

## Exchange Charge Contributions to the Failure of the Cauchy Relations in Alkali Halide Crystals\*

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Using a model originally constructed to deal with the theory of dielectric constants of alkali halide crystals, a theory of the elastic constants of these crystals is developed. Exchange charges arising from the requirements of the exclusion principle are approximated as point charges appropriately placed in a Born-Mayer model ionic crystal. The presence of these exchange charges and the manner in which their magnitude and position change in a strained crystal give rise to interionic forces of a many-body character. As a consequence the model predicts deviations from the Cauchy relation  $c_{12} = c_{44}$ .  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$  are calculated for 16 NaCl structured alkali-halides. In those cases where the method of calculation is expected to be valid the calculated values indicate that the exchange charge mechanism can account quantitatively for much of the observed deviation of  $c_{12} - c_{44}$  from zero for these crystals.

### I. INTRODUCTION

THE most general crystalline solid requires 21 independent elastic constants  $c_{ij}$  ( $i, j=1, \dots, 6$ ;  $c_{ij}=c_{ji}$ ) to describe its elastic behavior.<sup>1</sup> Crystal symmetry frequently reduces this number greatly. Under certain circumstances the maximum number of independent constants may reduce to 15.<sup>1-3</sup> These conditions are:

- (1) The interatomic forces in the crystal are of a central, single-body character;
- (2) Each atom in the crystal occupies a center of inversion symmetry;
- (3) The crystal is free from initial strains. In this case it follows that

$$\begin{aligned} c_{23} &= c_{44}, & c_{31} &= c_{55}, & c_{12} &= c_{66}, \\ c_{14} &= c_{56}, & c_{25} &= c_{64}, & c_{36} &= c_{45}. \end{aligned} \quad (1)$$

Equations (1) are called the Cauchy relations. For a crystal of cubic symmetry the number of independent elastic constants reduces to three:  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$ . If, in addition, the above conditions for the validity of the Cauchy relations are satisfied, then  $c_{12} = c_{44}$ .

The success of the Born-Mayer (BM) model in relating the cohesive energy of alkali halide crystals to their observed lattice constants and compressibilities is well known.<sup>1</sup> In its simplest form, this model contains only Coulomb, overlap repulsion, and van der Waals forces, all of them of central, single-body character, at least as employed in the model.<sup>4</sup> The alkali halides are cubic and the ions occupy centers of inversion symmetry so that the BM model leads one to expect that for these crystals  $c_{12}$  will equal  $c_{44}$ . The data shown in Table V show that this expectation is not born out by experiment.

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<sup>1</sup> M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).

<sup>2</sup> I. Stakgold, *Quart. Appl. Math.* **8**, 169 (1950).

<sup>3</sup> P. O. Löwdin, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 1.

<sup>4</sup> See, however, L. I. Podlubnyi, *Soviet Phys.—JETP* **37**, 633 (1960).

Three mechanisms have been proposed to account for the failure of the Cauchy relations in the alkali halides. Leibfried<sup>5,6</sup> and Hahn<sup>6</sup> have considered the role of the anharmonic contributions to the zero-point vibrations. Herpin<sup>7</sup> has pointed out that in a strained cubic crystal, ions are no longer at points of cubic symmetry and find themselves in inhomogeneous electric fields. These induce quadrupole moments on the ions which interact electrostatically with the ion monopoles and with one another in a non-single body manner. This leads to an expected failure of the Cauchy relation the magnitude of which Herpin has estimated. Löwdin<sup>3</sup> and Lundqvist<sup>8</sup> have shown that forces of a many-body character arising from nonorthogonality of Heitler-London crystal wave functions can account for a failure of the Cauchy relation. These three mechanisms have been treated distinctly but concurrently by Lothe<sup>9</sup> who finds that the contribution to the difference  $c_{12} - c_{44}$  (which is referred to as  $\Lambda$  hereafter) due to the zero-point vibration energy is small. Lothe also re-estimates the contribution from Herpin's mechanism and finds that Herpin somewhat underestimated this contribution to  $\Lambda$ . In this paper contributions to  $\Lambda$  which are qualitatively related to the mechanism of Löwdin and Lundqvist are investigated by means of a simple model which is an elaboration of the model of Born and Mayer.

