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Temperature dependence of the elastic constants of alkali halides

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The pseudopotential theory of Ruffa has been used to calculate the temperature dependence of the elastic constants of alkali halides crystallizing in CsCl-like and NaCl-like structures, using the Lundquist potential, and taking the thermal expansion as the experimental input. This potential contains the many-body interactions, which explains the violation of Cauchy's relations even at 0°K. The agreement between these calculated results and the available experimental data is much better than that of any other recent theories. In the case of the NaCl-like structure, our present model for the first time predicts the anomalous increase in C_{12} with temperature.

I. INTRODUCTION

Much theoretical work has been done on the temperature dependence of the elastic constants of alkali halides with two-body potentials,[1-5] but these potentials fail to explain the experimentally observed violation of Cauchy's relations ($C_{12}=C_{44}$). Earlier, Puri and Verma[6] explained the violation of Cauchy's relations even at 0 °K, through the Lundquist potential model with many-body interactions. The calculation of many-body interactions in the above theories[1-5] is very much involved. Recently Ruffa[7] has proposed the pseudopotential theory to explain the temperature dependence of the elastic shear moduli of cubic metals and we find that this pseudopotential theory is straightforward to work with many-body interactions in alkali halides. In the present work we use Ruffa's theory to calculate the temperature dependence of the elastic constants of alkali halides crystallizing in CsCl-like and NaCl-like structures using the Lundquist potential.[8,9] Care has been taken to use the equilibrium condition in accordance with lattice vibrations. Our results not only explain the violation of Cauchy's relation but also explain the anomalous temperature dependence of C_{12} in NaCl-like structures.

II. THEORY

The expressions for the elastic constants (of second order) determined by Puri *et al.*[8] and Garg *et al.*[9] with only nearest-neighbors repulsive interactions may be written

$$C_{11}=\frac{e^2}{4r^4}\left(0.7010\epsilon[\epsilon+16f(r)]+\frac{A(r)+2B(r)}{6}+3.1336\epsilon r\frac{\partial f}{\partial r}\right), \tag{1}$$

$$C_{12}=\frac{e^2}{4r^4}\left(-0.4636\epsilon[\epsilon+16f(r)]+\frac{A(r)}{6}+3.1336\epsilon r\frac{\partial f}{\partial r}\right), \tag{2}$$

$$C_{44}=\frac{e^2}{4r^4}\left(-0.1244\epsilon[\epsilon+16f(r)]+\frac{A(r)}{6}+B(r)\right) \tag{3}$$

for CsCl-like structure;

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

$$C_{12}=\frac{e^2}{4r^4}\left(3.721\epsilon[\epsilon+12f(r)]+2B(r)+9.3204\epsilon r\frac{\partial f}{\partial r}\right), \tag{5}$$

$$C_{44}=\frac{e^2}{4r^4}\{0.8085\epsilon[\epsilon+12f(r)]-\tfrac{1}{2}B(r)\} \tag{6}$$

for NaCl-like structures. The equilibrium condition is given by

$$B(r)=-0.3392\epsilon[\epsilon+16f(r)] \tag{7}$$

for CsCl-like structures and

$$B(r)=-1.165\epsilon[\epsilon+12f(r)] \tag{8}$$

for NaCl-like structures.

We see that in determining the equilibrium conditions (7) and (8) we have not taken into account the concept of lattice vibrations, and hence Eqs. (7) and (8) are satisfied only when $r=r_0$, r_0 being the position of potential minima. At a certain temperature the distance between nearest neighbors is no longer the position of potential minima. Therefore equilibrium conditions (7) and (8) are not obeyed at certain temperatures other than 0 °K.

