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Many-body effects on the third-order elastic constants and pressure derivatives of the second-order-elastic constants of NaCl-structure alkali halides

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Expressions for the third-order elastic (TOE) constants have been derived from the Lundqvist potential for ionic solids. It has been observed that the Cauchy relations among these constants are broken owing to the presence of the many-body term in the crystal potential. All the parameters, except one, appearing in the expressions for the TOE constants, can be determined from the values of the second-order elastic (SOE) constants, the equilibrium condition and a plausible assumption concerning the overlap repulsion. Determining the remaining parameter from the expression for dS'/dp, we can evaluate all the six TOE constants (C_{111}, C_{112}, C_{166}, C_{123}, C_{144}, C_{456}) and the remaining two independent pressure derivatives of the SOE constants. The values, so calculated, compare very well with the corresponding experimental results.

I. INTRODUCTION

In the infinitesimal theory of elastic deformation, the strain energy is expressed in a series of powers of the strains, with coefficients representing the elastic constants of orders corresponding to the powers of the strains in the respective terms. In particular, the third-order elastic (TOE) constants are the coefficients of the cubic terms in this series. Considerable attention has been given to the study of the TOE constants of the cubic crystals during the last few years. Chang[1] has experimentally determined the TOE constants of NaCl and KCl. Swartz[2] also determined experimentally the TOE constants of NaCl, while Dunham[3] experimentally determined the two ratios of linear combinations of SOE (second-order elastic) and TOE constants of NaCl. Naran'yan[4] and Ghate[5] have calculated the TOE constants for NaCl- and CsCl-type crystals, using the Born central-force model for which Cauchy relations ($C_{112} = C_{166}$ and $C_{144} = C_{123} = C_{456}$) are satisfied at 0 K.

It is well known that the many-body interactions in the ionic solids can account for the Cauchy discrepancy between the SOE constants to a good approximation.[6,7] It is natural to expect that these interactions could lead to deviations from the Cauchy relations among the TOE constants also. In fact, the breakdown of the first Cauchy relation $C_{112} = C_{166}$ has been reported by Paul,[8] who has based his analysis on an approximate formulation of many-body forces due to Sarkar and Sengupta.[9] These many-body forces are short range in nature, whereas the quantum-mechanical analysis of Lowdin[6] and Lundqvist[7] leads to a long-range many-body potential.

The effect of this long-range many-body potential on the TOE constants does not seem to have been studied so far. In the present paper, we are reporting a complete study of the SOE and TOE constants, and the pressure derivatives of the SOE constants of alkali-halide crystals, solidifying in the NaCl structure, as derived from the Lundqvist potential.[7] We show here that the many-body term in the crystal potential leads to deviations from both the Cauchy relations among the TOE constants, although an identity $C_{123} + 2C_{456} - 3C_{144} = 0$, connecting the constants, still exists. The preliminary results based on this study have already been reported (Puri and Verma[10]).

We have expressed the TOE constants and the pressure derivatives of the SOE constants in terms of six parameters derived from the short-range overlap potential and the three-body force (charge-transfer) parameter. Four of these parameters appear in the expressions for the SOE constants and the equilibrium condition and can be evaluated from them. The fifth parameter can be evaluated by taking a plausible empirical relation, concerning the overlap repulsion. Choosing one of the pressure derivatives of the SOE constants, dS'/dp, to obtain the sixth parameter, we can evaluate all the TOE constants and the pressure derivatives of the SOE constants of all the alkali-halide crystals solidifying in the NaCl structure. The values so obtained agree fairly well with the available experimental results.

Section II is devoted to deriving the expressions for the SOE and TOE constants in terms of various coefficients. In Secs. III and IV, we describe the Lundqvist potential-energy function which is then used to evaluate the various coefficients and therefrom the SOE and TOE constants, and the pressure derivatives of the SOE constants. The numerical results are reported in Sec. V, which is followed by a short discussion of these results.

II. EXPRESSIONS FOR THE SOE AND TOE CONSTANTS

An ion in the lattice will be designated by the pair of indices (l, κ), where $l=(l_1, l_2, l_3)$ represents the cell to which the ion belongs and $\kappa=1$ and 2 for the positive and negative ions, respectively. A position vector will be denoted by $x_\alpha (\alpha=1,2,3)$. Thus the position of the (l, κ)th ion will be given by $x_\alpha(l, \kappa)$. The vector joining the (l, κ)th ion to the (l', κ')th ion is denoted by

$$x_\alpha(l'-l, \kappa\kappa') = x_\alpha(l', \kappa') - x_\alpha(l, \kappa) . \tag{1}$$

The displacement of the (l, κ)th ion from the equilibrium position will be denoted by

$$U_\alpha(l, \kappa) = x_\alpha(l, \kappa) - x_\alpha^0(l, \kappa) . \tag{2}$$

The equilibrium value of a vector being denoted by a zero superscript. The relative displacement can be expressed as

$$U_\alpha(l'-l, \kappa\kappa') = U_\alpha(l', \kappa') - U_\alpha(l, \kappa) . \tag{3}$$

The modulus of a vector will be indicated by just dropping the vector suffix. Thus $|U_\alpha(l, \kappa)| = U(l, \kappa)$.

The potential energy ϕ of the crystal, due to the interactions among the ions in a given configuration, may be expanded in a series of powers of the displacements from the initial equilibrium configuration as

$$\phi = \phi_0 + \sum_{l,\kappa} \sum_{l',\kappa'} \phi_\alpha(l'-l, \kappa\kappa') U_\alpha(l'-l, \kappa\kappa') + \frac{1}{2!} \sum_{l,\kappa} \sum_{l',\kappa'} \sum_{l'',\kappa''} \phi_{\alpha\beta}(l'-l, \kappa\kappa', l''-l, \kappa\kappa'') U_\alpha(l'-l, \kappa\kappa') U_\beta(l''-l, \kappa\kappa'')$$

$$+ \frac{1}{3!} \sum_{l,\kappa} \sum_{l',\kappa'} \sum_{l'',\kappa''} \sum_{l''',\kappa'''} \phi_{\alpha\beta\gamma}(l'-l, \kappa\kappa', l''-l, \kappa\kappa'', l'''-l, \kappa\kappa''') U_\alpha(l'-l, \kappa\kappa') U_\beta(l''-l, \kappa\kappa'') U_\gamma(l'''-l, \kappa\kappa''') + \cdots , \tag{4}$$

where summations are always implied for repeated Greek suffixes. ϕ_0 is the crystal potential when the ions are all located at their equilibrium positions. The potential energy coefficients $\phi_\alpha(l'-l, \kappa\kappa')$, $\phi_{\alpha\beta}(l'-l, \kappa\kappa', l''-l, \kappa\kappa'')$, $\phi_{\alpha\beta\gamma}(l'-l, \kappa\kappa', l''-l, \kappa\kappa'', l'''-l, \kappa\kappa'''), \ldots$, are all evaluated from the equilibrium configuration, so that $\phi_\alpha(l'-l, \kappa\kappa')$ must vanish and

$$\phi_{\alpha\beta}(l'-l, \kappa\kappa', l''-l, \kappa\kappa'') = \left[\frac{\partial^2 \phi}{\partial x_\alpha(l'-l, \kappa\kappa') \partial x_\beta(l''-l, \kappa\kappa'')} \right]_0 , \tag{5a}$$

$$\phi_{\alpha\beta\gamma}(l'-l, \kappa\kappa', l''-l, \kappa\kappa'', l'''-l, \kappa\kappa''') = \left[\frac{\partial^3 \phi}{\partial x_\alpha(l'-l, \kappa\kappa') \partial x_\beta(l''-l, \kappa\kappa'') \partial x_\gamma(l'''-l, \kappa\kappa''')} \right]_0 . \tag{5b}$$

The suffix 0 indicates values corresponding to the equilibrium configuration. In these equations, the cell index l can be chosen to be any finite number without affecting the value of the potential-energy coefficients. It is, therefore, put equal to zero and is dropped.