Löwdin's quantum mechanical treatment of the cohesion and elastic constants of alkali halide crystals is far more fundamental than the semiempirical method of BM. Löwdin<sup>3</sup> points out that there is an important qualitative difference between the two approaches as well. This lies in the many-body forces which arise in the quantum mechanical treatment but not in the BM treatment. These many-body forces lead to deviations

<sup>5</sup> G. Leibfried, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. VII, Part 1, p. 287.

<sup>6</sup> G. Leibfried and H. Hahn, *Z. Physik* **150**, 497 (1958). 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.

<sup>7</sup> A. Herpin, *J. Phys. Radium* **14**, 611 (1953).

<sup>8</sup> S. O. Lundqvist, *Arkiv Fysik* **6**, 25 (1952).

<sup>9</sup> J. Lothe, *Arch. Math. Naturvidenskab.* **55**, 1 (1959).

from the Cauchy relations while the BM model predicts  $\Lambda=0$ . As well as being more fundamental, the quantum mechanical treatment is also very much more complicated than the BM treatment. The great services rendered by the BM model in understanding properties of ionic crystals have been possible because of its appealing simplicity. Two of the most conspicuous shortcomings of the BM model have been its inability to deal with the failure of the Cauchy relations and its deficiencies with regard to the predicted dielectric behavior of the alkali halides.<sup>10-15</sup> These two failures are to some extent related. Using an approach originally designed to deal with the dielectric theory<sup>12</sup> it is the purpose of this paper to show how a simple modification of the BM model can be made to introduce many-body forces and to account for the observed values of  $\Lambda$  with reasonable quantitative success. It is hoped that modifications of the BM model of this sort will enhance both its usefulness and that of the insights gained by the extensive work of Löwdin and his co-workers.

In Sec. II the model is described and in III the method of calculation is presented. Sections IV and V discuss the two stages of the calculation, the numerical results of which are presented in VI. The results are discussed in Sec. VII and VIII is a brief summary of principal conclusions.

## II. MODEL

The idea of the BM model modifications to be introduced can be given briefly as follows: In order for ions to repel in a crystal they must overlap. In the region of overlap the Pauli exclusion principle acts to reduce the electron charge density and (in the Heitler-London approximation) to distribute the removed charge with spherical symmetry on the ions. The region of reduced charge density may be considered electrostatically like a region of superposed positive charge and will be to some extent localized between neighboring ions. As a model incorporating this feature we consider small positive point charges, "exchange charges," located between neighboring ions on the line of centers. (see Fig. 1). Total electrical neutrality is maintained by a slight enhancement of electron charge on the ions. When the crystal is strained the magnitude and position of these exchange charges will change. Since the magnitude and position of the exchange charges depend on the positions of the ions nearest to these charges the interaction of two exchange charges with one another depends on the positions of four ions. Thus, exchange-charge interactions have a many-body character and their introduction into the BM model leads to a predicted  $\Lambda$  which is not zero. We now proceed to work out these ideas in detail.

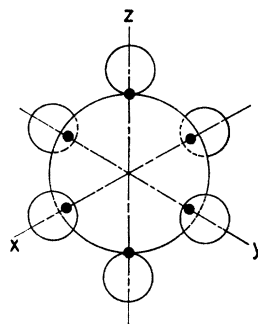


FIG. 1. Positions of exchange charges about a central negative ion in an unstrained crystal. The large and small spheres are negative and positive ions; the filled black circles are exchange charges. The positive ions have charge  $e-3q_0$  and the negative ion has a charge  $-e-3q_0$ .

The exchange charges are treated here exactly as in reference 12 (hereafter referred to as DO) to which the reader is referred for a detailed discussion. The important features of this treatment are:

(1) The regions of appreciable exchange charge density are approximated as point charges of magnitude  $q$  where

$$q = aB' \exp(-a/\rho)/\gamma e. \quad (2)$$

Here  $B'$  and  $\rho$  are the BM short-range repulsion parameters of the crystal,  $a$  is the nearest-neighbor ion separation,  $e$  is the electron charge, and  $\gamma$  is a dimensionless parameter estimated for the various alkali halide crystals in DO.

(2) The position of these point charges is taken to be on the line of centers of the ions and at a distance  $r_+a/a_0$  from the positive ion.  $r_+$  is the positive ion radius;  $a$  and  $a_0$  are the nearest-neighbor separations in the strained and unstrained crystals, respectively.