TABLE I. Input data at absolute zero or extrapolated value at absolute zero from low-temperature data.

	r_0 (10^{-8} cm)	C_{11} (10^{11} dyn/cm^2)	C_{12} (10^{11} dyn/cm^2)	C_{44} (10^{11} dyn/cm^2)
CsCl	3.5150[a]	4.112[b]	1.196[b]	1.125[b]
CsBr	3.6645[c]	3.417[b]	0.955[b]	1.033[b]
CsI	3.9018[c]	3.152[b]	1.040[b]	0.898[b]
LiCl	2.5467[d]	5.940[b]	2.010[b]	2.695[b]
LiBr	2.7136[d]	4.762[b]	1.620[e]	2.057[b]
NaF	2.3032[d]	11.340[b]	2.598[b]	2.459[b]
NaCl	2.7865[f]	5.745[g]	0.980[g]	1.316[b]
NaBr	2.9567[d]	4.964[b]	1.286[b]	1.069[b]
NaI	3.1967[a]	3.700[h]	0.816[b]	0.781[b]
KF	2.6568[d]	7.712[b]	1.590[b]	1.296[b]
KCl	3.1115[f]	4.940[i]	0.664[b]	0.662[b]
KBr	3.2580[j]	4.250[k]	0.510[k]	0.583[b]
KI	3.4840[j]	3.499[b]	0.299[b]	0.389[b]
RbCl	3.2564[f]	4.525[b]	0.675[b]	0.511[b]
RbI	3.6220[j]	3.181[b]	0.321[b]	0.283[b]

[a] Leibfried and Ludwig (Ref. 1).
[b] Botaki, Gyrbu, and Sharko (Ref. 10).
[c] Bijanki and Hardy (Ref. 11).
[d] Rapp and Merchant (Ref. 12).
[e] Marshall and Cleavelin (Ref. 13).
[f] Hardy and Karo (Ref. 14).
[g] Durand (Ref. 15).
[h] Claythor and Marshall (Ref. 16).
[i] Norwood and Briscoe (Ref. 17).
[j] Sarkar and Sengupta (Ref. 18).
[k] Galt (Ref. 19).

According to the theory of Ruffa,[7] we have

$$r_0 = r_n(1 - x), \tag{9}$$

where r_n is the distance between nearest neighbors and x is the fractional change in the position of potential minima and nearest neighbors. x is related to the linear-thermal-expansion coefficient α as follows:

$$\alpha = \frac{1}{1-x}\frac{\partial x}{\partial T}. \tag{10}$$

Using relations (9) and (10), the temperature derivatives of the elastic constants are given as

TABLE II. Calculated values of parameters from extrapolated values at absolute zero.

	A_0	B_0	$[-10^2 f(r_0)]$	$10^2 r_0(\partial f/\partial r_0)$	r_0/ρ
CsCl	4.2590	−0.2770	1.1462	0.6672	15.3758
CsBr	4.4213	−0.2763	1.1596	−0.8659	16.0039
CsI	4.9066	−0.3046	0.6375	2.0260	16.1083
LiCl	12.0714	−1.6484	−3.4578	−5.3673	7.3231
LiBr	12.0097	−1.6218	−3.2666	−4.4135	7.4058
NaF	9.8865	−1.0061	1.1368	0.7285	9.8267
NaCl	11.4270	−1.1536	0.0813	−3.7733	9.9052
NaBr	11.5113	−1.1880	−0.1643	3.0892	9.6900
NaI	11.8480	−1.1859	−0.1493	0.6808	9.9910
KF	10.5361	−0.9389	1.6176	2.7284	11.2221
KCl	11.8316	−0.9022	1.8797	0.0271	13.1139
KBr	12.6470	−0.9551	1.5014	−1.5320	13.2415
KI	12.8370	−0.8334	2.3722	−2.4699	15.4040
RbCl	11.9220	−0.8178	2.4838	3.3623	14.5781
RbI	12.4989	−0.7082	3.2675	1.2182	17.6482

$$\frac{\partial C_{11}}{\partial T}=-\frac{e^2}{4r_0^4}\left(2.804\epsilon[\epsilon+16f(r_0)]+\frac{A_0(1+r_0/\rho)+2B_0(2+r_0/\rho)}{6}+12.5344\epsilon r_0\frac{\partial f}{\partial r}\bigg|_0\right)(1-x)^3\frac{\partial x}{\partial T}, \tag{11}$$