For a homogeneous deformation of crystals with every ion at a center of inversion symmetry, the displacement of an ion, away from the boundary, can be expressed as

$$U_\alpha(l', \kappa\kappa') = u_{\alpha\beta} x_\beta(l', \kappa\kappa') , \tag{6a}$$

where $u_{\alpha\beta}$ are the displacement gradients

$$u_{\alpha\beta} = \frac{\partial U_\alpha(l', \kappa\kappa')}{\partial x_\beta(l', \kappa\kappa')} . \tag{6b}$$

Using Eq. (6a), we can express Eq. (4) as

$$\phi = \phi_0 + V A_{\alpha\beta} u_{\alpha\beta} + \tfrac{1}{2} V A_{\alpha\beta\gamma\delta} u_{\alpha\beta} u_{\gamma\delta}$$

$$+ \tfrac{1}{6} V A_{\alpha\beta\gamma\delta\lambda\mu} u_{\alpha\beta} u_{\gamma\delta} u_{\lambda\mu} + \cdots . \tag{7}$$

This equation defines the A coefficients in terms of the potential-energy coefficients as

$$A_{\alpha\beta} = V^{-1} \sum_{\kappa} \sum_{l',\kappa'} \phi_\alpha(l', \kappa\kappa') x_\beta(l', \kappa\kappa') , \tag{8a}$$

$$A_{\alpha\beta\gamma\delta} = V^{-1} \sum_{\kappa} \sum_{l',\kappa'} \sum_{l'',\kappa\kappa''} \phi_{\alpha\gamma}(l'\kappa\kappa', l'', \kappa\kappa'') \; x_\beta(l', \kappa\kappa') x_\delta(l'', \kappa\kappa'') , \tag{8b}$$

$$A_{\alpha\beta\gamma\delta\lambda\mu} = V^{-1} \sum_{\kappa} \sum_{l',\kappa'} \sum_{l'',\kappa''} \sum_{l''',\kappa'''} \phi_{\alpha\gamma\lambda}(l'\kappa\kappa', l'', \kappa\kappa'', l''', \kappa\kappa''')\, x_\beta(l', \kappa\kappa') x_\delta(l'', \kappa\kappa'') x_\mu(l''', \kappa\kappa''') , \tag{9}$$

where $\phi_{\alpha\gamma}$ and $\phi_{\alpha\gamma\lambda}$ are given by Eqs. (5a) and (5b).

For rotational invariance, the crystal potential must depend only on the symmetric finite strain parameters $\eta_{\alpha\beta}$, given by Wallace,[11]

$$\eta_{\alpha\beta} = \tfrac{1}{2}(u_{\alpha\beta} + u_{\beta\alpha} + u_{\gamma\alpha} u_{\gamma\beta}) . \tag{10}$$

Hence the potential energy may also be expanded in a series of powers of the symmetric finite strain parameters $\eta_{\alpha\beta}$,

$$\phi = \phi_0 + V C_{\alpha\beta} \eta_{\alpha\beta} + \tfrac{1}{2} V C_{\alpha\beta\gamma\delta} \eta_{\alpha\beta} \eta_{\gamma\delta} + \tfrac{1}{6} V C_{\alpha\beta\gamma\delta\lambda\mu} \eta_{\alpha\beta} \eta_{\gamma\delta} \eta_{\lambda\mu} + \cdots , \tag{11}$$

defining the C coefficients, which are the elastic constants of various orders in Brugger's definition.[12]

Equations (7), (10), and (11) lead to

$$A_{\alpha\beta} = C_{\alpha\beta} , \tag{12a}$$

$$A_{\alpha\beta\gamma\delta} = C_{\alpha\beta\gamma\delta} + C_{\beta\delta} \delta_{\alpha\gamma} , \tag{12b}$$

and

$$A_{\alpha\beta\gamma\delta\lambda\mu} = C_{\alpha\beta\gamma\delta\lambda\mu} + C_{\alpha\beta\delta\mu} \delta_{\gamma\lambda} + C_{\gamma\delta\beta\mu} \delta_{\alpha\lambda} + C_{\beta\delta\lambda\mu} \delta_{\alpha\gamma} , \tag{12c}$$

where $\delta_{\alpha\beta}$ are the Kronecker delta symbols. $C_{\alpha\beta}$ and $A_{\alpha\beta}$ must vanish for the equilibrium of the lattice in the absence of external stresses. Therefore Eq. (12b) can be written

$$A_{\alpha\beta\gamma\delta} = C_{\alpha\beta\gamma\delta} . \tag{13}$$

Changing to Voigt notation, we obtain from Eqs. (13) and (12c),

$$C_{11} = A_{11} , \quad C_{12} = A_{12} , \quad C_{44} = A_{44} \tag{14a}$$

and

$$C_{111} = A_{111} - 3C_{11} , \quad C_{112} = A_{112} - C_{12} , \quad C_{123} = A_{123} , \tag{14b}$$

$$C_{144} = A_{144} - C_{12} , \quad C_{456} = A_{456} , \quad C_{166} = A_{166} - C_{12} - 2C_{44} .$$

III. DERIVATIONS OF THE SOE AND THE TOE CONSTANTS OF NaCl-STRUCTURE SOLIDS

The potential energy of the crystal as given by Lundqvist[7] is

$$\phi = \frac{e^2}{2} \sum_{\kappa} \sum_{l',\kappa'} \frac{\epsilon(\kappa)\epsilon(\kappa')}{r(l', \kappa\kappa')} + e^2 \sum_{\kappa} \sum_{l',\kappa'} V^1(r(l', \kappa\kappa')) + e^2 \sum_{\kappa} \sum_{l',\kappa'} \sum_{l^{\mathrm{iv}},\kappa^{\mathrm{iv}}} f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}}, \kappa\kappa^{\mathrm{iv}})) \frac{\epsilon(\kappa')}{r(l', \kappa\kappa')} , \tag{15}$$

where $\epsilon(\kappa)$ is the valence of the κ type ion and $\epsilon = |\epsilon(\kappa)|$. The first term represents the Coulomb energy. The second term is the overlap repulsive energy, coupling the nearest neighbors, and the third term represents the three-body potential term. The function f can be defined in terms of the overlap integrals derived from the free-ion one-electron wave functions. However, in the present analysis this function and its derivatives have been chosen as disposable parameters.

The contribution of the various terms in the potential-energy expression (15) to the coefficients $A_{\alpha\beta\gamma\delta}$ and $A_{\alpha\beta\gamma\delta\lambda\mu}$, and hence to $C_{\alpha\beta\gamma\delta}$ and $C_{\alpha\beta\gamma\delta\lambda\mu}$ are obtained in Appendixes A–C.

The final expressions for the SOE and the TOE constants of the NaCl-type crystals are obtained as follows:

$$C_{11} = \frac{e^2}{4a^4} \left[-5.112\epsilon[\epsilon + 12f(a)] + A + 9.320\epsilon \left(a \frac{\partial f}{\partial a} \right) \right] , \tag{16}$$

$$C_{12} = \frac{e^2}{4a^4} \left[1.391\epsilon[\epsilon + 12f(a)] + 9.320\epsilon \left(a \frac{\partial f}{\partial a} \right) \right] , \tag{17}$$

$$C_{44} = \frac{e^2}{4a^4} \{ 2.556\epsilon[\epsilon + 12f(a)] + B \} , \tag{18}$$

$$C_{111} = \frac{e^2}{4a^4} \left[37.556\epsilon[\epsilon + 12f(a)] + C - 3A + 13.980\epsilon \left(a^2 \frac{\partial^2 f}{\partial a^2} \right) - 89.305\epsilon \left(a \frac{\partial f}{\partial a} \right) \right] , \tag{19}$$

$$C_{112} = \frac{e^2}{4a^4} \left[-4.836\epsilon[\epsilon + 12f(a)] + 4.660\epsilon \left(a^2 \frac{\partial^2 f}{\partial a^2} \right) - 18.640\epsilon \left(a \frac{\partial f}{\partial a} \right) \right] , \tag{20}$$

$$C_{166} = \frac{e^2}{4a^4} \left[-4.836\epsilon[\epsilon + 12f(a)] + 5.564\epsilon \left(a \frac{\partial f}{\partial a} \right) \right] , \tag{21}$$

$$C_{123} = \frac{e^2}{4a^4} \left[2.717\epsilon[\epsilon + 12f(a)] + 16.692\epsilon \left(a \frac{\partial f}{\partial a} \right) \right] , \tag{22}$$

$$C_{144} = \frac{e^2}{4a^4} \left[2.717\epsilon[\epsilon + 12f(a)] + 5.564\epsilon \left(a \frac{\partial f}{\partial a} \right) \right] , \tag{23}$$

$$C_{456} = \frac{e^2}{4a^4} \{ 2.717\epsilon[\epsilon + 12f(a)] \} . \tag{24}$$

The parameters A, B, C are defined as

$$\left[\frac{\partial^2 V(r)}{\partial r^2}\right]_{r=a} = \frac{1}{8a^3}A\,, \quad \left[\frac{\partial V(r)}{\partial r}\right]_{r=a} = \frac{1}{8a^2}B\,, \quad \left[\frac{\partial^3 V(r)}{\partial r^3}\right]_{r=a} = \frac{1}{8a^4}C\,, \tag{25}$$