This assumption about the positions of the exchange charges is a plausible one only when the positive ion-negative ion overlap is the most significant. It is not expected to be a reasonable supposition for the lithium salts in which the negative ions overlap with one another more than with the small lithium ion.

(3) The positive (negative) ions have modified charges

$$+(-)e - \frac{1}{2} \sum_i q_i, \quad (3)$$

where  $q_i$  is the exchange charge located on the line connecting the positive (negative) ion to its nearest neighbor  $i$ . The sum over  $i$  is over these nearest neighbors.

In DO an additional ion deformation mechanism is discussed which allows relative displacements of ion cores and shells. This mechanism is ignored here; it leads to contributions to  $\Lambda$  corresponding to the induced quadrupole mechanism of Herpin. This contribution is discussed in Sec. VII.

## III. METHOD OF CALCULATION

The method used for calculating the elastic constants uses the relations

$$c_{11} = \partial^2 U / \partial e_{xx}^2, \quad c_{12} = \partial^2 U / \partial e_{xx} \partial e_{yy}, \quad c_{44} = \partial^2 U / \partial e_{xy}^2, \quad (4)$$

<sup>10</sup> B. Szigeti, Trans. Faraday Soc. **45**, 155 (1945).

<sup>11</sup> B. Szigeti, Proc. Roy. Soc. (London) **A204**, 51 (1950).

<sup>12</sup> B. G. Dick and A. W. Overhauser, Phys. Rev. **112**, 90 (1958).

<sup>13</sup> J. E. Hanlon and A. W. Lawson, Phys. Rev. **113**, 472 (1959).

<sup>14</sup> E. E. Havinga, Phys. Rev. **119**, 1193 (1960).

<sup>15</sup> J. R. Hardy, Phil. Mag. **6**, 27 (1961).

where  $U$  is the energy density of strained crystal and  $e_{xx}$ ,  $e_{yy}$ ,  $e_{xy}$  are strain tensor components.<sup>16</sup> Energy densities for a strained crystal model in which exchange charges have been included are calculated here for NaCl structure alkali halides by treating the ionic and exchange charges as multipoles. The exchange charges have been associated with the positive ions. The resulting multipole expansion is most rapidly convergent for those cases in which the positive ions are smallest compared with the negative ions. As noted above, however, the positive ions should not be too small. The clusters of exchange charges near the positive sites give rise to monopoles, quadrupoles, hexadecapoles, etc., at these sites. For the strains considered dipole and all odd order multipole components are zero. The monopole-monopole ( $MM$ ), monopole-quadrupole ( $MQ$ ), and quadrupole-quadrupole ( $QQ$ ) interactions along with nearest-neighbor repulsive interactions have been included in calculating  $U$ . Since octupole components vanish we may say that multipole interactions up to and including octupole-octupole interactions have been included. Next-nearest neighbor repulsive interactions and van der Waals interactions have been omitted. Since they are central, one expects the contribution of these omitted interactions to the quantity  $\Lambda = c_{12} - c_{44}$  to be small, but not in general zero. Lothe<sup>9</sup> has pointed out that the presence of many-body forces can cause central forces to contribute through the presence of both kinds of forces in the equilibrium condition, the crystal not being in equilibrium under central forces alone.

The calculation has been carried out in two stages. In stage one, discussed in Sec. IV,  $U$  is calculated ignoring the fact that certain exchange charge interactions are counted more than once in the multipole expansion procedure just outlined. This situation arises from the fact, discussed in DO that the monopole-exchange charge interactions of nearest neighbors are already included in the BM repulsive interaction and are, in fact, responsible for it. In stage two, discussed in Sec. V, a correction is made to allow for the exclusion of these redundant interactions included in stage one.

It is convenient to define a dimensionless notation:

$$\begin{aligned} x &= a_0/\rho, \\ r &= r_+/a_0, \\ \kappa &= q_0/e, \\ q_0 r_+^2/ea_0^2 &= Q = \kappa r^2, \\ B' a_0/e^2 &= B, \end{aligned} \quad (5)$$

where  $q_0 = a_0 B' \exp(-a_0/\rho)/\gamma e$  is the exchange charge magnitude in the unstrained crystal.