$$\frac{\partial C_{12}}{\partial T}=-\frac{e^2}{4r_0^4}\left(-1.8543\epsilon[\epsilon+16f(r_0)]+\frac{A_0(1+r_0/\rho)}{6}+12.5344\epsilon r_0\frac{\partial f}{\partial r}\bigg|_0\right)(1-x)^3\frac{\partial x}{\partial T}, \tag{12}$$

$$\frac{\partial C_{44}}{\partial T}=-\frac{e^2}{4r_0^4}\left[-0.4975\epsilon[\epsilon+16f(r_0)]+\frac{A_0(1+r_0/\rho)}{6}+B_0\left(2+\frac{r_0}{\rho}\right)\right](1-x)^3\frac{\partial x}{\partial T}, \tag{13}$$

for CsCl-like structures;

$$\frac{\partial C_{11}}{\partial T}=-\frac{e^2}{4r_0^4}\left[-20.228\epsilon[\epsilon+12f(r_0)]+A_0\left(1+\frac{r_0}{\rho}\right)+37.2816\epsilon r_0\frac{\partial f}{\partial r}\bigg|_0\right](1-x)^3\frac{\partial x}{\partial T}, \tag{14}$$

$$\frac{\partial C_{12}}{\partial T}=-\frac{e^2}{4r_0^4}\left[14.884\epsilon[\epsilon+12f(r_0)]+2B_0\left(2+\frac{r_0}{\rho}\right)+37.2816\epsilon r_0\frac{\partial f}{\partial r}\bigg|_0\right](1-x)^3\frac{\partial x}{\partial T}, \tag{15}$$

$$\frac{\partial C_{44}}{\partial T}=-\frac{e^2}{4r_0^4}\left[3.234\epsilon[\epsilon+12f(r_0)]-\frac{B_0(2+r_0/\rho)}{2}\right](1-x)^3\frac{\partial x}{\partial T} \tag{16}$$

for NaCl-like structures.

Using above derivatives the elastic constants at any temperature may be given as

$$(C_{11})_T=(C_{11})_0\left(1-\alpha_{11}(1-2x)\int_0^T \alpha\, dT\right), \tag{17}$$

$$(C_{12})_T=(C_{12})_0\left(1-\alpha_{12}(1-2x)\int_0^T \alpha\, dT\right), \tag{18}$$

$$(C_{44})_T=(C_{44})_0\left(1-\alpha_{44}(1-2x)\int_0^T \alpha\, dT\right), \tag{19}$$

where the indices 0 and T represent the values at 0 °K and T °K, and α_{ij} are given as

$$\alpha_{ij}=\frac{\partial C_{ij}}{\partial T}\bigg/(C_{ij})_0(1-x)^3\frac{\partial x}{\partial T}. \tag{20}$$

III. CALCULATIONS

The parameters A_0, B_0, $f(r_0)$, and $r_0\,\partial f/\partial r_0$ are determined for both the structures by the expressions for second-order elastic constants and the equilibrium conditions [Eqs. (1)–(8)] from the ex-

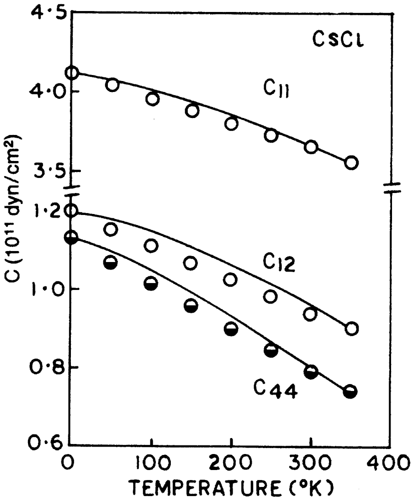

FIG. 1. Temperature dependence of the elastic constants of CsCl: ○, C_{11} and C_{12}; ◒, C_{44} according to Botaki, Gyrbu, and Sharko; ——, calculated by the present model.