where $V(r)$ is related to the Lundqvist repulsive potential in the following manner:

$$V(r) = V'(r) + (\alpha_M \epsilon/a) f(r)\,, \tag{26}$$

and α_M is the Madelung constant, equal to 1.7475 for NaCl-type crystals. The expressions for the SOE constants, obtained above by the finite deformation method, agree with those deduced by Verma and Singh[13] by the method of long waves, in view of the equilibrium condition

$$B = -1.165\epsilon[\epsilon + 12f(a)]\,. \tag{27}$$

The Cauchy discrepancies among the SOE and the TOE constants are therefore given by

$$C_{12} - C_{44} = \frac{e^2}{4a^4}\left[9.320\epsilon\left(a\frac{\partial f}{\partial a}\right)\right]\,, \tag{28}$$

$$C_{112} - C_{166} = \frac{e^2}{4a^4}\left[4.660\epsilon\left(a^2\frac{\partial^2 f}{\partial a^2}\right) - 24.204\epsilon\left(a\frac{\partial f}{\partial a}\right)\right]\,, \tag{29}$$

$$C_{123} - C_{456} = \frac{e^2}{4a^4}\left[16.692\epsilon\left(a\frac{\partial f}{\partial a}\right)\right]\,, \tag{30}$$

$$C_{144} - C_{456} = \frac{e^2}{4a^4}\left[5.564\epsilon\left(a\frac{\partial f}{\partial a}\right)\right]\,. \tag{31}$$

Equations (16)–(24) have been derived, ignoring the thermal vibrations, and are, therefore, expected to be best satisfied at 0K. Obviously the Cauchy relations break down both for the SOE constants and for the TOE constants in the presence of three-body interactions even at 0 K. However, if we put the function f and its derivatives equal to zero, the Cauchy relations are satisfied, leaving only two independent SOE constants and three independent TOE constants, a consequence of the central-force model used by Naran'yan[4] and Ghate.[5]

It is also obvious from Eqs. (30) and (31) that even in the presence of three-body forces, the TOE constants satisfy the following identity:

$$C_{123} + 2C_{456} - 3C_{144} = 0\,. \tag{32}$$

IV. PRESSURE DERIVATIVES OF THE SOE CONSTANTS

When a cubic crystal is subjected to hydrostatic pressure, the symmetry of the crystal is preserved. Birch[14] has derived a set of effective SOE constants C'_{ij} which determines the response of an initially stressed crystal to additional infinitesimal strains. The expressions for C'_{11}, C'_{12} and C'_{44} are given below:

$$C'_{11} = C_{11} + \eta(2C_{11} + 2C_{12} + C_{111} + 2C_{112})\,, \tag{33}$$

$$C'_{12} = C_{12} + \eta(-C_{11} - C_{12} + C_{123} + 2C_{112})\,, \tag{34}$$

$$C'_{44} = C_{44} + \eta(C_{11} + 2C_{12} + C_{44} + C_{144} + 2C_{166})\,, \tag{35}$$

where

$$\eta = \frac{-p}{C_{11} + 2C_{12}}$$

and the C_{ijk} are those defined by Brugger.[12] Hence the pressure derivatives of the SOE constants are

$$\frac{dC'_{44}}{dp} = -\left(\frac{C_{11} + 2C_{12} + C_{44} + C_{144} + 2C_{166}}{C_{11} + 2C_{12}}\right)\,, \tag{36}$$

$$\frac{dS'}{dp} = -\left(\frac{3C_{11} + 3C_{12} + C_{111} - C_{123}}{2(C_{11} + 2C_{12})}\right)\,, \tag{37}$$

$$\frac{dK'}{dp} = -\left(\frac{C_{111} + 6C_{112} + 2C_{123}}{3(C_{11} + 2C_{12})}\right)\,, \tag{38}$$

where $S' = \frac{1}{2}(C'_{11} - C'_{12})$ and $K' = \frac{1}{3}(C'_{11} + 2C'_{12})$. We can write pressure derivatives of the SOE constants in terms of the parameters A, B, C, $f(a)$, $a\partial f/\partial a$, and $a^2\partial^2 f/\partial a^2$ by substituting the expressions of the SOE constants and the TOE constants given by Eqs. (16)–(24). Thus

$$\frac{dC'_{44}}{dp} = -\left(\frac{-6.729\epsilon[\epsilon + 12f(a)] + A + B + 44.652\epsilon(a\partial f/\partial a)}{-2.330\epsilon[\epsilon + 12f(a)] + A + 27.961\epsilon(a\partial f/\partial a)}\right)\,, \tag{39}$$

$$\frac{dS'}{dp} = -\left(\frac{23.676\epsilon[\epsilon + 12f(a)] + C - 51.075\epsilon(a\partial f/\partial a) + 13.980\epsilon(a^2\partial^2 f/\partial a^2)}{2\{-2.330\epsilon[\epsilon + 12f(a)] + A + 27.961\epsilon(a\partial f/\partial a)\}}\right)\,, \tag{40}$$

$$\frac{dK'}{dp} = -\Bigg(\frac{13.975\epsilon[\epsilon + 12f(a)] + C - 3A - 167.764\epsilon(a\partial f/\partial a) + 41.940\epsilon(a^2\partial^2 f/\partial a^2}{3\{-2.330\epsilon[\epsilon + 12f(a)] + A + 27.961\epsilon(a\partial f/\partial a)\}}\Bigg)\,. \tag{41}$$

TABLE I. Input data at room temperature [lattice parameter (Ref. 16) in Å and the calculated values of the isothermal SOE constants (Refs. 15 and 16) in units of 10^{11} dyn cm^{-2}; original references for dS^1/dp values are given in parentheses alongside].

	a	C_{11}^T	C_{12}^T	C_{44}^T	$\frac{dS^1}{dp}$
LiF	2.013	10.655	4.632	6.350	3.60 (17)
LiCl	2.570	4.510	2.184	2.480	3.70 (17)
LiBr	2.751	3.528	1.770	1.930	3.75 (17)
NaF	2.317	9.176	2.394	2.810	4.79 (18)
NaCl	2.820	4.585	1.264	1.265	4.79 (18)
NaBr	2.989	3.704	1.066	0.990	4.83 (18)
NaI	3.236	2.762	0.856	0.740	4.80 (18)
KF	2.674	6.185	1.440	1.250	5.25 (18)
KCl	3.146	3.838	0.683	0.633	5.61 (18)
KBr	3.300	3.263	0.564	0.504	5.68 (18)
KI	3.533	2.577	0.445	0.370	6.03 (18)
RbF	2.826	5.251	1.377	0.925	4.93 (19)
RbCl	3.291	3.448	0.609	0.465	5.88 (19)
RbBr	3.445	2.986	0.491	0.380	6.03 (19)
RbI	3.671	2.412	0.366	0.278	6.26 (19)

V. RESULTS AND DISCUSSION

The application of the above theory demands evaluation of the six parameters A, B, C, $f(a)$, $a\partial f/\partial a$, and $a^2\partial^2 f/\partial a^2$. The parameters $A, B, f(a)$, $a\partial f/\partial a$ can be evaluated from the SOE constants [Eqs. (16)–(18)] and the equilibrium condition [Eq. (27)]. The parameter C can be evaluated by approximating the overlapped repulsive potential $V(r)$ as a two-parameter potential of the form

$$V(r) = be^{-r/\rho}, \tag{42}$$

so that

$$C = A^2/B. \tag{43}$$

The parameter $a^2\partial^2 f/\partial a^2$ may be evaluated from the experimental value of the pressure derivative of shear modulus dS'/dp (or the pressure derivative of bulk modulus dK'/dp), and all six TOE constants and the remaining two pressure derivatives of the SOE constants can, then, easily be calculated. The input data are given in Table I. The parameters, so calculated, are listed in Table II. The calculated values of the TOE constants and the pressure derivatives of the SOE constants, together with other theoretical and experimental values, are reported in Table III.