Three different cases of strain have been considered:

Case I. Hydrostatic compression; among the strain components only

$$e_{xx} = e_{yy} = e_{zz} = (a - a_0)/a_0 \text{ nonzero.}$$

<sup>16</sup> See, for example, C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed.

Case II. Only  $e_{xx}$  and  $e_{yy}$  nonzero.

Case III. Only  $e_{xy}$  nonzero.

Under the assumptions about the exchange and ionic charges outlined in Sec. II the monopoles and nonzero quadrupole components at the positive ion sites for the three cases of strain, to second order in strain components are as follows:

Case I.

$$\begin{aligned} e' &= 1 + 3\kappa(a/a_0) \exp[(a_0 - a)/\rho], \\ Q_{11} = Q_{22} = Q_{33} &= 2Q(a/a_0)^3 \exp[(a_0 - a)/\rho]. \end{aligned} \quad (6)$$

Case II.

$$\begin{aligned} e' &= 1 + 3\kappa + \kappa(1-x)(e_{xx} + e_{yy}) + \kappa x(\frac{1}{2}x-1)(e_{xx}^2 + e_{yy}^2), \\ Q_{11} &= 2Q[1 + (3-x)e_{xx} + (3-3x + \frac{1}{2}x^2)e_{xx}^2], \\ Q_{22} &= 2Q[1 + (3-x)e_{yy} + (3-3x + \frac{1}{2}x^2)e_{yy}^2], \\ Q_{33} &= 2Q. \end{aligned} \quad (7)$$

Case III.

$$\begin{aligned} e' &= 1 + 3\kappa + \frac{1}{4}\kappa(1-x)e_{xy}^2, \\ Q_{11} = Q_{22} &= 2Q[1 + \frac{1}{8}(3-x)e_{xy}^2], \\ Q_{33} &= 2Q, \\ Q_{12} &= 2Qe_{xy}. \end{aligned} \quad (8)$$

In Eqs. (6), (7), and (8) the monopole charges,  $e'$ , are in units of the electronic charge  $e$ . Although the modified monopole charges given by Eq. (3) are not equal, the grouping of the exchange charges with the positive ion makes the negative-ion monopole and positive ion-exchange charge aggregate monopole equal in magnitude, the magnitude being  $e'$ . Negative ions have only monopoles. The quadrupole components have been calculated from the definition

$$Q_{ij} = \int \rho(\mathbf{r}) x_i x_j d\tau. \quad (9)$$

In a strained crystal the ions and hence the multipoles are not in general at the sites of a cubic lattice. To calculate  $U$ , the positions as well as the magnitudes [Eqs. (6), (7), (8)] of the multipoles are needed. If we denote the position vector of an ion in a strained crystal by  $a_0(l_1', l_2', l_3')$  then the following array gives  $l_1'$ ,  $l_2'$ ,  $l_3'$  for the three strain cases:

	$l_1'$	$l_2'$	$l_3'$
Case I	$al_1/a_0$	$al_2/a_0$	$al_3/a_0$
Case II	$l_1(1+e_{xx})$	$l_2(1+e_{yy})$	$l_3$
Case III	$l_1 + \frac{1}{2}l_2 e_{xy}$	$l_2 + \frac{1}{2}l_1 e_{xy}$	$l_3$

Here  $l_1$ ,  $l_2$ ,  $l_3$  are positive or negative integers or zero.

In calculating the strain energy density it will be convenient to separate the short-range repulsive ( $SR$ ),  $MM$ ,  $MQ$ , and  $QQ$  interaction contributions. To find the elastic constants it is necessary to calculate, to second order in the strain components, the following quantities:

$$U_{SR} = \sum_i B \exp(-r_i/\rho) \quad (10)$$

(where the sum is over nearest neighbors  $r_i$ ),

$$U_{MM} = \frac{1}{2}(e')^2 \sum_{l_1 l_2 l_3} (-1)^\sigma (l')^{-1}, \quad (11)$$

$$U_{MQ} = -\frac{1}{4}(e') \sum_{i=1}^3 \sum_{l_1 l_2 l_3} (-1)^\sigma Q_{11}(3l_i'^2 - l'^2)(l')^{-5}, \quad (12)$$

