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Second-, third-, and fourth-order elastic constants of mixed alkali-halide crystals

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The second-order elastic constants (SOEC), third-order elastic constants (TOEC), and fourth-order elastic constants (FOEC) of mixed alkali-halide crystals are calculated using a phenomenological potential model which takes into account the effect of Lundqvist's three-body forces along with other relevant interactions in ionic solids. Values of three SOEC, six TOEC, eleven FOEC, and pressure derivatives of SOEC have been calculated for NaCl-NaBr, KCl-KBr, and KBr-KI mixed crystals for the entire range of compositions. The results are compared with available experimental values. The applicability of knowledge of TOEC and FOEC has been discussed for predicting the conductivity and thermal expansion coefficient of mixed crystals.

I. INTRODUCTION

For cubic ionic crystals like alkali halides there are three second-order elastic constants (SOEC) C_{ij}, six third-order elastic constants (TOEC) C_{ijk}, and eleven fourth-order elastic constants (FOEC) C_{ijkl}. Under certain conditions and assumptions[1-3] some of these elastic constants are equal to each other, and such equalities are known as Cauchy relations. The experimentally measured values of various-order elastic constants demonstrate the invalidity of Cauchy relations. The breakdown of Cauchy relations in ionic crystals can be explained by taking into account the effect of Lundqvist's many-body or three-body potentials.[4-6] The phenomenological models based on three-body potentials have been quite successful in predicting the higher-order elastic constants.[7-10] Studies on TOEC and FOEC provide useful information on the interatomic forces and on anharmonic properties of crystalline solids. The high-pressure equation of state also requires the knowledge of TOEC and FOEC, as the pressure and temperature derivatives of bulk modulus are derived from them. Since the contributions from third- and fourth-order coupling parameters to many anharmonic properties are of the same order of magnitude, the knowledge of FOEC is equally important as that of TOEC. In the present paper we evaluate TOEC and FOEC for mixed alkali-halide crystals, viz., NaCl-NaBr, KCl-KBr, and KBr-KI solid solutions using Lundqvist's model. Theory and method of calculations are described in Sec. II. The results are discussed and compared with available experimental data in Sec. III. The applicability of knowledge of TOEC and FOEC for mixed crystals has also been discussed.

II. THEORY AND METHOD OF CALCULATION

The potential energy of an ionic crystal based on Lundqvist's three-body potential can be expressed as follows:

$$\Phi=\frac{e^2}{2}\sum_{k}\sum_{l'k'}\frac{\epsilon(k)\epsilon(k')}{r(l',kk'')}+\sum_{k}\sum_{l',k'}V\{r(l',kk')\}+\sum_{k}\sum_{l',k'}\sum_{l'',k''}f_k\{r(l',kk')\}\frac{\epsilon(k'')}{r(l'',kk'')}\,, \tag{1}$$

where $\epsilon(k)$ is the valence of the k-type ion. The terms in this expression represent the Coulomb energy, the repulsive energy extended up to second neighbors, and three-body potential energy, respectively. The function f, related to the overlap integrals of the free-ion one-electron wave functions, is assumed significant only for the nearest neighbors.

Within the framework of a phenomenological model we express the elastic constants in terms of short-range force parameters A_1, B_1, C_1, D_1, A_2, B_2, C_2, and D_2. The subscripts 1 and 2 represent the connection with first-neighbor and second-neighbor interactions, respectively. The short-range force constants, for NaCl-type solids, are defined as follows[7,8]:

$$\frac{A_1}{8a^3}=\left[\frac{\partial^2 V_1'(r)}{\partial r^2}\right]_{r=a_1}, \tag{2}$$

$$\frac{B_1}{8a^2}=\left[\frac{\partial V_1'(r)}{\partial r}\right]_{r=a_1}, \tag{3}$$

$$\frac{C_1}{8a^4}=\left[\frac{\partial^3 V_1'(r)}{\partial r^3}\right]_{r=a_1}, \tag{4}$$

$$\frac{D_1}{8a^5}=\left[\frac{\partial^4 V_1'(r)}{\partial r^4}\right]_{r=a_1}, \tag{5}$$

$$\frac{A_2}{16a^3}=\left[\frac{\partial^2 V_2'(r)}{\partial r^2}\right]_{r=a_2}, \tag{6}$$

$$\frac{B_2\sqrt{2}}{16a^2}=\left[\frac{\partial V_2'(r)}{\partial r}\right]_{r=a_2}, \tag{7}$$

$$\frac{C_2\sqrt{2}}{32a^4}=\left[\frac{\partial^3 V_2'(r)}{\partial r^3}\right]_{r=a_2}, \tag{8}$$

$$\frac{D_2}{32a^5}=\left[\frac{\partial^4 V_2'(r)}{\partial r^4}\right]_{r=a_2}, \tag{9}$$

where a_1 and a_2 are the equilibrium values of first-neighbor and second-neighbor distances. $V_1'(r)$ and $V_2'(r)$ are the effective short-range interactions between first neighbors and second neighbors, respectively, and can be approximated by exponential forms of the Born-Mayer-type $b\exp(-r/\rho)$, where b and ρ are known as the repulsive strength and hardness parameters, respectively.[11] The use of the Born-Mayer exponential repulsion leads to the following relations among short-range force constants:

$$C_1=\frac{A_1^2}{B_1},\quad C_2=\left[\frac{A_2^2}{B_2}\right] \tag{10}$$

and

$$D_1=\frac{A_1^3}{B_1^2},\quad D_2=\frac{A_2^3}{B_2^2}\,. \tag{11}$$

Thus with the help of Eqs. (10) and (11) we can express the TOEC and FOEC in terms of A_1, B_1, A_2, and B_2 only. Following the method of homogeneous deformation[12] Garg *et al.*[7,8] have derived the expressions for TOEC and FOEC, which in view of Eqs. (10) and (11), can be reexpressed as follows:

$$C_{111}=\frac{e^2}{4a^4}\left[37.556\epsilon(\epsilon+12f)+\frac{A_1^2}{B_1}-3A_1+\frac{1}{4}\left[\frac{A_2^2}{B_2}-3A_2-9B_2\right]+13.98\epsilon\left[a^2\frac{\partial^2 f}{\partial r^2}\right]-89.305\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{12}$$

$$C_{112}=\frac{e^2}{4a^4}\left[-4.836\epsilon(\epsilon+12f)+\frac{1}{8}\left[\frac{A_2^2}{B_2}-3A_2+3B_2\right]+4.660\epsilon\left[\frac{a^2\partial^2 f}{\partial r^2}\right]-18.640\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{13}$$

$$C_{166}=\frac{e^2}{4a^4}\left[-7.116\epsilon(\epsilon+12f)-2(B_1+B_2)+\frac{1}{8}\left[\frac{A_2^2}{B_2}-3A_2+3B_2\right]+5.564\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{14}$$

$$C_{144}=\frac{e^2}{4a^4}\left[2.717\epsilon(\epsilon+12f)+5.564\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{15}$$

$$C_{456}=\frac{e^2}{4a^4}[2.717\epsilon(\epsilon+12f)], \tag{16}$$

$$C_{123}=\frac{e^2}{4a^4}\left[2.717\epsilon(\epsilon+12f)+16.692\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{17}$$

$$C_{1111}=\frac{e^2}{4a^4}\left[-305.321\epsilon(\epsilon+12f)+\frac{A_1^3}{B_1^2}-\frac{6A_1^2}{B_1}+15A_1+2R_2'-11.25B_2 + 18.6407\epsilon\left[a^3\frac{\partial^3 f}{\partial r^3}\right]-206.5714\epsilon\left[\frac{a^2\partial^2 f}{\partial r^2}\right]+863.498\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{18}$$

$$C_{1112}=\frac{e^2}{4a^4}\left[17.9304\epsilon(\epsilon+12f)+R_2'+4.6602\epsilon\left[a^3\frac{\partial^3 f}{\partial r^3}\right] + 2.7116\epsilon\left[\frac{a^2\partial^2 f}{\partial r^2}\right]+103.489\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{19}$$

$$C_{1166}=\frac{e^2}{4a^4}\left[27.2234\epsilon(\epsilon+12f)+8(B_1+B_2)+R_2'+5.564\epsilon\left[a^2\frac{\partial^2 f}{\partial r^2}\right]-44.2513\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{20}$$

$$C_{1122}=\frac{e^2}{4a^4}\left[22.4611\epsilon(\epsilon+12f)+R_2'-50.2166\epsilon\left[a^2\frac{\partial^2 f}{\partial r^2}\right]-27.158\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{21}$$

$$C_{1266}=\frac{e^2}{4a^4}\left[27.1211\epsilon(\epsilon+12f)+4(B_1+B_2)+R_2'-38.6873\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{22}$$

$$C_{4444}=\frac{e^2}{4a^4}\left[32.9562\epsilon(\epsilon+12f)+9(B_1+B_2)+R_2'+10.2242\epsilon\left[a^2\frac{\partial^2 f}{\partial r^2}\right]-10.2242\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{23}$$

$$C_{1123}=\frac{e^2}{4a^4}\left[-6.3406\epsilon(\epsilon+12f)+5.564\epsilon\left[a^2\frac{\partial^2 f}{\partial r^2}\right]-22.5157\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{24}$$

$$C_{1144}=\frac{e^2}{4a^4}\left[-6.3406\epsilon(\epsilon+12f)+5.564\epsilon\left[a^2\frac{\partial^2 f}{\partial r^2}\right]+16.692\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{25}$$

$$C_{1244}=\frac{e^2}{4a^4}\left[-6.3406\epsilon(\epsilon+12f)+8.4746\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{26}$$

$$C_{1456}=\frac{e^2}{4a^4}\left[-6.3406\epsilon(\epsilon+12f)+10.8678\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{27}$$

$$C_{4466}=\frac{e^2}{4a^4}\left[-4.0106\epsilon(\epsilon+12f)+2(B_1+B_2)+10.2242\epsilon\left[a^2\frac{\partial^2 f}{\partial r^2}\right]-10.2229\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{28}$$

where

$$R_2'=\frac{1}{16}\left[\frac{A_2^3}{B_2^2}-\frac{6A_2^2}{B_2}+15A_2-15B_2\right].$$

In above equations ϵ is the valence of ions and f is the three-body charge transfer parameter first introduced by Lundqvist.[4] The expressions for pressure derivatives of SOEC and TOEC can be directly obtained in terms of TOEC and FOEC with the use of definitions of effective elastic constants.[13–15] We note from (12) to (28) that various TOEC and FOEC, and therefore also the pressure derivatives of SOEC and TOEC, depend on eight parameters, viz., A_1, B_1, A_2, B_2, f, $\partial f/\partial r$, $\partial^2 f/\partial r^2$, and $\partial^3 f/\partial r^3$. We determine these parameters, first for pure crystals, using three SOEC, equilibrium condition, and Cochran's formula.[16,17] In essence we use the following relations:

$$C_{11}=\frac{e^2}{4a^4}\left[-5.112\epsilon(\epsilon+12f)+A_1 + \frac{A_2+B_2}{2}+9.3204\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{29}$$

$$C_{12}=\frac{e^2}{4a^4}\left[1.391\epsilon(\epsilon+12f)+\tfrac{1}{4}(A_2-B_2)+9.3204\epsilon\left[a\frac{\partial f}{\partial r}\right]\right], \tag{30}$$