Naran'yan[4] and Ghate[5] have deduced the expressions for TOE constants from the central Born-Mayer potential, for which the Cauchy relations ($C_{112} = C_{166}$, $C_{123} = C_{456} = C_{144}$) are satisfied at 0 K. They deduced the failure of the Cauchy relations at a finite temperature T by introducing the vibrational part of the energy. These changes came out in general very large, in some cases up to 40% too large, and are difficult to comprehend in crystals like alkali halides. Our study shows that much of the failure of the Cauchy relations could be due to many-body interactions, which lead to the breakdown of the Cauchy relations among the TOE constants even at 0 K. An identity $C_{123} + 2C_{456} - 3C_{144} = 0$, however, is still satisfied. This identity can be considered as a single Cauchy relation satisfied by the TOE constants derived from the Lundqvist potential.[7] Therefore, low-temperature measurements of the TOE constants through this identity can provide a direct check on the validity of the Lundqvist potential[7] in ionic crystals.

Our calculated values of the TOE constants and the pressure derivatives of the SOE constants agree fairly well with the experimental values, as compared to the theoretical values of Ghate[5] and

TABLE II. Calculated values of the parameters.

	A	B	C	$f(a)$	$a\frac{\partial f}{\partial a}$	$a^2\frac{\partial^2 f}{\partial a^2}$
LiF	10.167	−1.514	−68.266	2.498×10^{-2}	-5.248×10^{-2}	−0.4306
LiCl	10.529	−1.571	−70.5667	2.905×10^{-2}	-2.402×10^{-2}	−0.8788
LiBr	10.707	−1.6053	−71.4134	3.149×10^{-2}	-1.705×10^{-2}	−1.0536
NaF	9.954	−1.176	−84.249	7.939×10^{-4}	-2.2305×10^{-2}	−0.54678
NaCl	10.1269	−1.162	−88.275	-2.3096×10^{-4}	-1.1765×10^{-4}	−0.7201
NaBr	10.266	−1.147	−91.8475	-1.248×10^{-3}	-1.125×10^{-2}	−0.4300
NaI	10.644	−1.178	−96.141	9.5978×10^{-4}	-2.3725×10^{-2}	−0.1579
KF	9.7238	−0.928	−101.880	-1.6946×10^{-2}	-1.8071×10^{-2}	0.3427
KCl	10.386	−0.9005	−119.789	-1.892×10^{-2}	9.0573×10^{-3}	0.1994
KBr	10.395	−0.8680	−124.499	-2.124×10^{-2}	1.3238×10^{-2}	0.3547
KI	10.4348	−0.8371	−130.065	-2.345×10^{-2}	2.168×10^{-2}	0.0856
RbF	9.0705	−0.8567	−96.0305	-2.205×10^{-2}	5.362×10^{-2}	−0.4267
RbCl	10.195	−0.7921	−131.211	-2.667×10^{-2}	3.151×10^{-2}	0.3647
RbBr	10.4331	−0.7772	−140.043	-2.773×10^{-2}	2.898×10^{-2}	0.6350
RbI	10.5350	−0.7332	−151.371	-3.088×10^{-2}	2.980×10^{-2}	1.008

TABLE III. TOE constants (in units of 10^{12} dyn/cm^2) and pressure derivatives of the SOE constants at room temperature. ρ is in the units of 10^{-8} cm.

	ρ	C_{111}	C_{112}	C_{166}	C_{123}	C_{144}	C_{456}	$\frac{dC'_{44}}{dp}$	$\frac{dK'}{dp}$	Ref.
LiF	0.2507	−18.0130	−2.5687	−2.3100	0.9325	1.1377	1.2402	0.43	5.28	
	0.3333	−5.9770	−2.6180	−2.6400	0.9173	0.9768	0.9540	0.84	3.21	Theor. 5
	0.2800	−13.5300	−2.5950	−2.5420	0.8791	0.9803	0.9551	0.74	4.27	Theor. 5
		−20.7000	−2.5600	−2.4200	1.1100	1.3200	1.3200	0.45	5.66	Theor. 4
								1.38	5.30	Expt. 17
LiCl	0.3835	−8.1498	−1.3444	−0.8798	0.4314	0.4667	0.4844	0.177	5.76	
	0.3333	−6.3720	−0.9059	−0.9355	0.3142	0.3741	0.3617	0.32	3.93	Theor. 5
	0.3030	−8.572	−0.8592	−0.9014	0.2945	0.3742	0.3620	0.24	4.61	Theor. 5
								1.70	5.63	Expt. 17
LiBr	0.4124	−6.5440	−1.1333	−0.6805	0.3483	0.3674	0.3769	0.133	5.964	
	0.3333	−5.9850	−0.6670	−0.6980	0.2271	0.2870	0.2769	0.19	4.14	Theor. 5
	0.3050	−7.7210	−0.6272	−0.6699	0.2087	0.2867	0.2770	0.12	4.80	Theor. 5
								1.80	5.68	Expt. 17
NaF	0.2737	−16.3699	−1.4035	−1.0017	0.4743	0.5240	0.5488	−0.142	5.691	
	0.3333	−6.6710	−1.4310	−1.4570	0.5001	0.5601	0.5436	0.51	3.47	Theor. 5
	0.3120	−8.5630	−1.3940	−1.4290	0.4875	0.5606	0.5439	0.47	3.88	Theor. 5
		−7.1400	−1.4380	−1.2800	0.5580	0.7600	0.7600	0.11	3.51	Theor. 4
								0.205	5.18	Expt. 18
NaCl	0.3236	−8.3224	−0.7456	−0.4398	0.2468	0.2470	0.2710	−0.288	5.764	
	0.3333	−5.7980	−0.5837	−0.6153	0.1970	0.2568	0.2476	0.19	4.18	Theor. 5
	0.2880	−8.6050	−0.5220	−0.5744	0.1637	0.2563	0.2479	0.08	5.36	Theor. 5
		−5.4540	−0.6880	−0.6300	0.2690	0.3550	0.3540	0.22	4.25	Theor. 4
		−8.8000	−0.5710	−0.6110	0.2840	0.2580	0.2710	0.37	5.27	Expt. 1, 18
NaBr	0.3339	−6.5505	−0.4738	−0.3487	0.1798	0.1888	0.1934	−0.298	5.160	
	0.3333	−5.3830	−0.4418	−0.4744	0.1441	0.2039	0.1964	0.043	4.17	Theor. 5
	0.3080	−6.6230	−0.4139	−0.4566	0.1279	0.2036	0.1965	−0.013	4.83	Theor. 5
								0.46	5.29	Expt. 18
NaI	0.3581	−4.7425	−0.2727	−0.2642	0.1237	0.1376	0.1445	−0.292	4.567	
	0.3333	−4.7810	−0.2984	−0.3322	0.0891	0.1488	0.1432	−0.08	4.45	Theor. 5
	0.3410	−4.5120	−0.3045	−0.3358	0.0932	0.1489	0.1432	−0.06	4.35	Theor. 5
								0.61	5.40	Expt. 18
KF	0.2552	−10.6856	−0.2164	−0.4459	0.2101	0.2328	0.2441	−0.411	4.252	
	0.3333	−6.1380	−0.7461	−0.7767	0.2563	0.3162	0.3053	0.17	3.56	Theor. 5
	0.3410	−7.6220	−0.7134	−0.7532	0.2418	0.3161	0.3055	0.12	4.02	Theor. 5
								−0.43	5.26	Expt. 18
KCl	0.2728	−7.0615	−0.1753	−0.2171	0.1325	0.1266	0.1236	−0.530	5.028	
	0.3333	−4.9710	−0.3386	−0.3720	0.1047	0.1645	0.1583	−0.01	4.42	Theor. 5
	0.3090	−6.0130	−0.3152	−0.3581	0.0892	0.1641	0.1584	−0.06	4.95	Theor. 5
		−5.0700	−0.4580	−0.4000	0.1480	0.2270	0.2270	−0.02	4.82	Theor. 4
		−7.0100	−0.2440	−0.2450	0.1330	0.1270	0.1180	−0.39	5.34	Expt. 1, 18
KBr	0.2755	−6.0266	−0.0977	−0.1716	0.1092	0.1020	0.0984	−0.565	4.854	
	0.3333	−4.6170	−0.2675	−0.3015	0.0770	0.1315	0.1367	−0.030	4.74	Theor. 5
	0.3030	−5.8050	−0.2412	−0.2875	0.0568	0.1316	0.1362	−0.090	5.91	Theor. 5
		−4.5380	−0.3880	−0.3290	0.1110	0.1865	0.1865	−0.014	5.26	Theor. 4
								−0.328	5.38	Expt. 18
KI	0.2834	−5.0020	−0.1288	−0.1242	0.0856	0.0767	0.0723	−0.611	5.387	
	0.3333	−4.1030	−0.1869	−0.2214	0.0444	0.1041	0.1002	−0.16	4.76	Theor. 5
	0.3170	−4.6140	−0.1754	−0.2160	0.0345	0.1039	0.1002	−0.19	5.19	Theor. 5
		−4.7100	−0.3140	−0.2560	0.0740	0.1405	0.1445	−0.07	5.98	Theor. 4
								−0.244	5.47	Expt. 18