$$U_{QQ} = \frac{1}{8} \sum_{l_1 l_2 l_3}^{\text{fcc}} \sum_{i,j=1}^3 \sum_{\alpha,\beta=1}^3 Q_{ij} Q_{\alpha\beta} \\ \times \{ [(35l_\alpha' l_\beta' / l'^9) - (5\delta_{\alpha\beta} / l'^7)] (3l_i' l_j' - l'^2 \delta_{ij}) \\ - (5/l'^7) [3(\delta_{i\beta} l_\alpha' + \delta_{i\alpha} l_\beta') l_j' \\ + 3(\delta_{j\beta} l_\alpha' + \delta_{j\alpha} l_\beta') l_i' - 4l_\alpha' l_\beta' \delta_{ij}] \\ + (1/l'^5) (3\delta_{i\beta} \delta_{j\beta} + 3\delta_{j\alpha} \delta_{i\beta} - 2\delta_{\alpha\beta} \delta_{ij}) \}, \quad (13)$$

where the  $U$ 's are energy densities in units of  $e^2/a_0^4$ . Also

$$\sigma = l_1 + l_2 + l_3, \\ l' = (l_1'^2 + l_2'^2 + l_3'^2)^{1/2}, \quad (14)$$

and the sums over  $l_1 l_2 l_3$  are to be taken over all positive and negative integers excluding  $l_1 = l_2 = l_3 = 0$  except for the sum marked fcc where only those sets of  $l_1 l_2 l_3$  are taken for which  $\sigma$  is even. Equations (10)–(13) are derived by summing the energies of interaction of a positive-ion multipole aggregate with all the other ions in an infinite crystal. In this way the energy per positive ion aggregate is found. This is then divided by the volume per ion,  $2a_0^3$ , to give the energy density which is written as the sum of the several contributions, Eqs. (10)–(13),

$$U = U_{SR} + U_{MM} + U_{MQ} + U_{QQ}. \quad (15)$$

This  $U$  yields the results of stage one of the calculation when the differentiations of Eqs. (4) are performed.

#### IV. STAGE ONE

First consider the Case I strain, the hydrostatic compression. In this case  $U_{MQ} = U_{QQ} = 0$  because of the cubic symmetry of the quadrupoles (a cubically symmetric charge distribution has a zero external quadrupole field), and so  $U = U_{SR} + U_{MM}$ . The term in  $U$  linear in the strain component must vanish if zero strain is to be an equilibrium state. This equilibrium condition is

$$6Be^{-x} - S_1^{(0)}(1+3\kappa)(1-3\kappa+6\kappa x) = 0. \quad (16)$$

The quadratic term yields the bulk modulus

$$\mathfrak{B} = (e^2/a_0^4)(1/3)[Be^{-x^2} - \frac{1}{3}S_1^{(0)}(1+3\kappa x^2)]. \quad (17)$$

$S_1^{(0)}$  is defined in Eq. (22) and is Madelung's constant. Equations (16) and (17) are of use later.

From a consideration of Case II expressions for the various contributions to  $c_{11}$  and  $c_{12}$  can be derived. Substituting the quantities of Eq. (7) into Eqs. (10) to (13), expanding to second order in strain parameters,

and then differentiating according to Eq. (4), we find, after lengthy calculations, the following expressions for the various contributions to the elastic constants (expressed in units  $e^2/a_0^4$ ):

$$(c_{11})_{SR} = Be^{-x^2}, \\ (c_{11})_{MM} = \frac{1}{6}S_1^{(0)}[1+2\kappa(5+4x-3x^2) \\ + 3\kappa^2(5+12x-8x^2)] - \frac{3}{2}S_5^{(2)}(1+3\kappa)^2, \quad (18) \\ (c_{11})_{MQ} = \frac{3}{2}[5S_7^{(2)} - S_3^{(0)}]Q(1+3\kappa)(3-x), \\ (c_{11})_{QQ} = (21/2)[5S_9^{(2)} - S_5^{(0)}]Q^2(3-x)^2, \\ (c_{12})_{SR} = 0, \\ (c_{12})_{MM} = \frac{1}{3}S_1^{(0)}\kappa(1-x)(2+5\kappa+x\kappa) \\ - \frac{3}{2}(1+3\kappa)^2S_5^{(1,1)}, \quad (19) \\ (c_{12})_{MQ} = -\frac{1}{2}(c_{11})_{MQ}, \\ (c_{12})_{QQ} = -\frac{1}{2}(c_{11})_{QQ}.$$

