PHYSICAL REVIEW VOLUME 139, NUMBER 5A 30 AUGUST 1965

Third-Order Elastic Constants of Alkali Halide Crystals*

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(Received 11 March 1965)

Third-order elastic constants of NaCl-type and CsCl-type crystals have been calculated using the Born model of ionic solids. Short-range repulsive interactions have been included up to second-nearest neighbors. Assuming that the temperature variation of these constants is linear, we have calculated the temperature coefficients $a_{\alpha\beta\gamma}$ in the high-temperature limit. In the case of NaCl-type crystals, C_{111}, C_{112}, and C_{166} are negative and C_{123}, C_{456}, and C_{144} are positive, whereas all the third-order elastic constants of CsCl-type crystals are negative. The temperature coefficients $a_{\alpha\beta\gamma}$ are all positive for CsCl-type crystals, whereas a_{111}, a_{112}, and a_{166} are positive and the others are negative for NaCl-type crystals. The computed values of the third-order elastic constants have been used to calculate the pressure derivatives of the second-order elastic constants and a comparison is made with the available experimental data.

I. INTRODUCTION

In recent years considerable attention has been given to the study of third-order elastic constants[1,2] of cubic crystals. Since the classic work of Lazarus[3] on the effect of hydrostatic pressure on the second-order elastic constants of NaCl and KCl single crystals a number of measurements have been reported on the pressure derivatives of the second-order elastic constants of alkali halide single crystals.[4–6] For a cubic crystal there are six independent third-order elastic (T.O.E.) constants and the pressure derivatives of the second-order elastic constants enable us to obtain three combinations of the six T.O.E. constants. Recently, Chang[7] has experimentally determined two more combinations of the T.O.E. constants of NaCl and KCl crystals. Nran'yan[8] has calculated the T.O.E. constants for some of the NaCl-type crystals and CsCl-type crystals. He has used the Born model with nearest-neighbor interactions. We believe that his values of the electrostatic contribution to the T.O.E. constants are in error.

In the present article we have used Brugger's[9] definition of the T.O.E. coefficients. The advantage of using Brugger's definition should be apparent, later in the text, from the symmetry of the expressions for the elastic constants. The T.O.E. constants for 19 alkali halide crystals have been calculated using the Born model. For the short-range repulsive interactions we have used the Born-Mayer type of potential: $A\exp(-r/b)$. Interactions up to second-nearest neighbors have been included. For the NaCl-type of crystals we have used the values of the electrostatic contribution to T.O.E. constants as given by Blackman.[10] The necessary lattice sums to calculate the electrostatic part of the T.O.E. constants of CsCl-type crystals have been evaluated on a computer. The method of calculation of the lattice sums for CsCl-type crystals is outlined in the Appendix. The T.O.E. constants are assumed to vary linearly with temperature. The temperature coefficients are calculated by expanding the vibrational free energy up to cubic terms in the strains in the high-temperature limit by following the procedure developed by Leibfried and Hahn.[11,12] We have calculated the pressure derivatives of the second-order elastic constants at room temperature.

II. THIRD-ORDER ELASTIC CONSTANTS

The elastic-strain energy density for a cubic crystal up to cubic terms in strains is written as follows[1]:

$$\begin{aligned}U=&U_2+U_3\\ =&\tfrac{1}{2}C_{11}(\eta_{11}^2+\eta_{22}^2+\eta_{33}^2)+C_{12}(\eta_{11}\eta_{22}+\eta_{22}\eta_{33}+\eta_{33}\eta_{11})+2C_{44}(\eta_{12}^2+\eta_{23}^2+\eta_{31}^2)+\tfrac{1}{6}C_{111}(\eta_{11}^3+\eta_{22}^3+\eta_{33}^3)\\ &+\tfrac{1}{2}C_{112}\{\eta_{11}^2(\eta_{22}+\eta_{33})+\eta_{22}^2(\eta_{33}+\eta_{11})+\eta_{33}^2(\eta_{11}+\eta_{22})\}+C_{123}(\eta_{11}\eta_{22}\eta_{33})+8C_{456}(\eta_{12}\eta_{23}\eta_{31})\\ &+2C_{144}(\eta_{11}\eta_{23}^2+\eta_{22}\eta_{31}^2+\eta_{33}\eta_{12}^2)+2C_{166}\{\eta_{12}^2(\eta_{11}+\eta_{22})+\eta_{23}^2(\eta_{22}+\eta_{33})+\eta_{31}^2(\eta_{33}+\eta_{11})\}\cdots\end{aligned}\tag{1}$$

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* Work supported by the U. S. Atomic Energy Commission and the Advanced Research Projects Agency.

[1] F. Birch, Phys. Rev. **71**, 809 (1947).

[2] See the review article by H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, pp. 213–351.

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[9] K. Brugger, Phys. Rev. **133**, A1611 (1964).

[10] M. Blackman, Proc. Phys. Soc. **84**, 371 (1964).

[11] G. Leibfried and H. Hahn, Z. Physik **150**, 497 (1958).

[12] See also G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, pp. 275–444.

where $\eta_{\alpha\beta}$ are the Lagrangian strain components, $C_{\alpha\beta}$ are the usual second-order elastic constants, and $C_{\alpha\beta\gamma}$ are the T.O.E. constants in Brugger's[9] definition.[13]

We shall now derive the expressions for the T.O.E. constants of the alkali halides. This will be carried out in two steps. First the energy density of the deformed crystal at 0°K will be calculated. By expanding the energy density up to cubic terms in strains expressions for T.O.E. constants $C_{\alpha\beta\gamma}{}^0$ will be obtained by comparing with Eq. (1). The effect of temperature will be taken into account later. We shall assume that only central forces are acting and that the lattice is in equilibrium under vanishing external forces. The zero-point vibrational energy and its effect on the elastic constants will be ignored. We note that each atom is a center of symmetry. The energy density of the undeformed lattice can be written as follows:

$$U_0=(2V_C)^{-1}\sum_{\nu=1}^{2}\sum_{(\mu m)\neq(\nu 0)}\varphi_{\mu\nu}(r_{\mu\nu}{}^{m0})$$
$$=(2V_C)^{-1}\sum{}'\varphi_{\mu\nu}(r_{\mu\nu}{}^{m0}.)\quad(2)$$

Here $\varphi_{\mu\nu}(r_{\mu\nu}{}^{m0})$ represents the interaction energy between the νth particle in the zeroth cell and the μth particle in the mth cell. In our case μ, ν can take values 1 and 2, m takes all the values corresponding to the elementary cells in the crystal, and $\sum'$ denotes the summation over all lattice points except $m=0$, $\mu=\nu$. V_C is the volume of the elementary cell. When the lattice is subjected to a homogeneous deformation the new interatomic distances will be denoted by $R_{\mu\nu}{}^{m0}$. The Lagrangian strain parameters $\eta_{\alpha\beta}$ are defined by the following equation:

$$R^2-r^2=2\sum\xi_\alpha\xi_\beta\eta_{\alpha\beta}=2\rho_{\mu\nu}{}^{m0}.\quad(3)$$

(R and r denote $R_{\mu\nu}{}^{m0}$ and $r_{\mu\nu}{}^{m0}$ and $\alpha,\beta=1,2,3.$) ξ_α, ξ_β are the Cartesian coordinates of the particle in the undeformed state.

The potential-energy density

$$U=(2V_C)^{-1}\sum{}'\varphi_{\mu\nu}(R_{\mu\nu}{}^{m0})\quad(4)$$

can be expanded in a series of ascending powers of $(\rho_{\mu\nu}{}^{m0})$.[10,14]

$$U=U_0+U_1+U_2+U_3.\quad(5)$$

The condition of equilibrium yields the relation $U_1=0$ and U_2 contains quadratic terms in the strain components. Since we are interested in the T.O.E. constants we confine our attention to U_3:

$$U_3=(2V_C)^{-1}\sum{}'((\rho_{\mu\nu}{}^{m0})^3/3!)D^3\varphi_{\mu\nu}(R)\big|_{R=r_{\mu\nu}{}^{m0}}\quad(6)$$
$$=(12V_C)^{-1}\sum_{\alpha\beta}\sum_{\alpha'\beta'}\sum_{\alpha''\beta''}\eta_{\alpha\beta}\eta_{\alpha'\beta'}\eta_{\alpha''\beta''}$$
$$\times\Big[\sum{}'\xi_\alpha\xi_\beta\xi_{\alpha'}\xi_{\beta'}\xi_{\alpha''}\xi_{\beta''}D^3\varphi_{\mu\nu}(R)\big|_{R=r_{\mu\nu}{}^{m0}}\Big]\quad(7)$$

where $D=R^{-1}(d/dR)$.