$$C_{44}=\frac{e^2}{4a^4}[2.556\epsilon(\epsilon+12f)+B_1+\tfrac{1}{4}(A_2+3B_2)], \tag{31}$$

$$B_1+B_2=-1.165\epsilon(\epsilon+12f), \tag{32}$$

$$f=f_0\exp\left[-\frac{r}{\rho_{+-}}\right], \tag{33}$$

where f_0 is a constant and ρ_{+-} is the repulsive hardness parameter for cation and anion interactions. Equation (33) was first suggested by Cochran[16] and subsequently used by others.[6,9,10] The Born-Mayer exponential form for nearest-neighbor cation-anion repulsion leads to the following relation:

$$A_1=-\frac{a}{\rho_{+-}}B_1\,. \tag{34}$$

Values of ρ_{+-} have been taken from Hafemeister and Flygare.[18] The parameters A_1, B_1, A_2, B_2 and f_0, calculated for pure crystals, are listed in Table I along with input data[19,20] used in calculations.

Now we proceed to calculate the elastic constants of mixed crystals of alkali halides. We make use of the basic concept of the so-called pseudo-unit-cell model developed by Chang and Mitra.[21] According to their model a complete randomization is assumed in which all unit cells of a mixed crystal are identical. For a mixed crystal of AB and AC, mixed in the ratio of $(1-x)$ and x, the pseudo-unit-cell still contains two particles, maintains its symmetry, and has a unique dimension consistent with the single lattice constant of appropriate value in the case of a mixed crystal made of two cubic crystals. A pseudo-unit-cell thus contains one atom of A and one atom of $(1-x)B+xC$. X-ray diffraction measurements on mixed crystals do indeed indicate unique unit-cell dimensions throughout the composition range. Following the details of this model Varshney *et al.*[22] have taken the force constants and effective charge parameter to depend linearly on the concentration of constituent solids forming the mixed crystal. Thus one can write

$$P(AB_{1-x}C_x)=(1-x)P(AB)+xP(AC), \tag{35}$$

where x is the mole fraction of AC in the AB-AC mixed crystal and P denotes any force constant or effective charge parameter. Since the parameters of our present theory (Table I), A_1, B_2, A_2, B_2, f, and $\partial f/\partial r$ are either force constants or related to the effective charge parameter,[23] we can determine their values appropriate for mixed crystals using Eq. (35). The potential parameters for mixed crystals derived from Eq. (35) are then used to evaluate second- and higher-order elastic constants. The contributions to various-order elastic constants arising from the Coulomb interactions depend on (i) $\epsilon(\epsilon+12f)$, the modified magnitude of charge on the ions due to the effect of three-body forces,[23] and on (ii) the equilibrium nearest-neighbor distance a. Values of $\epsilon(\epsilon+12f)$ are determined from the interpolation scheme based on Eq. (35), and values of a for mixed crystals are taken from Ref. 19.

III. RESULTS AND DISCUSSION

The results obtained in the present work for $NaCl_{1-x}Br_x$, $KCl_{1-x}Br_x$, and $KBr_{1-x}I_x$ mixed crystals (for different values of mole fraction x varying from 0 to 1) are reported in Figs. 1(a)–1(c) and in Tables II–V. In Figs. 1(a)–1(c) we have compared the calculated values of SOEC with the corresponding experimental values graphically. For extreme cases with $x=0$ and 1 the parameters were fitted and therefore SOEC of pure crystals are

TABLE I. Values of input data (Refs. 19 and 20) and calculated potential parameters for pure crystals.

	10^{-8} cm	10^{11} dyn/cm^2								
Crystal	r_0	C_{11}	C_{12}	C_{44}	A_1	B_1	A_2	B_2	f	$\frac{\partial f}{\partial r}$
NaCl	2.820	4.585	1.264	1.265	10.082	-1.233	0.0522	0.0678	1.438×10^{-5}	-1.176×10^{-4}
NaBr	2.989	2.704	1.066	0.990	10.006	-1.194	0.0539	0.048	-1.348×10^{-3}	0.0113
KCl	3.147	3.838	0.683	0.633	11.822	-1.409	-0.9256	0.2588	-1.083×10^{-3}	0.0091
KBr	3.298	3.263	0.564	0.504	11.987	-1.406	-1.062	0.263	-1.58×10^{-3}	0.0132
KI	3.523	2.577	0.455	0.370	12.083	-1.398	-1.102	0.273	-2.85×10^{-3}	0.0246