TABLE III *(Continued)*

	ρ	C_{111}	C_{112}	C_{166}	C_{123}	C_{144}	C_{456}	$\frac{dC'_{44}}{dp}$	$\frac{dK'}{dp}$	Ref.
RbF	0.2669	−9.6190	−0.5918	−0.2946	0.2616	0.2076	0.1806	−0.64	5.27	
	0.3333	−5.7980	−0.5837	−0.6153	0.1970	0.2568	0.2476	0.06	3.56	Theor. 5
	0.2910	−8.3830	−0.5268	−0.5774	0.1666	0.2563	0.2479	−0.03	4.49	Theor. 5
								−0.70	5.69	Expt. 19
RbCl	0.2557	−6.8375	−0.1069	−0.1530	0.1167	0.0994	0.0908	−0.656	5.18	
	0.3333	−4.6260	−0.2689	−0.3028	0.0775	0.1372	0.1320	−0.13	4.16	Theor. 5
	0.2830	−6.7870	−0.2219	−0.2793	0.0388	0.1363	0.1322	−0.23	5.50	Theor. 5
								−0.56	5.62	Expt. 19
RbBr	0.2566	−5.7322	−0.2671	−0.1255	0.0940	0.0821	0.0742	−0.670	4.825	
	0.3333	−4.2810	−0.2116	−0.2460	0.0546	0.1142	0.1099	−0.180	4.390	Theor. 5
	0.2980	−5.5400	−0.1837	−0.2382	0.0301	0.1137	0.1100	−0.220	5.310	Theor. 5
								−0.550	5.590	Expt. 19
RbI	0.2555	−4.6992	0.0341	−0.0938	0.0701	0.0596	0.0543	−0.681	4.610	
	0.3333	−2.5800	−0.1389	−0.1737	0.0278	0.0875	0.0842	−0.33	3.57	Theor. 5
	0.2930	−5.0720	−0.1223	−0.1744	0.0002	0.0882	0.0856	−0.33	5.60	Theor. 5
								−0.51	5.60	Expt. 19

Naran'yan.[4] As a matter of fact, the agreement between our values and the experimental ones in the case of KCl is excellent. The values of dK'/dp are invariably positive, whereas dC'_{44}/dp is positive or negative, depending on the crystal. It is true that the degree of agreement between the theoretical and experimental values of dC'_{44}/dp falls short of that desired, but this should not be considered to be too serious because we have derived our expressions ignoring thermal vibrations and, therefore, our calculated values should necessarily show some deviations from the room-temperature experimental results.

APPENDIX A: COULOMB CONTRIBUTION

The expressions for $\phi_{\alpha\gamma}$ and $\phi_{\alpha\gamma\lambda}$ derived from the Coulomb energy term according to Eqs. (5a) and (5b) are

$$\phi^{C}_{\alpha\gamma}(l',\kappa\kappa',l'',\kappa\kappa'')=\frac{e^2}{2}\epsilon(\kappa)\epsilon(\kappa')\left[\frac{3\kappa_\alpha(l',\kappa\kappa')x_\gamma(l'',\kappa\kappa'')}{[r(l',\kappa\kappa')]^5}-\frac{\delta_{\alpha\gamma}}{[r(l',\kappa\kappa')]^3}\right]_0\delta_{l'l''}\delta_{\kappa'\kappa''}\,, \tag{A1}$$

$$\begin{aligned}\phi^{C}_{\alpha\gamma\lambda}&(l',\kappa\kappa',l'',\kappa\kappa'',l''',\kappa\kappa''')\\ &=\frac{e^2}{2}\epsilon(\kappa)\epsilon(\kappa')\left[\frac{3\delta_{\alpha\lambda}\delta_{l'l'''}\delta_{\kappa'\kappa'''}x_\gamma(l'',\kappa\kappa'')}{[r(l',\kappa\kappa')]^5}+\frac{3\delta_{\gamma\lambda}\delta_{l''l'''}\delta_{\kappa''\kappa'''}\kappa_\alpha(l',\kappa\kappa')}{[r(l',\kappa\kappa')]^5}\right.\\ &\qquad\left.+\frac{3\delta_{\alpha\gamma}\delta_{l'l'''}\delta_{\kappa'\kappa'''}\kappa_\lambda(l''',\kappa\kappa''')}{[r(l',\kappa\kappa')]^5}-\frac{15\delta_{l'l'''}\delta_{\kappa'\kappa'''}\kappa_\alpha(l',\kappa\kappa')x_\gamma(l'',\kappa\kappa'')x_\lambda(l''',\kappa\kappa''')}{[r(l',\kappa\kappa')]^7}\right]_0\delta_{l'l''}\delta_{\kappa\kappa''}\,.\end{aligned} \tag{A2}$$

Here the superscript C over $\phi_{\alpha\gamma}$ and $\phi_{\alpha\gamma\lambda}$ denotes the Coulomb part. The expressions of $A^C_{\alpha\beta\gamma\delta}$ and $A^C_{\alpha\beta\gamma\delta\lambda\mu}$ from Eqs. (8b) and (9) can be written as

$$A^C_{\alpha\beta\gamma\delta}=\frac{1}{2}\frac{e^2}{2a^3}\sum_{\kappa}\sum_{l',\kappa'}\epsilon(\kappa)\epsilon(\kappa')\left[\frac{3x_\alpha x_\gamma}{r^5}-\frac{\delta_{\alpha\gamma}}{r^3}\right]_0 x_\beta x_\delta\,, \tag{A3}$$

$$A^C_{\alpha\beta\gamma\delta\lambda\mu}=\frac{1}{2}\frac{e^2}{2a^3}\sum_{\kappa}\sum_{l',\kappa'}\epsilon(\kappa)\epsilon(\kappa')\left[\frac{3x_\alpha\delta_{\gamma\lambda}}{r^5}+\frac{3x_\gamma\delta_{\alpha\lambda}}{r^5}+\frac{3x_\lambda\delta_{\alpha\gamma}}{r^5}-\frac{15x_\alpha x_\gamma x_\lambda}{r^7}\right]_0 x_\beta x_\delta x_\mu\,. \tag{A4}$$

Here all the vectors are denoted by the same index numbers $(l',\kappa\kappa')$ and a denotes the nearest-neighbor distance. $2a^3$ is the volume of the elementary unit cell. Since NaCl-type crystals are diatomic, κ takes two values.

The $A^C_{\alpha\beta\gamma\delta}$ and $A^C_{\alpha\beta\gamma\delta\lambda\mu}$ can be evaluated by using various lattice sums, already determined by Verma and Lal.[20] Thus

$$A_{11}^{C}=-5.112\frac{e^2}{4a^4}\epsilon^2,\quad A_{12}^{C}=1.391\frac{e^2}{4a^4}\epsilon^2,\quad A_{44}^{C}=2.556\frac{e^2}{4a^4}\epsilon^2, \tag{A5}$$

$$\begin{aligned}&A_{111}^{C}=22.220\frac{e^2}{4a^4}\epsilon^2,\quad A_{112}^{C}=-3.445\frac{e^2}{4a^4}\epsilon^2,\quad A_{166}^{C}=-0.663\frac{e^2}{4a^4}\epsilon^2,\\ &A_{144}^{C}=4.108\frac{e^2}{4a^4}\epsilon^2,\quad A_{123}^{C}=2.717\frac{e^2}{4a^4}\epsilon^2,\quad A_{456}^{C}=2.717\frac{e^2}{4a^4}\epsilon^2.\end{aligned} \tag{A6}$$