We can compare the coefficients of $\eta_{\alpha\beta}\eta_{\alpha'\beta'}\eta_{\alpha''\beta''}$ in Eq. (7) with those in Eq. (1). After going through simple but somewhat lengthy algebra we get the following expressions for $C_{\alpha\beta\gamma}{}^0$:

$$\begin{aligned}
C_{111}{}^0&=(2V_C)^{-1}\sum{}'\xi_1{}^6D^3\varphi_{\mu\nu}(R)\big|_{R=r_{\mu\nu}{}^{m0}},\\
C_{112}{}^0&=(2V_C)^{-1}\sum{}'\xi_1{}^4\xi_2{}^2D^3\varphi_{\mu\nu}(R)\big|_{R=r_{\mu\nu}{}^{m0}},\\
C_{123}{}^0&=(2V_C)^{-1}\sum{}'\xi_1{}^2\xi_2{}^2\xi_3{}^2D^3\varphi_{\mu\nu}(R)\big|_{R=r_{\mu\nu}{}^{m0}},\\
C_{456}{}^0&=(2V_C)^{-1}\sum{}'\xi_1{}^2\xi_2{}^2\xi_3{}^2D^3\varphi_{\mu\nu}(R)\big|_{R=r_{\mu\nu}{}^{m0}},\\
C_{144}{}^0&=(2V_C)^{-1}\sum{}'\xi_1{}^2\xi_2{}^2\xi_3{}^2D^3\varphi_{\mu\nu}(R)\big|_{R=r_{\mu\nu}{}^{m0}},\\
C_{166}{}^0&=(2V_C)^{-1}\sum{}'\xi_1{}^4\xi_2{}^2D^3\varphi_{\mu\nu}(R)\big|_{R=r_{\mu\nu}{}^{m0}}.
\end{aligned}\quad(8)$$

The superscript zero for $C_{\alpha\beta\gamma}$ has been introduced to emphasize the fact that these constants correspond to 0°K. "Cauchy" relations for the T.O.E. constants follow from the above expressions.

$$C_{123}{}^0=C_{456}{}^0=C_{144}{}^0;\quad C_{112}{}^0=C_{166}{}^0.\quad(9)$$

For a central-force model there are only three independent T.O.E. constants.

In the case of alkali halides the potential energy between two ions $\mu,\nu(=1,2)$ with charges $\pm e$ and distance R apart is assumed to be made up of two parts, Coulombic and the non-Coulombic. Thus

$$\varphi_{\mu\nu}(R)=\varphi_{\mu\nu}{}^c(R)+\varphi_{\mu\nu}{}^{Nc}(R),\quad(10)$$

with $\varphi_{\mu\nu}{}^c(R)=\pm e^2/R$. The $\pm$ apply to like and unlike charges, respectively. The non-Coulombic part of the energy is assumed to have the form

$$\varphi_{\mu\nu}{}^{Nc}(R)=A\exp(-R/b).\quad(11)$$

We include the short range interactions up to the second nearest neighbors. The general expressions for the short-range interactions up to the second-nearest neighbors will be of three types:

(a) unlike ions: $A_{+-}\exp(-r_1/b_{+-})$,
(b) like positive ions: $A_{++}\exp(-r_2/b_{++})$,
(c) like negative ions: $A_{--}\exp(-r_2/b_{--})$.

Such a model would require six parameters. To keep the number of parameters to a minimum we have assumed that the short-range interactions (a), (b), and (c) can be approximated by expression of the type (11).

We are neglecting the van der Waal's forces, and many-body forces. In this simplified model we can write the elastic constants $C_{\alpha\beta\gamma}{}^0$ as

$$C_{\alpha\beta\gamma}{}^0=C_{\alpha\beta\gamma}{}^{c0}+C_{\alpha\beta\gamma}{}^{Nc0}.\quad(12)$$

A. NaCl-Type Crystals

The expressions for the Coulombic part of $C_{\alpha\beta\gamma}$ can be written down using the necessary lattice sums:

$$\begin{aligned}
C_{111}{}^{c0}&=-(15/V_C)(e^2/r_0)S_7{}^{(3)},\\
C_{112}{}^{c0}&=-(15/V_C)(e^2/r_0)S_7{}^{(2,1)},\\
C_{123}{}^{c0}&=-(15/V_C)(e^2/r_0)S_7{}^{(1,1,1)},\\
C_{456}{}^{c0}&=C_{123}{}^{c0}=C_{144}{}^{c0};\quad C_{166}{}^{c0}=C_{112}{}^{c0},
\end{aligned}\quad(13)$$

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[13] The T.O.E. constants ($C_{\alpha\beta\gamma}{}^{\mathrm{Bi}}$) defined by Birch (Ref. 1) are related to those ($C_{\alpha\beta\gamma}{}^{\mathrm{Br}}$) defined by Brugger (Ref. 9) in the following manner:

$C_{111}{}^{\mathrm{Br}}=6C_{111}{}^{\mathrm{Bi}}$ $\quad C_{456}{}^{\mathrm{Br}}=\frac{1}{4}C_{456}{}^{\mathrm{Bi}}$
$C_{112}{}^{\mathrm{Br}}=2C_{112}{}^{\mathrm{Bi}}$ $\quad C_{144}{}^{\mathrm{Br}}=\frac{1}{2}C_{144}{}^{\mathrm{Bi}}$
$C_{123}{}^{\mathrm{Br}}=C_{123}{}^{\mathrm{Bi}}$ $\quad C_{166}{}^{\mathrm{Br}}=\frac{1}{2}C_{166}{}^{\mathrm{Bi}}$.

[14] M. Born and R. D. Misra, Proc. Cambridge Phil. Soc. **36**, 466 (1940).

TABLE I. T.O.E. constants and their temperature coefficients. ($C_{\alpha\beta\gamma}^0$ in units of 10^{11} dyne/cm^2, $a_{\alpha\beta\gamma}$ in units of 10^7 dyne/cm^2 °K; r_0 and b in units of 10^{-8} cm.)