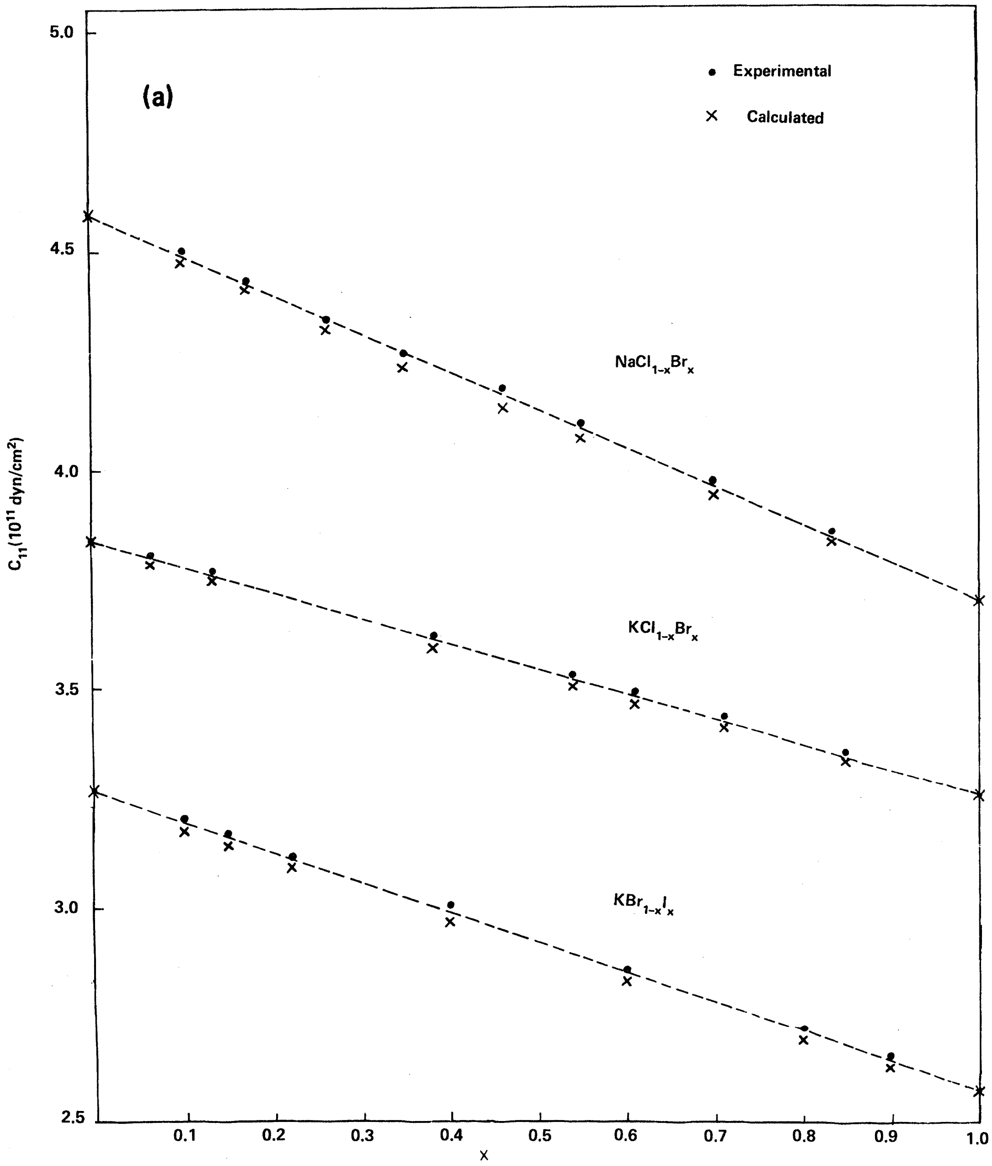

FIG. 1. (a) Plots of C_{11} (10^{11} dyn/cm^2) vs concentration x (mole fraction) for $NaCl_{1-x}Br_x$, KCl_{1-x}, and $KBr_{1-x}I_x$; ×, calculated; ●, experimental (Ref. 19). (b) Plots of C_{12} (10^{11} dyn/cm^2) vs concentration x (mole fraction) for $NaCl_{1-x}Br_x$, $KCl_{1-x}Br_x$, and $KBr_{1-x}I_x$; ×, calculated; ● experimental (Ref. 19). (c) Plots of C_{44} (10^{11} dyn/cm^2) vs concentration x (mole fraction) for $NaCl_{1-x}Br_x$, $KCl_{1-x}Br_x$, and $KBr_{1-x}I_x$; ×, calculated; ●, experimental (Ref. 19).

reproduced exactly. For mixed crystals the calculated SOEC agree with experimental values generally within 1%. The most striking feature of the experimental data on SOEC in mixed alkali halides is their smooth linear variation between values for pure crystals. The calculated values show only slight deviations from this linear variation, and therefore we may conclude that the interpolation scheme based on Eq. (35) is correct to a very good approximation. However, Eq. (35) does not hold in a strict sense.

The calculated values of TOEC are listed in Table II. Experimental values of TOEC are not available except for two pure crystals, NaCl and KCl. These experimental values[24] are given within parentheses in Table II. The overall agreement between calculated and experimental values of all the six TOEC for NaCl and KCl pure crystals is satis-