APPENDIX B: REPULSIVE CONTRIBUTION

The expressions for $\phi_{\alpha\gamma}$ and $\phi_{\alpha\gamma\lambda}$ derived from the short-range repulsive part of the Lundqvist potential energy[7] are

$$\begin{aligned}\phi_{\alpha\gamma}^{R}(l',\kappa\kappa',l'',\kappa\kappa'')=e^2\Bigg[&\frac{x_\alpha(l',\kappa\kappa')x_\gamma(l'',\kappa\kappa'')}{[r(l',\kappa\kappa')]^2}\frac{\partial^2V'(r(l',\kappa\kappa'))}{\partial[r(l',\kappa\kappa')]^2}\\ &+\frac{\delta_{\alpha\gamma}}{r(l',\kappa\kappa')}\frac{\partial V'(r(l',\kappa\kappa'))}{\partial r(l',\kappa\kappa')}-\frac{x_\alpha(l',\kappa\kappa')x_\gamma(l'',\kappa\kappa'')}{[r(l',\kappa\kappa')]^3}\frac{\partial V'(r(l',\kappa\kappa'))}{\partial r(l',\kappa\kappa')}\Bigg]_0\delta_{l'l''}\delta_{\kappa'\kappa''},\end{aligned} \tag{B1}$$

$$\begin{aligned}\phi_{\alpha\gamma\lambda}^{R}(l',\kappa\kappa',l'',\kappa\kappa'',l''',\kappa\kappa''')=e^2\Bigg[&\frac{3x_\alpha(l',\kappa\kappa')x_\gamma(l'',\kappa\kappa'')x_\lambda(l''',\kappa\kappa''')\delta_{l'l'''}\delta_{\kappa'\kappa'''}}{[r(l',\kappa\kappa')]^5}\frac{\partial V'(r(l',\kappa\kappa'))}{\partial r(l',\kappa\kappa')}\\ &+\frac{\delta_{\alpha\lambda}\delta_{l'l'''}\delta_{\kappa'\kappa'''}x_\gamma(l'',\kappa\kappa'')}{[r(l',\kappa\kappa')]^2}\frac{\partial^2V'(r(l',\kappa\kappa'))}{\partial[r(l',\kappa\kappa')]^2}\\ &+\frac{\delta_{\gamma\lambda}\delta_{l''l'''}\delta_{\kappa''\kappa'''}x_\alpha(l',\kappa\kappa')}{[r(l',\kappa\kappa')]^2}\frac{\partial^2V'(r(l',\kappa\kappa'))}{\partial[r(l',\kappa\kappa')]^2}\\ &+\frac{\delta_{\alpha\gamma}\delta_{l'l'''}\delta_{\kappa'\kappa'''}x_\lambda(l''',\kappa\kappa''')}{[r(l',\kappa\kappa')]^2}\frac{\partial^2V'(r(l',\kappa\kappa'))}{\partial[r(l',\kappa\kappa')]^2}\\ &+\frac{\delta_{l'l'''}\delta_{\kappa'\kappa'''}x_\alpha(l',\kappa\kappa')x_\gamma(l'',\kappa\kappa'')x_\lambda(l''',\kappa\kappa''')}{[r(l',\kappa\kappa')]^3}\frac{\partial^3V'(r(l',\kappa\kappa'))}{\partial[r(l',\kappa\kappa')]^3}\\ &-\frac{3x_\alpha(l',\kappa\kappa')x_\gamma(l'',\kappa\kappa'')x_\lambda(l''',\kappa\kappa''')\delta_{l'l'''}\delta_{\kappa'\kappa'''}}{[r(l',\kappa\kappa')]^4}\frac{\partial^2V'(r(l',\kappa\kappa'))}{\partial[r(l',\kappa\kappa')]^2}\\ &-\frac{\delta_{\alpha\lambda}\delta_{l'l'''}\delta_{\kappa'\kappa'''}x_\gamma(l'',\kappa\kappa'')}{[r(l',\kappa\kappa')]^3}\frac{\partial V'(r(l',\kappa\kappa'))}{\partial r(l',\kappa\kappa')}\\ &-\frac{\delta_{\gamma\lambda}\delta_{l''l'''}\delta_{\kappa''\kappa'''}x_\alpha(l',\kappa\kappa')}{[r(l',\kappa\kappa')]^3}\frac{\partial V'(r(l',\kappa\kappa'))}{\partial r(l',\kappa\kappa')}\\ &-\frac{\delta_{\alpha\gamma}\delta_{l'l'''}\delta_{\kappa'\kappa'''}x_\lambda(l''',\kappa\kappa''')}{[r(l',\kappa\kappa')]^3}\frac{\partial V'(r(l',\kappa\kappa'))}{\partial r(l',\kappa\kappa')}\Bigg]_0\delta_{l'l''}\delta_{\kappa'\kappa''}.\end{aligned} \tag{B2}$$

The superscript R indicates repulsive contribution. The expressions for $A_{\alpha\beta\gamma\delta}^{R}$ and $A_{\alpha\beta\gamma\delta\lambda\mu}^{R}$ can now be reduced to

$$A_{\alpha\beta\gamma\delta}^{R}=\frac{e^2}{2a^3}\sum_{\kappa}\sum_{l',\kappa'}\left[\left(\frac{x_\alpha x_\gamma}{r^2}\frac{\partial^2V'(r)}{\partial r^2}-\frac{x_\alpha x_\gamma}{r^3}\frac{\partial V'(r)}{\partial r}+\frac{1}{r}\delta_{\alpha\gamma}\frac{\partial V'(r)}{\partial r}\right)_0x_\beta x_\delta\right], \tag{B3}$$

$$\begin{aligned}A_{\alpha\beta\gamma\delta\lambda\mu}^{R}=\frac{e^2}{2a^3}\sum_{\kappa}\sum_{l',\kappa'}\Bigg[\Bigg(&\frac{3x_\alpha x_\gamma x_\lambda}{r^5}\frac{\partial V'(r)}{\partial r}-\frac{\delta_{\alpha\lambda}x_\gamma}{r^3}\frac{\partial V'(r)}{\partial r}-\frac{\delta_{\gamma\lambda}x_\alpha}{r^3}\frac{\partial V'(r)}{\partial r}-\frac{\delta_{\alpha\gamma}x_\lambda}{r^3}\frac{\partial V'(r)}{\partial r}+\frac{\delta_{\alpha\lambda}x_\gamma}{r^2}\frac{\partial^2V'(r)}{\partial r^2}\\ &+\frac{\delta_{\gamma\lambda}x_\alpha}{r^2}\frac{\partial^2V'(r)}{\partial r^2}+\frac{\delta_{\alpha\gamma}x_\lambda}{r^2}\frac{\partial^2V'(r)}{\partial r^2}-\frac{3x_\alpha x_\gamma x_\lambda}{r^4}\frac{\partial^2V'(r)}{\partial r^2}+\frac{x_\alpha x_\gamma x_\lambda}{r^3}\frac{\partial^3V'(r)}{\partial r^3}\Bigg)_0x_\beta x_\delta x_\mu\Bigg].\end{aligned} \tag{B4}$$

In these equations also, all the vectors are denoted by the same index number $(l',\kappa\kappa')$. The values of $A_{\alpha\beta\gamma\delta}^{R}$ and $A_{\alpha\beta\gamma\delta\lambda\mu}^{R}$, by carrying the lattice sums only up to the first-nearest-neighbor atoms, have been obtained in the form

$$A_{11}^{R}=\frac{e^2}{4a^4}A',\quad A_{12}^{R}=0,\quad A_{44}^{R}=\frac{e^2}{4a^4}B', \tag{B5}$$

$$A_{111}^{R}=\frac{e^2}{4a^4}C',\quad A_{112}^{R}=A_{166}^{R}=A_{123}^{R}=A_{144}^{R}=A_{456}^{R}=0, \tag{B6}$$

where parameters A', B', and C' are defined as

$$\left[\frac{\partial^2 V'(r)}{\partial r^2}\right]_{r=a}=\frac{1}{8a^3}A',\quad \left[\frac{\partial V'(r)}{\partial r}\right]_{r=a}=\frac{1}{8a^2}B',\quad \left[\frac{\partial^3 V'(r)}{\partial r^3}\right]_{r=a}=\frac{1}{8a^4}C'. \tag{B7}$$