	r_0	b	C_{111}^0	a_{111}	C_{112}^0	a_{112}	C_{123}^0	a_{123}	a_{456}	a_{144}	a_{166}
LiF	1.996	0.3333	−65.52	192.9	−27.72	51.71	9.859	−23.04	−10.72	−3.056	44.49
		0.280	−146.6	378.6	−26.76	60.57	9.859	−35.84	−10.36	−1.898	44.85
LiCl	2.539	0.3333	−70.59	230.3	−9.997	31.48	3.766	−20.94	−4.976	−0.833	21.55
		0.303	−95.03	312.4	−9.637	35.07	3.766	−27.53	−4.891	−0.806	20.93
LiBr	2.713	0.3333	−66.81	233.7	−7.499	27.83	2.889	−20.73	−4.029	−0.628	17.41
		0.305	−86.38	307.6	−7.196	30.99	2.889	−26.88	−3.968	−0.713	16.67
LiI	2.951	0.3333	−60.88	235.6	−5.152	23.94	2.064	−20.61	−3.087	−0.549	12.99
		0.366	−46.39	176.3	−5.367	21.35	2.064	−15.68	−3.136	−0.506	13.52
NaF	2.295	0.3333	−73.27	220.2	−15.46	38.56	5.641	−21.48	−6.866	−1.354	29.60
		0.312	−93.90	277.4	−15.16	41.12	5.641	−25.70	−6.777	−1.173	29.39
NaCl	2.789	0.3333	−64.97	234.6	−6.624	26.42	2.586	−20.69	−3.692	−0.607	15.81
		0.288	−96.92	364.7	−6.178	32.14	2.586	−31.85	−3.602	−0.797	14.54
NaBr	2.954	0.3333	−60.85	235.6	−5.130	23.90	2.055	−20.60	−3.075	−0.546	12.95
		0.308	−75.12	298.4	−4.933	26.66	2.055	−26.04	−3.036	−0.654	12.32
NaI	3.194	0.3333	−54.82	235.4	−3.613	21.08	1.504	−20.55	−2.403	−0.513	9.767
		0.341	−51.67	220.1	−3.653	20.38	1.504	−19.20	−2.411	−0.488	9.907
KF	2.648	0.3333	−68.32	232.7	−8.328	29.07	3.183	−20.80	−4.353	−0.700	18.82
		0.310	−84.92	292.3	−8.077	31.65	3.183	−25.67	−4.297	−0.723	18.29
KCl	3.116	0.3333	−56.73	235.7	−4.038	21.91	1.660	−20.56	−2.598	−0.519	10.70
		0.309	−68.90	294.4	−3.883	24.54	1.660	−25.77	−2.566	−0.638	10.11
KBr	3.262	0.3333	−53.18	235.1	−3.284	20.42	1.382	−20.54	−2.248	−0.512	9.026
		0.303	−67.28	309.9	−3.123	23.86	1.382	−27.33	−2.214	−0.669	8.326
KI	3.489	0.3333	−47.99	233.7	−2.423	18.59	1.056	−20.53	−1.819	−0.504	6.991
		0.317	−54.18	269.8	−2.359	20.28	1.056	−23.87	−1.803	−0.582	6.663
RbF	2.789	0.3333	−64.97	234.6	−6.624	26.42	2.586	−20.69	−3.692	−0.607	15.81
		0.291	−94.37	353.8	−6.211	31.65	2.586	−30.88	−3.608	−0.775	14.65
RbCl	3.259	0.3333	−53.27	235.2	−3.298	20.44	1.387	−20.54	−2.254	−0.511	9.056
		0.283	−79.09	376.6	−3.026	27.08	1.387	−33.55	−2.197	−0.807	7.810
RbBr	3.410	0.3333	−49.79	234.3	−2.687	19.17	1.157	−20.53	−1.953	−0.506	7.629
		0.298	−65.03	322.9	−2.533	23.35	1.157	−28.73	−1.920	−0.692	6.863
RbI	3.628	0.3333	−32.53	225.9	−1.939	18.47	0.903	−20.97	−2.045	−0.941	6.770
		0.293	−60.71	335.0	−1.899	22.71	0.903	−30.24	−1.576	−0.701	5.226
CsCl	2.034	0.3333	−37.20	132.1	−5.598	44.64	−3.913	25.64	15.87	52.42	55.32
		0.256	−43.30	192.1	−11.09	89.62	−9.409	64.53	38.67	124.0	126.8
CsBr	2.118	0.3333	−32.41	123.8	−5.323	44.07	−3.891	26.35	16.27	53.19	55.74
		0.267	−36.79	169.8	−9.399	79.04	−7.966	56.85	34.08	109.3	111.7
CsI	2.251	0.3333	−26.30	112.2	−4.912	43.15	−3.790	27.33	16.77	54.23	56.33
		0.263	−30.15	158.4	−8.831	80.33	−7.708	60.76	35.96	115.6	117.6

where

$$S_N^{(n_1,n_2,n_3)}=\sum_{l_1,l_2,l_3}(-1)^{l_1+l_2+l_3}\frac{l_1^{2n_1}l_2^{2n_2}l_3^{2n_3}}{(l_1^2+l_2^2+l_3^2)^{N/2}}. \tag{14}$$

Summation is taken over all the lattice points. n_1, n_2, n_3 and N are positive integers and $(n_1+n_2+n_3)\leq\frac{1}{2}(N-1)$. In this notation, Madelung's constant is given by $-S_1^{(0)}=1.74756$. Here r_0 denotes the nearest-neighbor distance; hence $2r_0^3$ is the volume of the elementary cell. For NaCl-type crystals the lattice sums are readily available[10]

$$\begin{aligned}S_7^{(3)}&=-1.36852,\\ S_7^{(2,1)}&=0.16115,\\ S_7^{(1,1,1)}&=-0.09045.\end{aligned} \tag{15}$$

Thus we have

$$\begin{aligned}C_{111}^{c0}&=+10.26390(e^2/r_0^4),\\ C_{112}^{c0}&=-1.208625(e^2/r_0^4),\\ C_{123}^{c0}&=+0.678375(e^2/r_0^4).\end{aligned} \tag{16}$$

Values of C_{456}^{c0}, C_{144}^{c0}, and C_{166}^{c0} can be easily obtained. We list the values of $C_{\alpha\beta\gamma}^{c0}$ obtained by Nran'yan[8] for comparison. His values are multiplied by appropriate numerical factors to convert from Birch's[1] definition of $C_{\alpha\beta\gamma}$ to that of Brugger.[9] According to Nran'yan[8]

$$\begin{aligned}C_{111}^{c0}&=11.00(e^2/r_0^4),\\ C_{112}^{c0}&=-1.71(e^2/r_0^4),\\ C_{123}^{c0}&=0.88(e^2/r_0^4).\end{aligned} \tag{17}$$

It is easy to check that Nran'yan's values of $S_7^{(3)}$,

$S_7^{(2,1)}$, and $S_7^{(1,1,1)}$ fail to satisfy the identity[14]

$$3S_7^{(3)}+18S_7^{(2,1)}+6S_7^{(1,1,1)}=S_1^{(0)}. \tag{18}$$

The final expressions for $C_{\alpha\beta\gamma}{}^0$, including the terms due to short-range interactions, are

$$\begin{aligned} C_{111}{}^0&=10.2639\frac{e^2}{r_0^4}-\frac{\varphi(r_0)}{b}\left[\frac{3}{r_0^2}+\frac{3}{br_0}+\frac{1}{b^2}\right]\\ &\quad-\frac{\varphi(r_0\sqrt{2})}{2b}\left[\frac{3\sqrt{2}}{r_0^2}+\frac{6}{br_0}+\frac{2\sqrt{2}}{b^2}\right],\\ C_{112}{}^0&=-1.208625\frac{e^2}{r_0^4}-\frac{\varphi(r_0\sqrt{2})}{4b}\left[\frac{3\sqrt{2}}{r_0^2}+\frac{6}{br_0}+\frac{2\sqrt{2}}{b^2}\right],\\ C_{123}{}^0&=0.678375(e^2/r_0^4),\\ C_{456}{}^0&=C_{123}{}^0=C_{144}{}^0;\quad C_{166}{}^0=C_{112}{}^0, \end{aligned} \tag{19}$$

where $\varphi(r)=A\exp(-r/b)$.

The values of $C_{\alpha\beta\gamma}{}^0$ for sixteen NaCl-type crystals are listed in Table I. We have used the room-temperature data of the lattice parameter and the coefficient of thermal expansion[15] to extrapolate the value of r_0. The hardness parameter b for the alkali halides is about $(1/3)\times10^{-8}$ cm. We have used $b=0.3333\times10^{-8}$ cm and the value of the pre-exponential parameter A is calculated from the equilibrium condition.

$$A=bZ_0(e^2/r_0^2)[6\exp(-r_0/b)+12\sqrt{2}\exp(-r_0\sqrt{2}/b)]^{-1} \tag{20}$$

where Z_0 = Madelung's constant for NaCl-type crystal $=1.74756$, and e = electronic charge $=4.803\times10^{-10}$ esu. We have used this value of A to calculate the short-range repulsive interaction energy $\varphi(r)$.

Tosi[15] has shown that different values of b result if one uses different equations of state. We have used the set of "b" obtained by Tosi[15] making use of the Hilderbrand equation of state. The different values of b for different crystal systems and the corresponding values of $C_{\alpha\beta\gamma}{}^0$ are also listed in Table I. In passing we note that the contribution of the short-range repulsive interactions to T.O.E. constants is quite predominant as compared to that of the electrostatic interactions.