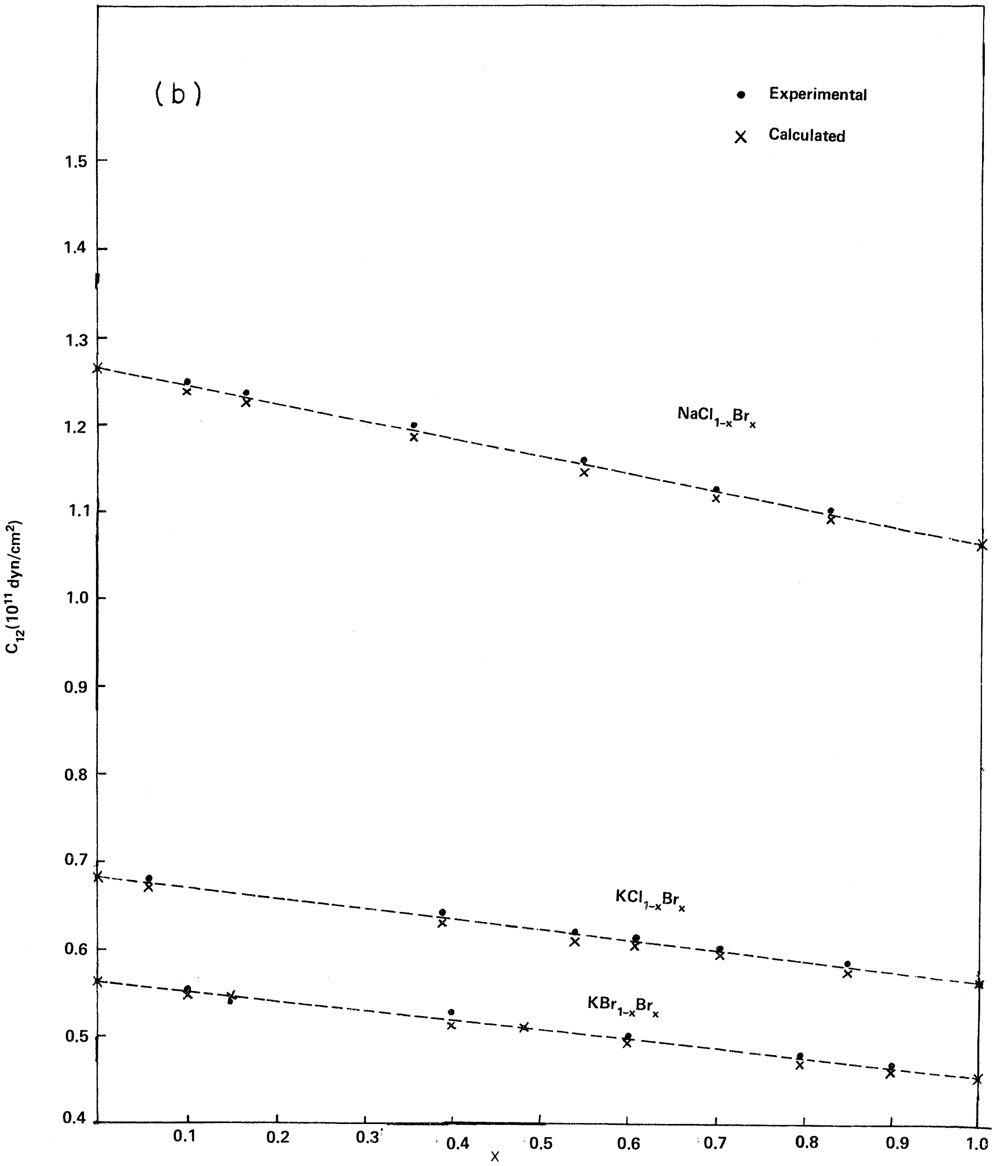

FIG. 1. (*Continued.*)

factory. It is particularly remarkable to mention that we have not used any TOEC in fitting the parameters of the model. The order of agreement is at least as good as that obtained by other workers.[2]

In Tables III and IV we report the calculated values of first and second pressure derivatives of SOEC for all the mixed crystals. The experimental values available for extreme cases, i.e., for pure crystals,[25–27] have also been listed for the sake of comparison. While the first pressure derivatives of SOEC have been measured experimentally for all the pure alkali halides, the second pressure derivatives of SOEC have been measured only for a few alkali halides.[25,28] The agreement is fair between our calculated pressure derivatives of SOEC and their experimental values, except the calculated pressure derivative of C_{44} in $NaCl_{1-x}Br_x$ has the incorrect sign. It became known from the experimental study performed by Roberts and Smith[27] that dC_{44}/dP is positive for sodium halides and negative for potassium halides. The magnitude of this quantity is much smaller as compared to pressure derivatives of other SOEC. This feature seems to be characteristic of all the NaCl-structure alkali-