The value of the parameter B' can be obtained from the equilibrium condition

$$\left(\frac{\partial\phi}{\partial r}\right)_{r=a}=0, \tag{B8}$$

where ϕ is defined by Eq. (15). Thus

$$B'=-1.165\epsilon^2. \tag{B9}$$

APPENDIX C: THREE-BODY POTENTIAL CONTRIBUTION

The expression for $\phi_{\alpha\gamma}$ and $\phi_{\alpha\gamma\lambda}$ arising from the three-body potential term of the Lundqvist potential-energy[7] expression are given by

$$\begin{aligned}\phi^T_{\alpha\gamma}(l',\kappa\kappa',l'',\kappa\kappa'')\\ =e^2\sum_{l^{\mathrm{iv}},\kappa^{\mathrm{iv}}}\Bigg\{&[f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}},\kappa\kappa^{\mathrm{iv}}))]\left[\frac{\partial^2}{\partial x_\alpha(l',\kappa\kappa')\partial x_\gamma(l'',\kappa\kappa'')}\left(\frac{\epsilon(\kappa')}{r(l',\kappa\kappa')}\right)\right]_{\mathrm{I}}+\left[\frac{\epsilon(\kappa')}{r(l',\kappa\kappa')}\right]\left[\frac{\partial^2 f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}},\kappa\kappa^{\mathrm{iv}}))}{\partial x_\alpha(l',\kappa\kappa')\partial x_\gamma(l'',\kappa\kappa'')}\right]_{\mathrm{II}}\\ &+\left[\frac{\partial f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}},\kappa\kappa^{\mathrm{iv}}))}{\partial x_\alpha(l',\kappa\kappa')}\right]\left[\frac{\partial}{\partial x_\gamma(l'',\kappa\kappa'')}\left(\frac{\epsilon(\kappa')}{r(l',\kappa\kappa')}\right)\right]_{\mathrm{III}}+\left[\frac{\partial f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}},\kappa\kappa^{\mathrm{iv}}))}{\partial x_\gamma(l'',\kappa\kappa'')}\right]\left[\frac{\partial}{\partial x_\alpha(l',\kappa\kappa')}\left(\frac{\epsilon(\kappa')}{r(l',\kappa\kappa')}\right)\right]_{\mathrm{IV}}\Bigg\},\end{aligned} \tag{C1}$$

$$\begin{aligned}\phi^T_{\alpha\gamma\lambda}(l',\kappa\kappa',l'',\kappa\kappa'',l''',\kappa\kappa''')=e^2\sum_{l^{\mathrm{iv}},\kappa^{\mathrm{iv}}}\Bigg\{&[f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}},\kappa\kappa^{\mathrm{iv}}))]\left[\frac{\partial^3}{\partial x_\alpha(l',\kappa\kappa')\partial x_\gamma(l'',\kappa\kappa'')\partial x_\lambda(l''',\kappa\kappa''')}\left(\frac{\epsilon(\kappa')}{r(l',\kappa\kappa')}\right)\right]_{\mathrm{I}}\\ &+\left[\frac{\epsilon(\kappa')}{r(l',\kappa\kappa')}\right]\left[\frac{\partial^3 f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}},\kappa\kappa^{\mathrm{iv}}))}{\partial x_\alpha(l',\kappa\kappa')\partial x_\gamma(l'',\kappa\kappa'')\partial x_\lambda(l''',\kappa\kappa''')}\right]_{\mathrm{II}}\\ &+\left[\frac{\partial^2 f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}},\kappa\kappa^{\mathrm{iv}}))}{\partial x_\gamma(l'',\kappa\kappa'')\partial x_\lambda(l''',\kappa\kappa''')}\right]\left[\frac{\partial}{\partial x_\alpha(l',\kappa\kappa')}\left(\frac{\epsilon(\kappa')}{r(l',\kappa\kappa')}\right)\right]_{\mathrm{III}}\\ &+\left[\frac{\partial f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}},\kappa\kappa^{\mathrm{iv}}))}{\partial x_\alpha(l',\kappa\kappa')}\right]\left[\frac{\partial^2}{\partial x_\gamma(l'',\kappa\kappa'')\partial x_\lambda(l''',\kappa\kappa''')}\left(\frac{\epsilon(\kappa')}{r(l',\kappa\kappa')}\right)\right]_{\mathrm{IV}}\\ &+\left[\frac{\partial^2 f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}},\kappa\kappa^{\mathrm{iv}}))}{\partial x_\alpha(l',\kappa\kappa')\partial x_\lambda(l''',\kappa\kappa''')}\right]\left[\frac{\partial}{\partial x_\gamma(l'',\kappa\kappa'')}\left(\frac{\epsilon(\kappa')}{r(l',\kappa\kappa')}\right)\right]_{\mathrm{V}}\\ &+\left[\frac{\partial f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}},\kappa\kappa^{\mathrm{iv}}))}{\partial x_\gamma(l'',\kappa\kappa'')}\right]\left[\frac{\partial^2}{\partial x_\alpha(l',\kappa\kappa')\partial x_\lambda(l''',\kappa\kappa''')}\left(\frac{\epsilon(\kappa')}{r(l',\kappa\kappa')}\right)\right]_{\mathrm{VI}}\\ &+\left[\frac{\partial^2 f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}},\kappa\kappa^{\mathrm{iv}}))}{\partial x_\alpha(l',\kappa\kappa')\partial x_\gamma(l'',\kappa\kappa'')}\right]\left[\frac{\partial}{\partial x_\lambda(l''',\kappa\kappa''')}\left(\frac{\epsilon(\kappa')}{r(l',\kappa\kappa')}\right)\right]_{\mathrm{VII}}\\ &+\left[\frac{\partial f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}},\kappa\kappa^{\mathrm{iv}}))}{\partial x_\lambda(l''',\kappa\kappa''')}\right]\left[\frac{\partial^2}{\partial x_\alpha(l',\kappa\kappa')\partial x_\gamma(l'',\kappa\kappa'')}\left(\frac{\epsilon(\kappa')}{r(l',\kappa\kappa')}\right)\right]_{\mathrm{VIII}}\Bigg\}.\end{aligned} \tag{C2}$$

Here the superscript T over $\phi_{\alpha\gamma}$ and $\phi_{\alpha\gamma\lambda}$ denotes the three-body potential term. We have divided the expressions of $\phi^T_{\alpha\gamma}$ and $\phi^T_{\alpha\gamma\lambda}$ into four and eight different parts, respectively, and now we will calculate the contribution of each part to $A^T_{\alpha\beta\gamma\delta}$ and $A^T_{\alpha\beta\gamma\delta\lambda\mu}$ separately.

First part. Since the function f is defined in terms of overlap integrals which are assumed significant only for the nearest neighbors, the contribution of the first part of $\phi^T_{\alpha\gamma}$ and $\phi^T_{\alpha\gamma\lambda}$ can be expressed as

$$\phi^{T\mathrm{I}}_{\alpha\gamma}=e^2\times 6f(a)\left[\frac{\partial^2}{\partial x_\alpha(l',\kappa\kappa')\partial x_\gamma(l'',\kappa\kappa'')}\left(\frac{\epsilon(\kappa')}{r(l',\kappa\kappa')}\right)\right]_0=\frac{12f(a)}{\epsilon(\kappa)}\phi^C_{\alpha\gamma}, \tag{C3}$$

$$\phi^{T_I}_{\alpha\gamma\lambda}=e^2\times 6f(a)\left[\frac{\partial^3}{\partial x_\alpha(l',\kappa\kappa')\partial x_\gamma(l'',\kappa\kappa'')\partial x_\lambda(l''',\kappa\kappa''')}\left(\frac{\epsilon(\kappa')}{r(l',\kappa\kappa')}\right)\right]_0=\frac{12f(a)}{\epsilon(\kappa)}\phi^C_{\alpha\gamma\lambda}. \tag{C4}$$

These terms can be added to the Coulomb part modifying ϵ^2 to $\epsilon[\epsilon+12f(a)]$.

Second part. Evaluating the lattice sums, we get

$$\phi^{T\,\mathrm{II}}_{\alpha\gamma} = e^2 \frac{\alpha_M \epsilon}{a} \left[\frac{\partial^2 f_{\kappa'}(r(l', \kappa\kappa'))}{\partial x_\alpha(l', \kappa\kappa') \partial x_\gamma(l'', \kappa\kappa'')} \right]_0 , \tag{C5}$$

$$\phi^{T\,\mathrm{II}}_{\alpha\gamma\lambda} = e^2 \frac{\alpha_M \epsilon}{a} \left[\frac{\partial^3 f_{\kappa'}(r(l', \kappa\kappa'))}{\partial x_\alpha(l', \kappa\kappa') \partial x_\gamma(l'', \kappa\kappa'') \partial x_\lambda(l''', \kappa\kappa''')} \right]_0 , \tag{C6}$$

which may be added to the repulsive potential part, so that the total contribution can be derived from the overlapped repulsion $V(r)$ given by Eq. (26).