B. CsCl-Type Crystals

The expressions for the $C_{\alpha\beta\gamma}{}^0$ of CsCl-type crystals can be easily written down. The elementary cell is chosen to have a cube edge of $2r_0$ and hence of volume $8r_0^3$. The nearest-neighbor distance is $r_1=r_0\sqrt{3}$. The necessary lattice sums and the Coulombic part of $C_{\alpha\beta\gamma}{}^0$ are given below.

$$\begin{aligned} &S_1^{(0)}=-Z_0=-1.01768, && S_7^{(2,1)}=-0.09336,\\ &S_7^{(3)}=0.5409, && S_7^{(1,1,1)}=-0.16000, \end{aligned} \tag{21}$$

$$\begin{aligned} C_{111}{}^{c0}&=-1.01419(e^2/r_0^4),\\ C_{112}{}^{c0}&=0.17505(e^2/r_0^4),\\ C_{123}{}^{c0}&=0.30000(e^2/r_0^4). \end{aligned} \tag{22}$$

Nran'yan's[8] values are listed below for comparison.

$$\begin{aligned} C_{111}{}^{c0}&=-2.8520(e^2/r_0^4),\\ C_{112}{}^{c0}&=+0.4359(e^2/r_0^4),\\ C_{123}{}^{c0}&=0.2944(e^2/r_0^4). \end{aligned} \tag{23}$$

The expressions for $C_{\alpha\beta\gamma}{}^0$ including the contribution of the short-range repulsive forces are as follows:

$$\begin{aligned} C_{111}{}^0&=-1.01419\frac{e^2}{r_0^4}-\frac{\varphi(r_1)}{9b}\left[\frac{\sqrt{3}}{r_0^2}+\frac{3}{br_0}+\frac{\sqrt{3}}{b^2}\right]\\ &\quad-\frac{\varphi(r_2)}{2b}\left[\frac{3}{r_0^2}+\frac{6}{br_0}+\frac{4}{b^2}\right],\\ C_{112}{}^0&=0.17505\frac{e^2}{r_0^4}-\frac{\varphi(r_1)}{9b}\left[\frac{\sqrt{3}}{r_0^2}+\frac{3}{br_0}+\frac{\sqrt{3}}{b^2}\right],\\ C_{123}{}^0&=0.30000\frac{e^2}{r_0^4}-\frac{\varphi(r_1)}{9b}\left[\frac{\sqrt{3}}{r_0^2}+\frac{3}{br_0}+\frac{\sqrt{3}}{b^2}\right],\\ C_{456}{}^0&=C_{123}{}^0=C_{144}{}^0;\quad C_{166}{}^0=C_{112}{}^0, \end{aligned} \tag{24}$$

where

$$\varphi(r_1)=A\exp(-r_0\sqrt{3}/b)$$

and

$$\varphi(r_2)=A\exp(-2r_0/b). \tag{25}$$

The pre-exponential parameter A is obtained from the equilibrium condition given below:

$$A=bZ_0(e^2/r_0^2)[8\sqrt{3}\exp(-r_0\sqrt{3}/b)+12\exp(-2r_0/b)]^{-1}. \tag{26}$$

The value of r_0 is obtained by extrapolation using the room-temperature lattice-parameter and thermal-expansion data.[15] The values of $C_{\alpha\beta\gamma}{}^0$ for CsCl, CsBr, and CsI along with those of other NaCl-type halides are listed in Table I.

III. TEMPERATURE VARIATION OF THE THIRD-ORDER ELASTIC CONSTANTS

The temperature variation of the T.O.E. constants is calculated by following the procedure developed by Leibfried and Hahn[11,12] for the temperature variation of the second-order elastic constants. The free energy of a crystal containing N cells, with s atoms ($s=2$ for alkali halides) per unit cell, can be written as

$$F=V_cNU+F^{\text{vib}} \tag{27}$$

where

$$\begin{aligned} F^{\text{vib}}&=kT\sum_{i=1}^{3sN}\ln 2\sinh\{\hbar\omega_i/2kT\}\\ &=kT\sum_{i=1}^{3sN}\ln\{\hbar\omega_i/kT\}\quad\text{for}\quad \hbar\omega_i\ll kT. \end{aligned} \tag{28}$$

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[15] M. P. Tosi, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1965), Vol. 16, pp. 1–120.

It should be emphasized that expression (28) for the vibrational free energy and hence, the subsequent expressions for the temperature coefficients of the T.O.E. constants are valid only in the high-temperature limit. At this stage one invokes the theorem that the spur of a matrix is invariant under a coordinate transformation and hence $\sum\omega_i^2=3sN\langle\omega^2\rangle_{\mathrm{av}}$. Following the suggestion of Born, ω_i in Eq. (28) is replaced by $[\langle\omega^2\rangle_{\mathrm{av}}]^{1/2}$.[2,12]

We write down the expression for $\langle\omega^2\rangle_{\mathrm{av}}$, the average of the ω_i^2:

$$\langle\omega^2\rangle_{\mathrm{av}}=(3s)^{-1}\sum_{m;\mu\nu}{}'(M_\nu)^{-1}\Delta\varphi_{\mu\nu}(R_{\mu\nu}^{m0}) \tag{29}$$

where $\Delta\varphi_{\mu\nu}$ is the Laplacian of the potential seen by $({}^{0}_{\nu})$th atom which results from its interactions with other atoms and M_ν is the mass of the νth atom. In the case of alkali halides, by the use of Poisson's equation, the Laplacian of that part of the potential arising from the electrostatic forces vanishes.[11,12] With this convient simplification one has to consider only the short-range interactions in the evaluation of $\langle\omega^2\rangle_{\mathrm{av}}$.

At absolute zero the lattice parameter is r_0. At temperature T°K, r_0 changes to $r_0+\delta r$. For cubic crystals the thermal expansion is isotropic. If we assume that the coefficient of thermal expansion is independent of temperature, then

$$\delta r=l_1kT\,, \tag{30}$$

where k is Boltzmann's constant and l_1 is a constant characteristic of the alkali halide. The thermal strain

$$\eta_{ij}^{\mathrm{th}}\delta_{ij}=\delta r/r_0\,, \tag{31}$$

δ_{ij}= Kronecker delta. We now impose the condition that the lattice be in equilibrium at this temperature. This is done by expanding the free energy given by (28) in powers of thermal strains and setting the linear term equal to zero. The condition of equilibrium reduces to

$$V_c\sum_{jl}C_{ik,jl}\eta_{jl}^{\mathrm{th}}-3skT\gamma_{ik}=0\,, \tag{32}$$

where

$$\gamma_{ik}=-\tfrac{1}{2}(\partial\ln\langle\omega^2\rangle_{\mathrm{av}}/\partial\eta_{ik}) \tag{33}$$

is the generalized Grüneisen constant, and $C_{ik,jl}$ are the second-order elastic coefficients. For cubic crystals $\gamma_{ik}=\delta_{ik}\gamma$. Then

$$\delta r/r_0=\eta_{11}^{\mathrm{th}}=(skT/V_c)(\text{bulk modulus})^{-1}\gamma\,. \tag{34}$$

The expressions for l_1 can now be easily written down. For NaCl-type crystals

$$l_1=-\frac{b}{2}\frac{[(2+2\rho_0-\rho_0^2)\varphi(r_0)+2\sqrt{2}(1+\sqrt{2}\rho_0-\rho_0^2)\varphi(r_0\sqrt{2})]}{[(\rho_0-2)\varphi(r_0)+2(\rho_0-\sqrt{2})\varphi(r_0\sqrt{2})][(\rho_0-2)\varphi(r_0)+4(\rho_0-\sqrt{2})\varphi(r_0\sqrt{2})]}\,, \tag{35}$$

where

$$\rho_0=r_0/b\quad\text{and}\quad\varphi(r)=A\exp(-r/b)\,.$$

For CsCl-type crystals

$$l_1=-r_0[(8/3)(2\rho_1+2\rho_1^2-\rho_1^3)\varphi(r_1)+\tfrac{3}{2}(2\rho_2+2\rho_2^2-\rho_2^3)\varphi(r_2)]Y^{-1}\,, \tag{36}$$

where

$$Y=[(8/3)(\rho_1^2-2\rho_1)\varphi(r_1)+\tfrac{3}{2}(\rho_2^2-2\rho_2)\varphi(r_2)][(8/3)(\rho_1^2-2\rho_1)\varphi(r_1)+2(\rho_2^2-2\rho_2)\varphi(r_2)]$$

and

$$r_1=r_0\sqrt{3}\,,\quad r_2=2r_0\,,\quad \rho_1=r_1/b\,,\quad \rho_2=r_2/b\,,\quad\text{and}\quad\varphi(r)=A\exp(-r/b)\,.$$

We now expand the vibrational part of the free energy of the deformed crystal up to cubic terms in the strains For the T.O.E. constants only f_3^{vib} is of interest.