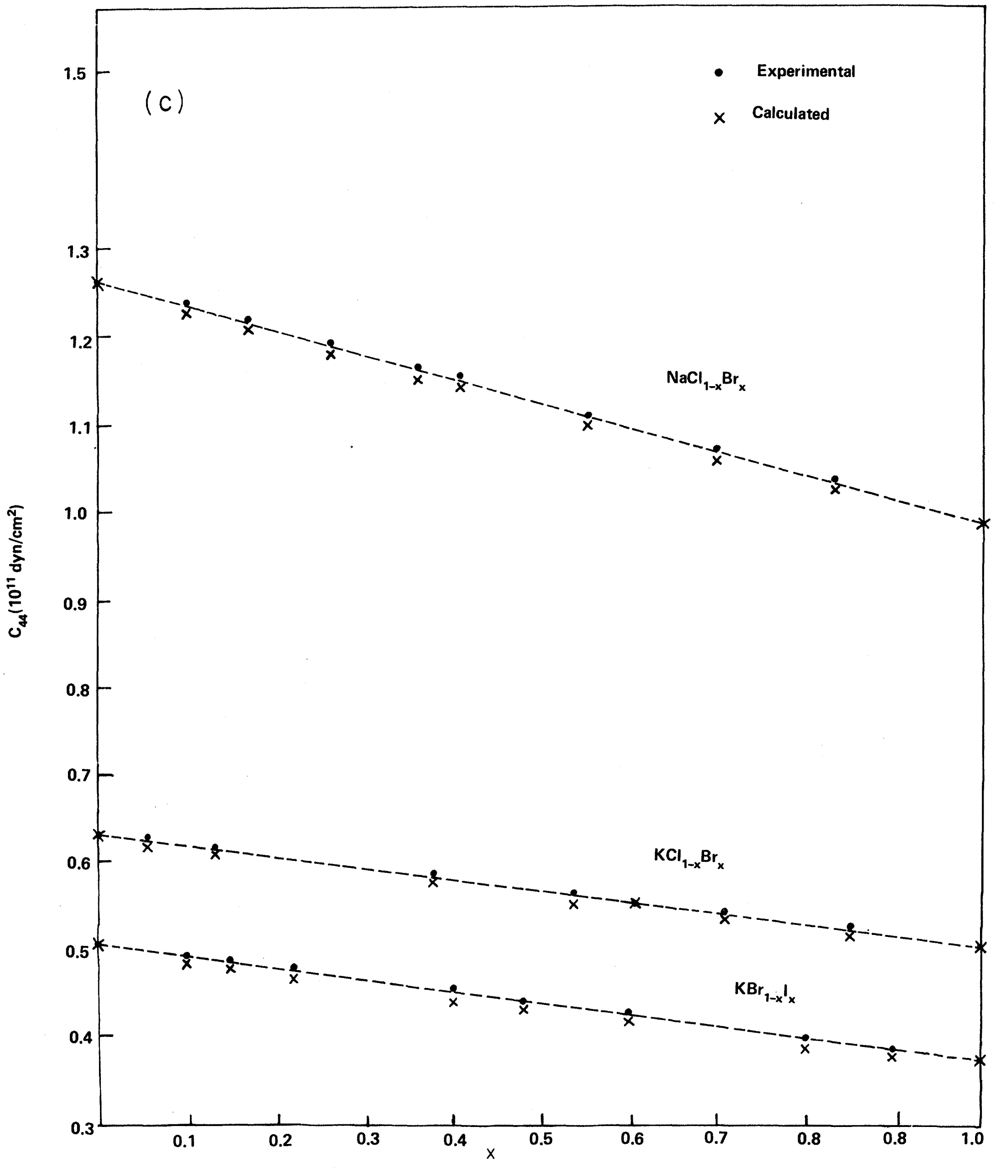

FIG. 1. (*Continued.*)

halide crystals, as has already been reported by Roberts and Smith[27]. To explain the values of dC_{44}/dP on the basis of interionic potentials we have to make a careful analysis of the expression for C_{44}. Equations (31) and (32) yield

$$C_{44}=\frac{e^2}{4a^4}[1.391\epsilon(\epsilon+12f)+\tfrac{1}{4}(A_2-B_2)] \ . \tag{36}$$

It is evident from Eq. (36) that C_{44} depends on the second-neighbor force constants A_2 and B_2 and does not contain the first-neighbor potential parameters A_1 and B_1. On the basis of a detailed analysis of elastic constants in alkali halides, Catlow *et al.*[29] have emphasized the necessity of including the van der Waals interactions in the second-neighbor potential. The importance of these interactions in calculating higher-order elastic constants has also been discussed by Hollinger and Barseh.[26] In the present work we have not considered the van der Waals interactions, and the discrepancy between calculated and experimental values may be attributed to this fact.

TABLE II. Calculated values of third-order elastic constants (10^{12} dyn/cm^2). Experimental values for pure crystals are given within parentheses.

Mixed crystal	Values of x	C_{111}	C_{112}	C_{166}	C_{123}	C_{144}	C_{456}
$NaCl_{1-x}Br_x$	0.00	-6.850	-0.439	-0.439	0.247	0.248	0.248
		(-8.8)	(-0.571)	(-0.611)	(0.284)	(0.258)	(0.271)
	0.10	-6.729	-0.433	-0.427	0.243	0.241	0.24
	0.17	-6.640	-0.429	-0.419	0.239	0.237	0.236
	0.24	-6.517	-0.424	-0.409	0.235	0.232	0.231
	0.36	-6.392	-0.419	-0.398	0.231	0.227	0.225
	0.46	-6.286	-0.415	-0.388	0.227	0.222	0.220
	0.55	-6.187	-0.410	-0.379	0.223	0.218	0.215
	0.70	-6.027	-0.403	-0.364	0.217	0.211	0.207
	0.83	-5.887	-0.396	-0.352	0.213	0.205	0.201
	1.00	-5.725	-0.390	-0.338	0.207	0.198	0.193
$KCl_{1-x}Br_x$	0.00	-5.74	-0.237	-0.203	0.167	0.161	0.158
		(-7.01)	(-0.244)	(-0.245)	(0.133)	(0.127)	(0.118)
	0.06	-5.69	-0.234	-0.199	0.165	0.157	0.155
	0.13	-5.63	-0.230	-0.195	0.163	0.156	0.154
	0.38	-5.42	-0.219	-0.181	0.156	0.149	0.146
	0.54	-5.29	-0.212	-0.173	0.155	0.145	0.142
	0.61	-5.24	-0.209	-0.169	0.149	0.143	0.140
	0.71	-5.16	-0.205	-0.164	0.147	0.140	0.137
	0.85	-5.07	-0.197	-0.158	0.144	0.137	0.134
	1.00	-4.96	-0.194	-0.151	0.140	0.133	0.130
$KBr_{1-x}I_x$	0.00	-4.96	-0.194	-0.151	0.140	0.133	0.130
	0.10	-4.84	-0.189	-0.146	0.137	0.130	0.126
	0.15	-4.79	-0.188	-0.143	0.136	0.128	0.124
	0.22	-4.71	-0.186	-0.140	0.134	0.125	0.122
	0.40	-4.52	-0.181	-0.132	0.128	0.119	0.115
	0.48	-4.45	-0.180	-0.128	0.126	0.117	0.113
	0.60	-4.34	-0.177	-0.123	0.123	0.114	0.109
	0.80	-4.13	-0.170	-0.114	0.117	0.107	0.102
	0.90	-4.08	-0.169	-0.112	0.116	0.106	0.101
	1.00	-3.97	-0.166	-0.108	0.112	0.102	0.097