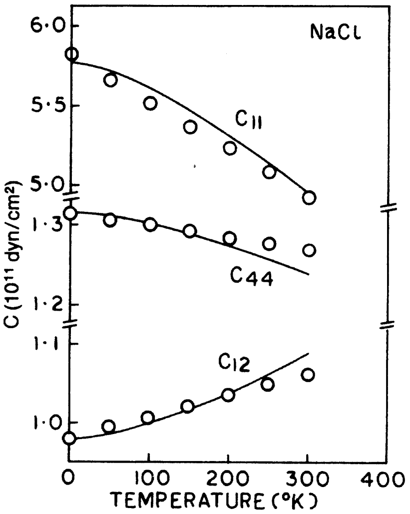

FIG. 2. Temperature dependence of the elastic constants of NaCl: ○, C_{11} according to Haussuhl; ○, C_{12} according to the temperature derivatives of Haussuhl; and ○, C_{44} according to Botaki, Gyrbu, and Sharko; ——, calculated by the present model.

TABLE III. Calculated values of the coefficients C_1 of the linear fitted equation ($C=C_0+C_1T$), where the C_0 are from Table I, along with available theoretical and experimental results.

	C_{11} (10^8 dyn/cm^2 °K)	C_{12} (10^8 dyn/cm^2 °K)	C_{44} (10^8 dyn/cm^2 °K)	Reference
CsCl	−1.490	−0.780	−1.077	Present
	−0.648	−0.278	−0.150	Theor. (Ref. 1)
	−1.523	−0.849	−1.062	Expt. (Ref. 10)
CsBr	−1.429	−0.783	−1.054	Present
	−1.220	−0.692	−0.931	Expt. (Ref. 10)
CsI	−1.303	−0.696	−0.951	Present
	−1.078	−0.575	−0.806	Expt. (Ref. 21)
LiCl	−2.849	0.478	−0.502	Present
	−3.815	0.342	−0.645	Expt. (Refs. 10 and 22)
LiBr	−3.369	0.544	−0.577	Present
	−3.681	−1.216	−0.775	Theor. (Ref. 2)
	−2.861	1.245	−0.674	Expt. (Ref. 10)
NaF	−4.633	0.432	−0.354	Present
	−5.351	0.437	−0.571	Expt. (Refs. 10 and 22)
NaCl	−2.636	0.362	−0.258	Present
	−2.593	−0.950	−0.120	Theor. (Ref. 1)
	−3.504	0.219	−0.344	Expt. (Refs. 10 and 22)
NaBr	−2.773	0.307	−0.275	Present
	−3.409	0.109	−0.249	Expt. (Refs. 10 and 22)
NaI	−2.049	0.244	−0.194	Present
	−2.593	−0.370	−0.120	Theor. (Ref. 1)
	−2.848	0.581	−0.163	Expt. (Ref. 22)
KF	−2.795	0.291	−0.217	Present
	−4.789	0.394	−0.262	Expt. (Ref. 22)
KCl	−2.369	0.247	−0.146	Present
	−3.390	−0.128	−0.145	Theor. (Ref. 2)
	−2.778	−0.740	−0.150	Theor. (Ref. 1)
	−3.300	0.240	−0.123	Expt. (Ref. 10)
KBr	−2.315	0.249	−0.141	Present
	−2.300	−0.463	−0.185	Theor. (Ref. 1)
	−2.763	0.123	−0.107	Expt. (Ref. 10)
KI	−2.348	0.232	−0.115	Present
	−1.389	−0.740	−0.370	Theor. (Ref. 1)
	−2.541	0.347	−0.063	Expt. (Ref. 10)
RbCl	−2.282	0.222	−0.118	Present
	−3.158	0.353	−0.108	Expt. (Ref. 10)
RbI	−2.246	0.186	−0.090	Present
	−2.451	0.321	−0.058	Expt. (Ref. 10)