Third part. The expressions $\phi^{T\,\mathrm{III}}_{\alpha\gamma}$ and $\phi^{T\,\mathrm{III}}_{\alpha\gamma\lambda}$ are

$$\phi^{T\,\mathrm{III}}_{\alpha\gamma}(l', \kappa\kappa', l'', \kappa\kappa'') = e^2 \sum_{l^{\mathrm{iv}}, \kappa^{\mathrm{iv}}} \left[\left(\frac{x_\alpha(l', \kappa\kappa') \delta_{l' l^{\mathrm{iv}}} \delta_{\kappa' \kappa^{\mathrm{iv}}}}{r(l^{\mathrm{iv}}, \kappa\kappa^{\mathrm{iv}})} \frac{\partial f_{\kappa^{\mathrm{iv}}}(r(l', \kappa\kappa'))}{\partial r(l^{\mathrm{iv}} \kappa\kappa^{\mathrm{iv}})} \right) \left(\frac{-\epsilon(\kappa') x_\gamma(l'', \kappa\kappa'') \delta_{l' l''} \delta_{\kappa\kappa''}}{[r(l', \kappa\kappa')]^3} \right) \right]_0 , \tag{C7}$$

$$\begin{aligned} \phi^{T\,\mathrm{III}}_{\alpha\gamma\lambda}&(l', \kappa\kappa', l'', \kappa\kappa'', l''', \kappa\kappa''') \\ = e^2 \sum_{l^{\mathrm{iv}}, \kappa^{\mathrm{iv}}} \Bigg[\Bigg(& \frac{x_\gamma(l'', \kappa\kappa'') x_\lambda(l''', \kappa\kappa''') \delta_{l'' l^{\mathrm{iv}}} \delta_{\kappa'' \kappa^{\mathrm{iv}}} \delta_{l''' l^{\mathrm{iv}}} \delta_\kappa \delta_{\kappa''' \kappa^{\mathrm{iv}}}}{[r(l^{\mathrm{iv}}, \kappa\kappa^{\mathrm{iv}})]^2} \frac{\partial^2 f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}}, \kappa\kappa^{\mathrm{iv}}))}{\partial [r(l^{\mathrm{iv}}, \kappa\kappa^{\mathrm{iv}})]^2} \\ & + \frac{\delta_{\gamma\lambda} \delta_{l'' l^{\mathrm{iv}}} \delta_{\kappa'' \kappa^{\mathrm{iv}}} \delta_{l'' l'''} \delta_{\kappa'' \kappa'''}}{r(l^{\mathrm{iv}}, \kappa\kappa^{\mathrm{iv}})} \frac{\partial f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}}, \kappa\kappa^{\mathrm{iv}}))}{\partial [r(l^{\mathrm{iv}}, \kappa\kappa^{\mathrm{iv}})]} \\ & - \frac{x_\gamma(l'', \kappa\kappa'') x_\lambda(l''', \kappa\kappa''') \delta_{l'' l^{\mathrm{iv}}} \delta_{\kappa'' \kappa^{\mathrm{iv}}} \delta_{l''' l^{\mathrm{iv}}} \delta_{\kappa''' \kappa^{\mathrm{iv}}}}{[r(l^{\mathrm{iv}}, \kappa\kappa^{\mathrm{iv}})]^3} \frac{\partial f_{\kappa^{\mathrm{iv}}}(r(l^{\mathrm{iv}}, \kappa\kappa^{\mathrm{iv}}))}{\partial [r(l^{\mathrm{iv}}, \kappa\kappa^{\mathrm{iv}})]} \Bigg) \left(\frac{-\epsilon(\kappa') x_\alpha(l', \kappa\kappa')}{[r(l', \kappa\kappa')]^3} \right) \Bigg]_0 . \end{aligned} \tag{C8}$$

Hence the expressions for $A^{T\,\mathrm{III}}_{\alpha\beta\gamma\delta}$ and $A^{T\,\mathrm{III}}_{\alpha\beta\gamma\delta\lambda\mu}$ can be obtained from Eqs. (8b) and (9) as

$$A^{T\,\mathrm{III}}_{\alpha\beta\gamma\delta} = \frac{e^2}{2a^3} \sum_\kappa \left[\sum_{l^{\mathrm{iv}}, \kappa^{\mathrm{iv}}} \left(\frac{x_\alpha}{r} \frac{\partial f(r)}{\partial r} \right) x_\beta \right]_0 \left[\sum_{l', \kappa'} \left(\frac{-\epsilon(\kappa') x_\gamma}{r^3} \right) x_\delta \right]_0 , \tag{C9}$$

$$A^{T\,\mathrm{III}}_{\alpha\beta\gamma\delta\lambda\mu} = \frac{e^2}{2a^3} \sum_\kappa \left[\sum_{l^{\mathrm{iv}}, \kappa^{\mathrm{iv}}} \left(\frac{x_\gamma x_\lambda}{r^2} \frac{\partial^2 f(r)}{\partial r^2} - \frac{x_\gamma x_\lambda}{r^3} \frac{\partial f(r)}{\partial r} + \frac{1}{r} \frac{\partial f(r)}{\partial r} \delta_{\gamma\lambda} \right) x_\delta x_\mu \right]_0 \left[\sum_{l', \kappa'} \left(\frac{-\epsilon(\kappa') x_\alpha}{r^3} \right) x_\beta \right]_0 . \tag{C10}$$

All the vectors within the first square brackets are denoted by the same index number $(l^{\mathrm{iv}}, \kappa\kappa^{\mathrm{iv}})$ and within the second square brackets, by the index number $(l', \kappa\kappa')$. By summing the first-bracket expressions over nearest neighbors and the second-bracket expressions over the whole lattice, and writing $r df(r)/dr$ evaluated at $r = a$ as $a \partial f/\partial a$, we get

$$A^{T\,\mathrm{III}}_{11} = 4.660 \frac{e^2}{4a^4} \epsilon \left(a \frac{\partial f}{\partial a} \right), \quad A^{T\,\mathrm{III}}_{12} = 4.660 \frac{e^2}{4a^4} \epsilon \left(a \frac{\partial f}{\partial a} \right), \quad A^{T\,\mathrm{III}}_{44} = 0 , \tag{C11}$$

$$A^{T\,\mathrm{III}}_{111} = 4.660 \frac{e^2}{4a^4} \epsilon \left(a^2 \frac{\partial^2 f}{\partial a^2} \right), \quad A^{T\,\mathrm{III}}_{166} = A^{T\,\mathrm{III}}_{144} = 4.660 \frac{e^2}{4a^4} \epsilon \left(a \frac{\partial f}{\partial a} \right), \quad A^{T\,\mathrm{III}}_{112} = A^{T\,\mathrm{III}}_{123} = A^{T\,\mathrm{III}}_{456} = 0 . \tag{C12}$$

Similary, we can get the contributions of the remaining parts of $\phi^T_{\alpha\gamma}$ and $\phi^T_{\alpha\gamma\lambda}$ to the $A^T_{\alpha\beta\gamma\delta}$ and $A^T_{\alpha\beta\gamma\delta\lambda\mu}$. Thus, the total contributions of $\phi^T_{\alpha\gamma}$ and $\phi^T_{\alpha\gamma\lambda}$ to the various A coefficients are

$$A^T_{11} = 9.320 \frac{e^2}{4a^4} \epsilon \left(a \frac{\partial f}{\partial a} \right), \quad A^T_{12} = 9.320 \frac{e^2}{4a^4} \epsilon \left(a \frac{\partial f}{\partial a} \right), \quad A^T_{44} = 0 , \tag{C13}$$

$$A^T_{111} = \frac{e^2}{4a^4} \left[13.980 \epsilon \left(a^2 \frac{\partial^2 f}{\partial a^2} \right) - 61.344 \epsilon \left(a \frac{\partial f}{\partial a} \right) \right] , \tag{C14}$$

$$A^T_{112} = \frac{e^2}{4a^4} \left[4.660 \epsilon \left(a^2 \frac{\partial^2 f}{\partial a^2} \right) - 9.320 \epsilon \left(a \frac{\partial f}{\partial a} \right) \right] , \tag{C15}$$

$$A^T_{166} = \frac{e^2}{4a^4} \left[14.884 \epsilon \left(a \frac{\partial f}{\partial a} \right) \right] , \tag{C16}$$

$$A^T_{123} = \frac{e^2}{4a^4} \left[14.884 \epsilon \left(a \frac{\partial f}{\partial a} \right) \right] , \tag{C17}$$

$$A^T_{144} = \frac{e^2}{4a^4} \left[14.884 \epsilon \left(a \frac{\partial f}{\partial a} \right) \right] , \tag{C18}$$

$$A^{T}_{456}=0\,. \tag{C19}$$

Combining these three contributions to A coefficients, the SOE and the TOE constants can be obtained by transforming these A coefficients to the C coefficients.

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