In Table V we report the calculated values of 11 FOEC. There is no experimental data on these quantities available for comparison. The FOEC are useful quantities for studying the high-pressure equation of state, temperature and pressure derivatives of bulk modulus, and many other thermoelastic and anharmonic properties of solids.[25–28] The knowledge of FOEC can be applied to determine the conductivity or diffusivity and thermal expansivity of mixed alkali halides.[30–32]. Recently Varotsos[30,31] has derived the following relations:

$$x_m=\frac{\mu-2}{\lambda\mu}\,, \tag{37}$$

$$\beta=\frac{\beta^0\left\{1+x\lambda\left[1+\frac{d}{dT}\left[\frac{dK}{dP}\right]\Big/\beta^0\left[\frac{dK}{dP}-1\right]\right]\right\}}{1+x\lambda}\,, \tag{38}$$

$$\mu=\frac{1-K\frac{d^2K}{dp^2}}{\left[\frac{dk}{dp}-1\right]}\,, \tag{39}$$

$$\lambda=\frac{V_2}{V_1}-1\,, \tag{40}$$

TABLE III. Calculated values of first pressure derivatives of second-order elastic constants. Experimental values (Ref. 27) for extreme cases are given within parentheses; $S=(\frac{1}{2})(C_{11}-C_{12})$ and $K=(\frac{1}{3})(C_{11}+2C_{12})$.

Mixed crystal	Values of x	$\frac{\partial C_{44}}{\partial P}$	$\frac{\partial S}{\partial P}$	$\frac{\partial K}{\partial P}$
$NaCl_{1-x}Br_x$	0.00	−0.289	3.755	4.216
		(0.37)	(4.79)	(5.27)
	0.10	−0.290	3.767	4.217
	0.17	−0.301	3.780	4.245
	0.24	−0.306	3.781	4.251
	0.36	−0.312	3.789	4.271
	0.46	−0.316	3.806	4.290
	0.55	−0.323	3.814	4.302
	0.70	−0.333	3.823	4.325
	0.83	−0.340	3.843	4.343
	1.00	−0.349	3.856	4.370
		(0.46)	(4.83)	(5.29)
$KCl_{1-x}Br_x$	0.00	−0.651	4.376	4.374
		(−0.39)	(5.61)	(5.34)
	0.06	−0.655	4.385	4.379
	0.13	−0.661	4.395	4.382
	0.38	−0.681	4.427	4.403
	0.56	−0.693	4.448	4.407
	0.61	−0.699	4.458	4.418
	0.71	−0.706	4.470	4.421
	0.85	−0.718	4.488	4.430
	1.00	−0.729	4.502	4.436
		(−0.33)	(5.68)	(5.38)
$KBr_{1-x}I_x$	0.00	−0.729	4.502	4.436
		(−0.33)	(5.68)	(5.38)
	0.10	−0.735	4.505	4.437
	0.15	−0.738	4.507	4.446
	0.22	−0.742	4.510	4.447
	0.40	−0.751	4.513	4.465
	0.48	−0.758	4.519	4.471
	0.60	−0.764	4.531	4.494
	0.80	−0.774	4.540	4.505
	0.90	−0.777	4.541	4.508
	1.00	−0.782	4.546	4.538
		(−0.24)	(6.03)	(5.47)

where x_m is the value of mole fraction x for which the conductvity or diffusivity of the mixed crystal is maximum. β and β^0 are thermal expansion coefficients of mixed and pure crystals, respectively. K is the bulk modulus. V_1 and V_2 are volumes at $x=0$ and 1, respectively. In order to calculate x_m and β we have to know the quantities such as dK/dP, d^2K/dP^2, and $(d/dT)(dK/dP)$. These are related to TOEC and FOEC.[13−15] Using our calculated TOEC, FOEC, and Eqs. 37−40 we obtain $x_m \approx 0.5$, and $\beta/\beta^0=1.03$ (for $x=0.25$) for the $KCl_{1-x}Br_x$ crystal. The quantities thus estimated are in good agreement with experimental data.[30,31] It should be emphasized here that calculated TOEC and FOEC are only approximate estimates of these constants. For performing accurate and reliable studies on mixed crystals it is desirable to measure experimentally their TOEC and FOEC.

TABLE IV. Calculated values of second pressure derivatives of second-order elastic constants (10^{-11} cm^2/dyn). Experimental values (Ref. 25) for KI are given within parentheses.

Mixed crystal	Values of x	$\frac{\partial^2 C_{11}}{\partial P^2}$	$\frac{\partial^2 C_{12}}{\partial P^2}$	$\frac{\partial^2 C_{44}}{\partial P^2}$
$NaCl_{1-x}Br_x$	0.00	-4.07	-0.863	-0.867
	0.10	-4.18	-0.843	-0.855
	0.17	-4.29	-0.895	-0.878
	0.24	-4.37	-0.968	-0.928
	0.36	-4.42	-0.969	-0.951
	0.46	-4.61	-0.975	-0.932
	0.55	-4.67	-0.989	-0.938
	0.70	-4.85	-1.036	-0.951
	0.83	-4.97	-1.056	-0.963
	1.00	-5.13	-1.111	-1.008
$KCl_{1-x}Br_x$	0.00	-6.07	-0.512	-0.458
	0.06	-6.13	-0.509	-0.463
	0.13	-6.49	-0.508	-0.455
	0.38	-6.52	-0.505	-0.428
	0.56	-6.63	-0.502	-0.426
	0.61	-6.77	-0.500	-0.409
	0.71	-6.85	-0.499	-0.412
	0.85	-7.05	-0.492	-0.401
	1.00	-7.14	-0.489	-0.388
$KBr_{1-x}I_x$	0.00	-7.14	-0.489	-0.388
	0.10	-7.29	-0.525	-0.434
	0.15	-7.52	-0.541	-0.436
	0.22	-7.56	-0.546	-0.452
	0.40	-7.86	-0.581	-0.459
	0.48	-7.97	-0.612	-0.462
	0.60	-8.35	-0.643	-0.464
	0.80	-8.90	-0.640	-0.472
	0.90	-8.92	-0.653	-0.474
	1.00	-9.34	-0.711	-0.505
		(-12.7 ± 1.5)	(-1.6 ± 1.2)	(-1.08 ± 0.04)