$$\begin{aligned}f_3^{\mathrm{vib}}=(kT/24\omega_0^2)\sum_{\alpha\beta}\sum_{\alpha'\beta'}\sum_{\alpha''\beta''}\eta_{\alpha\beta}\eta_{\alpha'\beta'}\eta_{\alpha''\beta''}\Big\{&\sum_{\nu=1}^{2}\sum_{({}^{m}_{\mu})\neq({}^{0}_{\nu})}M_\nu^{-1}\xi_\alpha\xi_\beta\xi_{\alpha'}\xi_{\beta'}\xi_{\alpha''}\xi_{\beta''}D^3\Delta\varphi_{\mu\nu}(R)\big|_{R=r_{\mu\nu}^{m0}}\\ &-(2\omega_0^2)^{-1}\Big[\sum_{\nu\nu'}^{2}\sum_{({}^{m}_{\mu})\neq({}^{0}_{\nu})}\sum_{({}^{m'}_{\mu'})\neq({}^{0}_{\nu'})}M_\nu^{-1}M_{\nu'}^{-1}\xi_\alpha\xi_\beta\xi_{\alpha'}'\xi_{\beta'}'\xi_{\alpha''}'\xi_{\beta''}'D^2\Delta\varphi_{\mu'\nu'}(R)\big|_{R=r_{\mu'\nu'}^{m'0}}D\Delta\varphi_{\mu\nu}(R)\big|_{R=r_{\mu\nu}^{m0}}\Big]\\ &+(18\omega_0^4)^{-1}\Big[\sum_{\nu\nu'\nu''}^{2}\sum_{({}^{m}_{\mu})\neq({}^{0}_{\nu})}\sum_{({}^{m'}_{\mu'})\neq({}^{0}_{\nu'})}\sum_{({}^{m''}_{\mu''})\neq({}^{0}_{\nu''})}M_\nu^{-1}M_{\nu'}^{-1}M_{\nu''}^{-1}\xi_\alpha\xi_\beta\xi_{\alpha'}'\xi_{\beta'}'\xi_{\alpha''}''\xi_{\beta''}''\\ &\times D\Delta\varphi_{\mu\nu}(R)\big|_{R=r_{\mu\nu}^{m0}}D\Delta\varphi_{\mu'\nu'}(R)\big|_{R=r_{\mu'\nu'}^{m'0}}D\Delta\varphi_{\mu''\nu''}(R)\big|_{R=r_{\mu''\nu''}^{m''0}}\Big]\Big\}\,,\end{aligned} \tag{37}$$

where ω_0^2 is the mean-square frequency of the undeformed crystal ($\omega_0^2=\langle\omega^2\rangle$) and

$$\xi_i=\xi_{\mu\nu i}^{m0}\,,\quad \xi_i'=\xi_{\mu'\nu' i}^{m'0}\,,\quad \xi_i''=\xi_{\mu''\nu'' i}^{m''0}\,,$$

$$i=\alpha,\beta,\alpha',\beta',\alpha'',\beta''.$$

Here f^{vib} corresponds to the vibrational energy per unit cell. We rearrange the terms as follows:

$$\begin{aligned}f_3^{\mathrm{vib}}=\tfrac{1}{6}f_{111}^{\mathrm{vib}}(\eta_{11}^3+\eta_{22}^3+\eta_{33}^3)+\tfrac{1}{2}f_{112}^{\mathrm{vib}}\{&\eta_{11}^2(\eta_{22}+\eta_{33})\\ &+\eta_{22}^2(\eta_{33}+\eta_{11})+\eta_{33}^2(\eta_{11}+\eta_{22})\}+\text{etc.},\end{aligned} \tag{38}$$

where

$$f_{111}^{\mathrm{vib}}=\tfrac{1}{4}kT\{\Omega_3-\tfrac{1}{2}(\Omega_2)(\Omega_1)+(\Omega_1)^3/18\}\,, \tag{39}$$

TABLE II. Third-order elastic constants $C_{\alpha\beta\gamma}$ at 25°C. ($C_{\alpha\beta\gamma}$ are expressed in units of 10^{11} dyn/cm². b is in units of 10^{-8} cm.)

	b	C_{111}	C_{112}	C_{123}	C_{456}	C_{144}	C_{166}
LiF	0.3333	−59.77	−26.18	9.173	9.540	9.768	−26.40
	0.280	−135.3	−24.95	8.791	9.551	9.803	−25.42
	N	−207.0	−25.6	11.1	13.2	13.2	−24.2
LiCl	0.3333	−63.72	−9.059	3.142	3.617	3.741	−9.355
	0.303	−85.72	−8.592	2.945	3.620	3.742	−9.014
LiBr	0.3333	−59.85	−6.670	2.271	2.769	2.870	−6.980
	0.305	−77.21	−6.272	2.087	2.770	2.867	−6.699
LiI	0.3333	−53.86	−4.439	1.449	1.972	2.047	−4.765
	0.366	−41.14	−4.730	1.596	1.970	2.048	−4.964
NaF	0.3333	−66.71	−14.31	5.001	5.436	5.601	−14.57
	0.312	−85.63	−13.94	4.875	5.439	5.606	−14.29
	N	−71.4	−14.38	6.58	7.6	7.6	−12.8
NaCl	0.3333	−57.98	−5.837	1.970	2.476	2.568	−6.153
	0.288	−86.05	−5.220	1.637	2.479	2.563	−5.744
	N	−54.54	−6.88	2.69	3.55	3.54	−6.3
NaBr	0.3333	−53.83	−4.418	1.441	1.964	2.039	−4.744
	0.308	−66.23	−4.139	1.279	1.965	2.036	−4.566
NaI	0.3333	−47.81	−2.984	0.891	1.432	1.488	−3.322
	0.341	−45.12	−3.045	0.932	1.432	1.489	−3.358
KF	0.3333	−61.38	−7.461	2.563	3.053	3.162	−7.767
	0.310	−76.22	−7.134	2.418	3.055	3.161	−7.532
KCl	0.3333	−49.71	−3.386	1.047	1.583	1.645	−3.720
	0.309	−60.13	−3.152	0.892	1.584	1.641	−3.581
	N	−50.70	−4.58	1.48	2.27	2.27	−4.00
KBr	0.3333	−46.17	−2.675	0.770	1.315	1.367	−3.015
	0.303	−58.05	−2.412	0.568	1.316	1.362	−2.875
	N	−46.38	−3.88	1.11	1.865	1.865	−3.29
KI	0.3333	−41.03	−1.869	0.444	1.002	1.041	−2.214
	0.317	−46.14	−1.754	0.345	1.002	1.039	−2.160
	N	−47.10	−3.14	0.74	1.445	1.405	−2.56
RbF	0.3333	−57.98	−5.837	1.970	2.476	2.568	−6.153
	0.291	−83.83	−5.268	1.666	2.479	2.563	−5.774
RbCl	0.3333	−46.26	−2.689	0.775	1.320	1.372	−3.028
	0.283	−67.87	−2.219	0.388	1.322	1.363	−2.793
RbBr	0.3333	−42.81	−2.116	0.546	1.099	1.142	−2.460
	0.298	−55.40	−1.837	0.301	1.100	1.137	−2.382
RbI	0.3333	−25.80	−1.389	0.278	0.842	0.875	−1.737
	0.293	−50.72	−1.223	0.002	0.856	0.882	−1.744
CsCl	0.3333	−33.26	−4.267	−3.150	−3.441	−2.351	−3.949
	0.256	−37.57	−8.422	−7.486	−8.257	−5.713	−7.314
	N	−27.16	−3.76	−5.58	−4.8	−4.95	−3.06
CsBr	0.3333	−28.73	−4.010	−3.105	−3.406	−2.305	−3.662
	0.267	−31.74	−7.043	−6.272	−6.951	−4.710	−6.068
	N	−33.22	−3.88	−5.47	−4.7	−4.90	−3.295
CsI	0.3333	−22.96	−3.626	−2.975	−3.290	−2.174	−3.234
	0.263	−25.43	−6.437	−5.898	−6.637	−4.263	−5.325
	N	−19.08	−3.86	−5.11	−4.325	−4.6	−3.35

$$f_{112}{}^{\mathrm{vib}}=\tfrac{1}{4}kT\{\Omega_{2,1}-\tfrac{1}{3}(\Omega_{1,1})(\Omega_1)-\tfrac{1}{6}(\Omega_2)(\Omega_1)+(\Omega_1)^3/18\}, \quad (40)$$

$$f_{123}{}^{\mathrm{vib}}=\tfrac{1}{4}kT\{\Omega_{1,1,1}-\tfrac{1}{2}(\Omega_{1,1})(\Omega_1)+(\Omega_1)^3/18\}, \quad (41)$$

$$f_{456}{}^{\mathrm{vib}}=\tfrac{1}{4}kT\{\Omega_{1,1,1}\}, \quad (42)$$

$$f_{144}{}^{\mathrm{vib}}=\tfrac{1}{4}kT\{\Omega_{1,1,1}-\tfrac{1}{2}(\Omega_{1,1})(\Omega_1)\}, \quad (43)$$