perimental value of r_0 and $(C_{ij})_0$ given in Table I. These parameters are presented in Table II along with r_0/ρ which is given by the relation[6]

$$A_0=(-r_0/\rho)B_0\,. \tag{21}$$

Since the quantum-mechanical states for the potential are not known, $\int_0^T \alpha\, dT$ is computed at different temperatures from 0 to 300 °K, from the experimental values of Rapp and Merchant[12] except for RbCl (Cooper and Yates[20]). The value of x is determined by the relation (10). The elastic constants are computed at various temperatures using Eqs. (17)–(19), for all the three alkali-metal halides in CsCl-like structure and 12 out of 16 in NaCl-like structure. These results are fitted in the following equations in the temperature:

$$C=C_0+C_1T\,, \tag{22}$$

where the C_0 values are already given in Table I. The coefficients C_1 are presented in Table III along with other theoretical and experimental results[21,22] for comparison. The typical curves show the variation of these elastic constants with temperature, for selected members of alkali halides (CsCl, NaCl, KBr, and RbI) are also shown in Figs. 1–4.

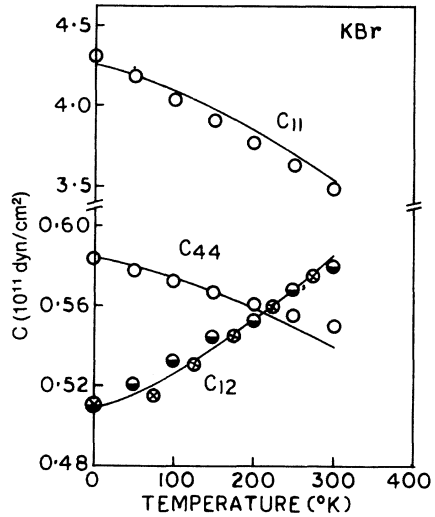

FIG. 3. Temperature dependence of the elastic constants of KBr: ○, C_{11} and C_{44}; and ⊗, C_{12} according to Botaki, Gyrbu, and Sharko; ◒, C_{12} according to Galt; ——, calculated by the present model.

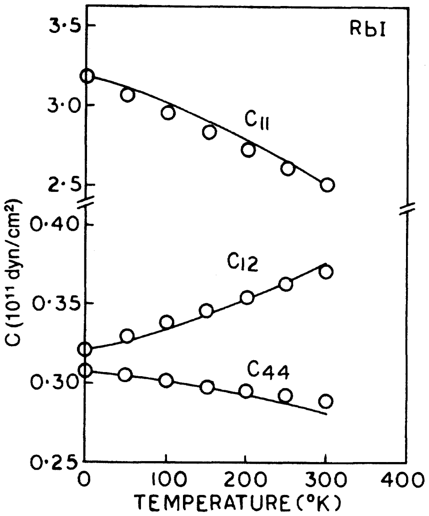

FIG. 4. Temperature dependence of the elastic constants of RbI: ○, C_{11} according to Botaki, Gyrbu, and Sharko; ○, C_{12} and C_{44} are according to Haussuhl; ——, calculated by the present model.

IV. RESULTS AND CONCLUSIONS

We see that our results give excellent agreement with the experimental results. This agreement is much better than that of previous workers,[1,2] especially in the case of NaCl-like structure. Our model for the first time predicts the observed anomalous increase in C_{12} with temperature.

We conclude that Ruffa's pseudopotential treatment is a useful tool to investigate the many-body interactions. Inclusion of many-body interaction ensures three distinct elastic constants even at 0 °K. Since at certain finite temperature the nearest-neighbor distance is not the position of potential minima, the equilibrium conditions (7) and (8) fail to account for the stability of the lattice in view of lattice vibrations. The failure of relations (7) and (8) leads to the different rates of temperature variations of C_{12} and C_{44}. These rates are found to be of opposite nature in NaCl-like structure.

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