Finally, it should be mentioned that our present calculations differ from the two-body potential models in two respects. First, the use of the three-body potential parameter f and its derivative $\partial f/\partial r$ provides complete fitting of the three SOEC (C_{11}, C_{12}, and C_{44}). On the other hand, the values of SOEC calculated from the two-body potentials[26] show large deviations from the experimental values. The second point is concerned with the Cauchy relations that are satisifed only when we use two-body potentials. If we put f and its derivatives equal to zero in Eqs. 12–31, we obtain the following well-known Cauchy equations:

$$C_{12}=C_{44}\ , \tag{41}$$

$$C_{112}=C_{166}\ , \tag{42}$$

$$C_{123}=C_{144}=C_{456}\ , \tag{43}$$

$$C_{1112}=C_{1166}\ , \tag{44}$$

$$C_{1122}=C_{1266}=C_{4444}\ , \tag{45}$$

$$C_{1123}=C_{1144}=C_{1244}=C_{1456}=C_{4466}\ . \tag{46}$$

The use of Lundqvist's three-body potential breaks down the Cauchy relations [(40)–(46)] and therefore we have obtained distinct values for elastic constants of various orders.

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TABLE V. Calculated values of fourth-order elastic constants (10^{11} dyn/cm^2).

Mixed crystal	Values of x	C_{1111}	C_{1112}	C_{1166}	C_{1122}	C_{1266}	C_{4444}	C_{1123}	C_{1144}	C_{1244}	C_{1456}	C_{4466}
$NaCl_{1-x}Br_x$	0.00	924.3	16.3	16.3	20.42	20.1	20.5	−5.78	−5.78	−5.78	−5.785	−5.77
	0.10	905.2	16.233	15.9	20.25	19.9	20.0	−5.69	−5.65	−5.63	−5.62	−5.52
	0.17	898.1	16.231	15.6	20.17	19.5	19.7	−5.64	−5.57	−5.54	−5.51	−5.40
	0.26	887.5	16.216	15.2	19.98	18.6	19.3	−5.56	−5.46	−5.42	−5.37	−5.23
	0.36	870.9	16.195	14.8	19.93	18.5	18.8	−5.49	−5.36	−5.29	−5.23	−5.02
	0.46	857.4	16.194	14.5	19.81	18.0	18.6	−5.43	−5.26	−5.17	−5.08	−4.82
	0.55	846.0	16.169	14.2	19.69	17.6	18.3	−5.36	−5.16	−5.06	−4.96	−4.64
	0.70	827.3	16.12	13.6	19.50	16.9	17.7	−5.26	−5.01	−4.89	−4.77	−4.37
	0.83	816.1	16.07	13.2	19.37	16.5	17.1	−5.17	−4.89	−4.74	−4.61	−4.15
	1.00	792.3	16.04	12.7	19.17	15.6	16.6	−5.07	−4.75	−4.58	−4.44	−3.89
$Kcl_{1-x}Br_x$	0.00	782.4	11.04	8.37	13.61	11.29	10.99	−4.05	−3.84	−3.72	−3.62	−4.19
	0.06	776.3	10.95	8.23	13.54	11.13	10.82	−4.01	−3.80	−3.68	−3.58	−4.16
	0.13	761.4	10.83	8.06	13.35	10.93	10.61	−3.97	−3.75	−3.63	−3.52	−4.12
	0.38	742.6	10.44	7.59	12.87	10.26	9.91	−3.82	−3.59	−3.45	−3.35	−3.99
	0.54	727.3	10.22	7.16	12.58	9.86	9.49	−3.73	−3.50	−3.36	−3.24	−3.91
	0.61	720.5	10.12	7.12	12.46	9.69	9.32	−3.69	−3.46	−3.31	−3.19	−3.87
	0.71	711.3	9.97	6.82	12.28	9.45	9.06	−3.64	−3.40	−3.25	−3.13	−3.82
	0.85	699.6	9.79	6.55	12.06	9.14	8.75	−3.57	−3.33	−3.17	−3.05	−3.76
	1.00	686.9	9.62	6.29	11.84	8.84	8.42	−3.50	−3.25	−3.08	−2.96	−3.69
$KBr_{1-x}I_x$	0.00	686.9	9.62	6.29	11.84	8.84	8.42	−3.5	−3.26	−3.08	−2.96	−3.69
	0.10	669.2	9.33	5.82	11.29	8.29	7.89	−3.42	−3.15	−2.99	2.87	−3.61
	0.15	663.4	9.29	5.69	11.22	8.15	7.74	−3.39	−3.11	−2.96	−2.82	−3.58
	0.22	653.9	9.27	5.54	11.14	7.96	7.54	−3.34	−3.06	−2.90	−2.76	−3.54
	0.40	629.7	9.17	5.15	10.93	7.51	7.05	−3.24	−2.93	−2.76	−2.61	−3.45
	0.48	620.2	9.17	4.98	10.48	7.30	6.84	−3.20	−2.88	−2.71	−2.54	−3.42
	0.60	605.7	9.11	4.75	10.70	7.03	6.55	−3.14	−2.78	−2.62	−2.54	−3.36
	0.80	576.9	8.81	4.37	10.41	6.55	6.04	−3.00	−2.66	−2.46	−2.29	−3.24
	0.90	572.9	8.80	4.25	10.40	6.42	5.88	−2.99	−2.63	−2.43	−2.25	−3.23
	1.00	556.6	8.79	4.05	10.23	6.17	5.63	−2.91	−2.53	−2.34	−2.17	−3.16

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