$$f_{166}{}^{\mathrm{vib}}=\tfrac{1}{4}kT\{\Omega_{N,1}-\tfrac{1}{2}(\Omega_{1,1})(\Omega_1)\}, \quad (44)$$

and

$$\Omega_3=\omega_0{}^{-2}\sum{}' M_\nu{}^{-1}\xi_1{}^6D^3\Delta\varphi_{\mu\nu}|_{R=r_{\mu\nu}{}^{m0}}, \quad (45)$$

$$\Omega_{2,1}=\omega_0{}^{-2}\sum{}' M_\nu{}^{-1}\xi_1{}^4\xi_2{}^2D^3\Delta\varphi_{\mu\nu}|_{R=r_{\mu\nu}{}^{m0}}, \quad (46)$$

$$\Omega_{1,1,1}=\omega_0{}^{-2}\sum{}' M_\nu{}^{-1}\xi_1{}^2\xi_2{}^2\xi_3{}^2D^3\Delta\varphi_{\mu\nu}|_{R=r_{\mu\nu}{}^{m0}}, \quad (47)$$

$$\Omega_2=\omega_0{}^{-2}\sum{}' M_\nu{}^{-1}\xi_1{}^4D^2\Delta\varphi_{\mu\nu}|_{R=r_{\mu\nu}{}^{m0}}, \quad (48)$$

$$\Omega_{1,1}=\omega_0{}^{-2}\sum{}' M_\nu{}^{-1}\xi_1{}^2\xi_2{}^2D^2\Delta\varphi_{\mu\nu}|_{R=r_{\mu\nu}{}^{m0}}, \quad (49)$$

$$\Omega_1=\omega_0{}^{-2}\sum{}' M_\nu{}^{-1}\xi_1{}^2D\Delta\varphi_{\mu\nu}|_{R=r_{\mu\nu}{}^{m0}}. \quad (50)$$

We have evaluated Ω_3, $\Omega_{2,1}$, $\Omega_{1,1,1}$, Ω_2, $\Omega_{1,1}$, and Ω_1 in the approximation of second-nearest-neighbor interactions.

For NaCl-type crystals we get

$$\Omega_3=\{2\varphi(r_0)[30\rho_0+30\rho_0{}^2+9\rho_0{}^3-\rho_0{}^4-\rho_0{}^5]+\tfrac{1}{2}\varphi(r_0\sqrt{2})\times[30\rho_2+30\rho_2{}^2+9\rho_2{}^3-\rho_2{}^4-\rho_2{}^5]\}\Lambda, \quad (51)$$

$$\Omega_{2,1}=[\tfrac{1}{4}\varphi(r_0\sqrt{2})(30\rho_2+30\rho_2{}^2+9\rho_2{}^3-\rho_2{}^3-\rho_2{}^5)]\Lambda, \quad (52)$$

$$\Omega_{1,1,1}=0, \quad (53)$$

$$\Omega_2=[2\varphi(r_0)(-6\rho_0-6\rho_0{}^2-\rho_0{}^3+\rho_0{}^4)+\varphi(r_0\sqrt{2})(-6\rho_2-6\rho_2{}^2-\rho_2{}^3+\rho_2{}^4)]\Lambda, \quad (54)$$

$$\Omega_{1,1}=\tfrac{1}{2}\varphi(r_0\sqrt{2})[-6\rho_2-6\rho_2{}^2-\rho_2{}^3+\rho_2{}^4]\Lambda, \quad (55)$$

$$\Omega_1=[2\varphi(r_0)(2\rho_0+2\rho_0{}^2-\rho_0{}^3)+2\varphi(r_0\sqrt{2})(2\rho_2+2\rho_2{}^2-\rho_2{}^3)]\Lambda, \quad (56)$$

where

$$\Lambda=[\varphi(r_0)(\rho_0{}^2-2\rho_0)+(r_0\sqrt{2})(\rho_2{}^2-2\rho_2)]^{-1}, \quad (57)$$

$$\rho_0=r_0/b, \; \rho_2=(r_0\sqrt{2})/b, \text{ and } \varphi(r)=A\exp(-r/b). \quad (58)$$

For CsCl-type crystals

$$\Omega_3=[(8\varphi(r_1)/81)(30\rho_1+30\rho_1{}^2+9\rho_1{}^3-\rho_1{}^4-\rho_1{}^5)+\tfrac{1}{2}\varphi(r_2)(30\rho_2+30\rho_2{}^2+9\rho_2{}^3-\rho_2{}^4-\rho_2{}^5)]Z, \quad (59)$$

$$\Omega_{2,1}=[(8\varphi(r_1)/81)\times(30\rho_1+30\rho_1{}^2+9\rho_1{}^3-\rho_1{}^4-\rho_1{}^5)]Z, \quad (60)$$

$$\Omega_{1,1,1}=\Omega_{2,1}, \quad (61)$$

$$\Omega_2=[(8/27)\varphi(r_1)(-6\rho_1-6\rho_1{}^2-\rho_1{}^3+\rho_1{}^4)+\tfrac{1}{2}\varphi(r_2)(-6\rho_2-6\rho_2{}^2-\rho_2{}^3+\rho_2{}^4)]Z, \quad (62)$$

$$\Omega_{1,1}=[(8/27)\varphi(r_1)(-6\rho_1-6\rho_1{}^2-\rho_1{}^3+\rho_1{}^4)]Z, \quad (63)$$

$$\Omega_1=[(8/9)\varphi(r_1)(2\rho_1+2\rho_1{}^2-\rho_1{}^3)+\tfrac{1}{2}\varphi(r_2)(2\rho_2+2\rho_2{}^2-\rho_2{}^3)]Z, \quad (64)$$

where

$$Z=[(4/9)\varphi(r_1)(\rho_1{}^2-2\rho_1)+\tfrac{1}{4}\varphi(r_2)(\rho_2{}^2-2\rho_2)]^{-1}, \quad (65)$$

and r_1, r_2, ρ_1, ρ_2, and $\varphi(r)$ have the same meaning as defined in Eq. (36).

The free energy per unit cell for an alkali halide crystal can be written as

$$F_c=V_cU+f^{\mathrm{vib}}, \quad (66)$$

where

$$f^{\mathrm{vib}}=3kT\ln(\hbar^2\langle\omega^2\rangle_{\mathrm{av}}/k^2T^2). \quad (67)$$

The T.O.E. constants at temperature T with lattice parameter $r=r_0+\delta r$ can be written as

$$C_{\alpha\beta\gamma}(T,r)=C_{\alpha\beta\gamma}{}^0(r_0)+\delta r(\partial C_{\alpha\beta\gamma}{}^0/\partial r)_{r=r_0}+f_{\alpha\beta\gamma}{}^{\mathrm{vib}}/V_c, \quad (68)$$

$$=C_{\alpha\beta\gamma}{}^0+a_{\alpha\beta\gamma}T, \quad (69)$$

where

$$a_{\alpha\beta\gamma}=[l_1k(\partial C_{\alpha\beta\gamma}{}^0/\partial r)_{r=r_0}+f_{\alpha\beta\gamma}{}^{\mathrm{vib}}/TV_c]. \quad (70)$$

The values of $a_{\alpha\beta\gamma}$ have been calculated and these are listed in Table I. Once the values of $a_{\alpha\beta\gamma}$ are determined, it is easy to calculate the room temperature values of $C_{\alpha\beta\gamma}$ and these are listed in Table II. Nran'yan's[8] values of $C_{\alpha\beta\gamma}$ are also listed for comparison.

TABLE III. Second-order elastic constants of alkali halides in units of 10^{11} dyne/cm^2.

	C_{11}	C_{12}	C_{44}	Reference
LiF	11.049	4.435	6.368	[a,b]
LiCl	4.94	2.28	2.46	[b]
LiBr	3.94	1.87	1.93	[b]
LiI	2.85	1.40	1.35	[c]
NaF	9.450	2.129	2.822	[a,b]
NaCl	4.792	1.151	1.278	[d]
NaBr	4.01	1.09	0.99	[b]
NaI	3.03	0.88	0.74	[b,e,f]
KF	6.56	1.46	1.25	[b]
KCl	3.981	0.610	0.632	[d]
KBr	3.357	0.457	0.508	[g]
KI	2.677	0.405	0.369	[g]
RbF	5.53	1.40	0.93	[b]
RbCl	3.63	0.62	0.47	[b]
RbBr	3.15	0.493	0.384	[b,h]
RbI	2.54	0.407	0.276	[b,h]
CsCl	3.64	0.92	0.80	[i]
CsBr	3.091	0.841	0.747	[h,i,j,k]
CsI	2.434	0.636	0.632	[h,i]

[a] See Ref. 5.
[b] S. Haussühl, Z. Physik **159**, 223 (1960).
[c] S. Haussühl, Z. Krist. **110**, 1 (1958).
[d] See Ref. 7.
[e] R. Dalven and C. W. Garland, J. Chem. Phys. **30**, 346 (1959).
[f] R. N. Claythor and B. J. Marshall, Phys. Rev. **120**, 332 (1960).
[g] See Ref. 6.
[h] K. Reinitz, Phys. Rev. **123**, 1615 (1961).
[i] S. Haussühl, Acta Cryst. **13**, 685 (1960).
[j] B. J. Marshall, Phys. Rev. **121**, 72 (1961).
[k] K. M. Koliwad (private communication).

TABLE IV. Pressure derivatives of the second-order elastic constants ($dC_{\alpha b}/dp$ are dimensionless. b is in units of 10^{-8} cm).

	b	$\frac{dC_{11}}{dp}$	$\frac{dC_{12}}{dp}$	$\frac{dC_{44}}{dp}$	$\frac{dC'}{dp}$	$\frac{dB}{dp}$	Reference
LiF	0.3333	4.07	2.95	0.84	0.56	3.21	
	0.280	7.74	2.84	0.74	2.45	4.27	
				1.38	3.62	5.14	Expt. (5)
		11.41	2.79	0.45	4.31	5.66	*N* (8)
LiCl	0.3333	7.10	2.34	0.32	2.38	3.93	
	0.303	9.32	2.26	0.24	3.53	4.61	
LiBr	0.3333	8.02	2.20	0.19	2.91	4.14	
	0.305	10.17	2.12	0.12	4.03	4.80	
LiI	0.3333	9.60	2.07	0.09	3.77	4.58	
	0.366	7.45	2.14	0.16	2.65	3.91	
NaF	0.3333	5.26	2.57	0.51	1.35	3.47	
	0.312	6.59	2.52	0.47	2.03	3.88	
				0.205	4.79	5.18	Expt. (5)
		5.62	2.46	0.11	1.58	3.51	*N* (8)
NaCl	0.3333	8.14	2.21	0.19	2.97	4.18	
	0.288	11.93	2.08	0.08	4.93	5.36	
		12.18	2.25	0.19	4.97	5.56	Expt. (3)
		7.98	2.40	0.22	2.78	4.25	*N* (8)
NaBr	0.3333	8.48	2.02	0.043	3.23	4.17	
	0.308	10.39	2.09	−0.013	4.15	4.83	
NaI	0.3333	9.59	1.88	−0.08	3.86	4.45	
	0.341	9.06	1.89	−0.06	3.58	4.35	
KF	0.3333	6.36	2.15	0.17	2.11	3.56	
	0.310	7.85	2.10	0.12	2.88	4.02	
KCl	0.3333	9.29	1.98	−0.01	3.65	4.42	
	0.309	11.01	1.92	−0.06	4.54	4.95	
		12.52	1.38	−0.38	5.57	5.09	Expt. (3)
		9.74	2.36	−0.02	3.69	4.82	*N* (8)
KBr	0.3333	10.28	1.97	−0.03	4.16	4.74	
	0.303	12.94	1.90	−0.09	5.57	5.91	
		12.96	1.591	−0.328			Expt. (6)
		10.89	2.45	−0.014	4.23	5.26	*N* (8)
KI	0.3333	10.73	1.78	−0.16	4.48	4.76	
	0.317	12.09	1.74	−0.19	5.18	5.19	
		13.66	2.096	−0.241			Expt. (6)
		13.14	2.40	−0.07	5.37	5.98	*N* (8)
RbF	0.3333	6.70	2.00	0.06	2.35	3.56	
	0.291	9.66	1.90	−0.03	3.88	4.49	
RbCl	0.3333	8.86	1.82	−0.13	3.52	4.16	
	0.283	13.10	1.70	−0.23	5.70	5.50	
RbBr	0.3333	9.61	1.77	−0.18	3.92	4.39	
	0.298	12.52	1.70	−0.22	5.41	5.31	
RbI	0.3333	6.54	1.59	−0.33	2.47	3.57	
	0.293	13.66	1.58	−0.33	6.04	5.60	
CsCl	0.3333	5.96	2.96	0.72	1.50	3.96	
	0.256	8.27	5.27	2.57	1.50	6.27	
		4.66	3.22	0.87	0.72	3.70	*N* (8)
CsBr	0.3333	6.05	3.15	0.86	1.45	4.12	
	0.267	7.95	5.09	2.37	1.43	6.04	
		6.94	3.60	1.25	1.67	4.71	*N* (8)
CsI	0.3333	6.50	3.59	1.16	1.46	4.57	
	0.263	8.68	5.89	2.85	1.39	6.82	
		5.57	4.29	1.88	0.64	4.72	*N* (8)

IV. PRESSURE DERIVATIVES OF THE SECOND-ORDER ELASTIC CONSTANTS

When a cubic crystal is subjected to hydrostatic pressure, the symmetry of the crystal is preserved. Birch[1] has calculated the expressions for the effective second-order elastic constants $C_{\alpha\beta}'$ that are needed to relate the additional stresses with the additional infinitesimal strains. The expressions for C_{11}', C_{12}', and C_{44}' are given below. The $C_{\alpha\beta\gamma}$ are those defined by Brugger.[9]

$$C_{11}'=C_{11}+\eta(2C_{11}+2C_{12}+C_{111}+2C_{112})\,, \tag{71}$$

$$C_{12}'=C_{12}+\eta(-C_{11}-C_{12}+C_{123}+2C_{112})\,, \tag{72}$$

$$C_{44}'=C_{44}+\eta(C_{11}+2C_{12}+C_{44}+C_{144}+2C_{166})\,, \tag{73}$$

where

$$\eta=-p/(C_{11}+2C_{12})\,.$$

Hence the pressure derivatives of the second-order elastic constants are

$$\frac{dC_{11}'}{dp}=-\frac{2C_{11}+2C_{12}+C_{111}+2C_{112}}{C_{11}+2C_{12}}\,, \tag{74}$$

$$\frac{dC_{12}'}{dp}=-\frac{[-C_{11}-C_{12}+C_{123}+2C_{112}]}{C_{11}+2C_{12}}\,, \tag{75}$$

$$\frac{dC_{44}'}{dp}=-\frac{C_{11}+2C_{12}+C_{44}+C_{144}+2C_{166}}{C_{11}+2C_{12}}\,, \tag{76}$$

$$\frac{dC'}{dp}=-\frac{[3C_{11}+3C_{12}+C_{111}-C_{123}]}{2[C_{11}+2C_{12}]}\,, \tag{77}$$

$$\frac{dB}{dp}=-\frac{C_{111}+6C_{112}+2C_{123}}{3(C_{11}+2C_{12})}\,, \tag{78}$$

TABLE V. Theoretical values of T.O.E. constants and the experimental values of $C_{\alpha\beta\gamma}$ determined by Chang (Ref. 7) for NaCl and KCl crystals. ($C_{\alpha\beta\gamma}$ are in units of 10^{11} dyne/cm^2.)

	NaCl			KCl		
	Theory			Theory		
	$b=0.3333A$	$b=0.288A$	Expt.	$b=0.3333A$	$b=0.310A$	Expt.
$C_{111}+2C_{112}$	-69.65	-96.49	-99.1	-56.48	-66.43	-74.4
$C_{111}-C_{123}$	-59.95	-87.69	-91.0	-50.76	-61.02	-71.5
C_{456}	2.48	2.48	2.71	1.58	1.58	1.18
C_{144}	2.57	2.56	2.58	1.65	1.64	1.27
C_{166}	-6.15	-5.74	-6.11	-3.72	-3.58	-2.45

where

$$C'=\tfrac{1}{2}(C_{11}'-C_{12}') \quad \text{and} \quad B=\tfrac{1}{3}(C_{11}'+2C_{12}').$$

The room-temperature and atmospheric-pressure data on the second-order elastic constants are listed in Table III. The values of $C_{\alpha\beta\gamma}$ given in Table II and the second-order elastic constants given in Table III have been used to calculate the pressure derivatives of the second-order elastic constants for different alkali halides and these are listed in Table IV. Pressure derivatives calculated by using Nran'yan's[8] values of $C_{\alpha\beta\gamma}$ are listed in Table IV for comparison.

In Table V we have listed the experimental values of Chang[7] of $C_{\alpha\beta\gamma}$ for NaCl and KCl crystals and the calculated values of $C_{\alpha\beta\gamma}$ for these crystals.

V. DISCUSSION

We have calculated the third-order elastic (T.O.E.) constants of the alkali halide crystals in the framework of the Born model. We have included the short-range repulsive interactions up to second nearest neighbors. The temperature variation of these constants is calculated by following the procedure developed by Leibfried and Hahn.[11,12] We find that C_{123}, C_{456}, and $C_{144}>0$, and C_{111}, C_{112}, and $C_{166}<0$ for NaCl-type crystals whereas all the six T.O.E. constants for CsCl-type crystals are negative. It is interesting to note that the ratio $|C_{111}|/C_{11}$ varies roughly from 5 to 15 as one passes from fluorides to iodides. The absolute values of the rest of the T.O.E. constants are of the same order of magnitude as that of C_{11} for those crystals. Tables I and II show that the values of the $C_{\alpha\beta\gamma}{}^0$ and $a_{\alpha\beta\gamma}$ are sensitive to the value of the repulsive parameter b. Within the framework of our model, for NaCl-type crystals $C_{123}{}^0$ does not depend on the short-range interactions at all, whereas $C_{111}{}^0$ is very sensitive to the value of b. For CsCl-type crystals, $C_{112}{}^0$ and $C_{123}{}^0$ are more sensitive to the value of b as compared to $C_{111}{}^0$.

For the central force model chosen for the alkali halides, the Cauchy relations for the T.O.E. constants ($C_{112}{}^0=C_{166}{}^0$; $C_{123}{}^0=C_{456}{}^0=C_{144}{}^0$) are satisfied at 0°K. The failure of the Cauchy relations at a finite temperature T is due to the vibrational part of the energy. The temperature coefficients $a_{\alpha\beta\gamma}$ of the T.O.E. constants are all positive for CsCl-type crystals, whereas a_{111}, a_{112}, and $a_{166}>0$, and a_{123}, a_{456}, and $a_{144}<0$ for NaCl-type crystals. Our calculations indicate that, for NaCl-type crystals, C_{123} is most sensitive to temperature followed by C_{112} and other $C_{\alpha\beta\gamma}$. For a temperature difference of 300°K, C_{123} changes by about 30% and C_{112} changes by about 10%. For the CsCl-type crystals we find that C_{144} is most sensitive to temperature followed by C_{166}, C_{112}, and other $C_{\alpha\beta\gamma}$. For a temperature change of 300°K, there is a change in the value of C_{144} of about 40%. For the same temperature difference the other T.O.E. constants change by about 20%. Our conclusions differ from those arrived at by Nran'yan.[8] He finds that a_{112} and a_{123} are negative and that the other $a_{\alpha\beta\gamma}$ are positive for the CsCl-type crystals, contrary to our results, namely, that all $a_{\alpha\beta\gamma}$ are positive for the CsCl-type crystals. His values of C_{456} and C_{144} for NaCl-type crystals are in error because of an error in the sign of a_{456} and a_{144}. At the present time no experimental data are available to compare our conclusions with on the temperature variation of these T.O.E. constants. We have compared the experimental values of Chang[7] with our calculated values of $C_{\alpha\beta\gamma}$ for NaCl and KCl crystals The numerical agreement is considered to be satisfactory.

It is gratifying to note however that the pressure derivatives calculated using the values of T.O.E. constants from Table II, compare fairly well with the experiments. We note that (dC_{11}/dp) and (dC_{12}/dp) are positive whereas (dC_{44}/dp) is positive or negative depending on the crystal system. Our calculations indicate that C_{44} increases with hydrostatic pressure for the CsCl-type crystals and for LiF to NaCl crystals. The experiments on LiF, NaF, and NaCl support our conclusions. For NaBr we find that $(dC_{44}/dp)>0$ for $b=0.3333$ A and $(dC_{44}/dp)<0$ for $b=0.308$ A. For NaI $(dC_{44}/dp)<0$. For KF, C_{44} increases with pressure. From KCl to RbI, C_{44} decreases with pressure. RbF is another exception for which $(dC_{44}/dp)>0$ for $b=3333$ A and $(dC_{44}/dp)<0$ for $b=0.291$ A. We believe that the second set of values of the repulsive parameter b, used from Tosi's[15] paper, has to be weighed heavily as compared to the flat value of $b=0.3333$ A. If this premise is accepted, then we conclude that for NaBr to RbI, with the exception of KF, C_{44} decreases with pressure. These conclusions are consistent with the available experimental data on KCl, KBr, and KI crystals. The inclusion of the second-nearest-neighbor interactions has improved the agreement between theory and experiment. (Compare Nran'yan's values. He has included the nearest-neighbor interactions only.) It is true, however, that the agreement between the theoretical and experimental values of $(dC_{\alpha\beta}/dp)$ falls short of something that is desired. This is not considered to be too serious because we have used only two parameters b and r_0 to calculate the T.O.E. constants and have neglected the polarizability of the ions, van der Waal's forces, and many-body forces.

ACKNOWLEDGMENTS

The author wishes to thank Dr. A. L. Ruoff for his interest and encouragement in carrying out this work. It is a pleasure to thank R. C. Lincoln for his cheerful assistance in carrying out the computations, and Dr. Z. P. Chang, Dr. P. J. Reddy, and K. M. Koliwad, for making their experimental data available to me prior to publication. The opportunity to see a preprint of a paper by Dr. Mario P. Tosi is gratefully acknowledged.

APPENDIX

A convenient elementary cell for CsCl structure is a cubic cell of edge length $2r_0$. The positive (or negative) ion is located at the center of the cube and eight negative (or positive) ions are located at the corners. To calculate the Madelung constant and other lattice sums by Evjen's method, the choice of a larger neutral cube turns out to be an inconvenient one. An appropriate choice of a cell, for such calculations, is a parallelepiped whose adjacent edges are lines joining the center of the cubic cell to any three adjacent corners of the cube, i.e., the lines joining the origin (0,0,0) to points (1,1,1), $(1,\bar{1},1)$, and $(1,1,\bar{1})$. Distances are measured in units of r_0. For a further discussion on the choice of such a cell, the reader may refer to the articles by Krishnan and Roy[16] and Roy.[17] Lattice sums of the following type are of interest:

$$S_N^{(n,n_2,n_3)} = \sum_{l_1,l_2,l_3} (-1)^{l_1+l_2+l_3} \frac{l_1^{2n_1} l_2^{2n_2} l_3^{2n_3}}{(l_1^2+l_2^2+l_3^2)^{N/2}},$$

where n_1, n_2, n_3, and N are positive integers and $n_1+n_2+n_3 \leq \frac{1}{2}(N-1)$; l_1, l_2, and l_3 form an unmixed set of all possible (positive or negative) integers. In this notation Madelung's constant $= -S_1^{(0)}$. To calculate the lattice sums, we proceed as follows. We consider a larger neutral parallelepiped, with N^3 elementary parallelepipeds, with a positive ion at the center. We calculate the sum of this series. We choose a successively larger parallelepiped by increasing N in steps of 1. We find that the series converges fairly rapidly. We list below the lattice sums obtained in this manner for $N=11$. The sums are reliable up to 0.001%.

$S_1^{(0)} = -1.017678$
$S_3^{(0)} = -0.642941$
$S_5^{(0)} = -0.298164$
$S_7^{(0)} = -0.119704$
$S_9^{(0)} = -0.044633$
$S_5^{(2)} = 0.354190$
$S_7^{(2)} = 0.075054$
$S_9^{(2)} = 0.006960$
$S_7^{(3)} = 0.540901$
$S_9^{(3)} = 0.163790$
$S_9^{(4)} = 0.640849$

$S_5^{(1,1)} = -0.346708$
$S_7^{(1,1)} = -0.144684$
$S_9^{(1,1)} = -0.053174$
$S_7^{(2,1)} = -0.093356$
$S_9^{(2,1)} = -0.044368$
$S_9^{(2,2)} = -0.009950$
$S_9^{(3,1)} = -0.049974$
$S_7^{(1,1,1)} = -0.159996$
$S_9^{(1,1,1)} = -0.055948.$

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[16] K. S. Krishnan and S. K. Roy, Phys. Rev. **87**, 581 (1952).
[17] S. K. Roy, Can. J. Phys. **32**, 509 (1954).