Similarly Case II strains give

$$(c_{44})_{SR} = -Be^{-x}, \\ (c_{44})_{MM} = \frac{1}{2}S_1^{(0)}\kappa(x-1)(1+3\kappa) \\ + \frac{1}{12}[S_1^{(0)} - 18S_5^{(1,1)}](1+3\kappa)^2, \quad (20) \\ (c_{44})_{MQ} = \frac{1}{2}[57S_9^{(2,1)} + 9S_9^{(1,1,1)} + \frac{3}{2}39S_9^{(3)}]Q(1+3\kappa), \\ (c_{44})_{QQ} = 0.$$

Equations (18), (19), and (20) have been simplified to a considerable extent through the use of identities such as Eq. (23).

First notice that the  $MQ$  and  $QQ$  terms make no contribution to  $\mathfrak{B} = \frac{1}{3}(c_{11} + 2c_{12})$  as we have argued above should be the case. Notice also that  $(c_{44})_{SR} + (c_{44})_{MM}$  may be considerably simplified by use of the equilibrium condition Eq. (16):

$$(c_{44})_{SR} + (c_{44})_{MM} = -\frac{3}{2}S_5^{(1,1)}(1+3\kappa)^2. \quad (21)$$

Finally, notice that if  $\kappa = 0$ ,  $c_{12} = c_{44}$ ; the Cauchy relation is satisfied if the exchange charge magnitude were zero.

In Eqs. (18), (19), and (20) the sums appearing are defined as

$$S_\alpha^{(\beta)} \equiv \sum (-1)^{\sigma+1} l_1^{2\beta} (l_1^2 + l_2^2 + l_3^2)^{-\frac{1}{2}\alpha}, \\ S_\alpha^{(\beta,\gamma)} \equiv \sum (-1)^{\sigma+1} l_1^{2\beta} l_2^{2\gamma} (l_1^2 + l_2^2 + l_3^2)^{-\frac{1}{2}\alpha}, \quad (22) \\ S_\alpha^{(\beta,\gamma,\delta)} \equiv \sum (-1)^{\sigma+1} l_1^{2\beta} l_2^{2\gamma} l_3^{2\delta} (l_1^2 + l_2^2 + l_3^2)^{-\frac{1}{2}\alpha},$$

where  $\sigma$  is given in Eq. (14) and the summations are over all positive and negative integers ( $l_1, l_2, l_3$ ) excluding (0,0,0). The  $S$  sums are the same except that the factor  $(-1)^{\sigma+1}$  is absent in their definitions and the summations are to be taken over those sets ( $l_1, l_2, l_3$ ) for which  $\sigma$  is even, (000) excluded.

The  $S$  sums have been calculated by Born and Misra.<sup>17</sup> Of the  $S$  sums needed  $S_1^{(0)}$  is Madelung's constant for the NaCl structure,<sup>16</sup>  $S_5^{(2)}$  is given by Löwdin,<sup>3</sup> and  $S_3^{(0)}$  has been calculated by Cohen and

<sup>17</sup> M. Born and R. D. Misra, Proc. Cambridge Phil. Soc. **36**, 466 (1940).

Keffer.<sup>18</sup>  $S_7^{(2)}$  and  $S_9^{(2,1)}$  were calculated by direct summation using a digital computer and were carried to 2196 and 3374 terms, respectively. Incidentally it was found that these sums may be obtained to a few percent accuracy by use of Evjen's method<sup>16</sup> going to only two shells. The remaining sums may be deduced from  $S_3^{(0)}$ ,  $S_5^{(2)}$ ,  $S_7^{(2)}$ , and  $S_9^{(2,1)}$  by use of the identities

$$\begin{aligned} S_\alpha^{(0)} &= 3S_{\alpha+4}^{(2)} + 6S_{\alpha+4}^{(1,1)}, \\ S_7^{(2)} &= 2S_9^{(2,1)} + S_9^{(3)}, \\ S_7^{(1,1)} &= 2S_9^{(2,1)} + S_9^{(1,1,1)}, \end{aligned} \quad (23)$$

which may be easily verified from the definitions Eq. (22).

The required lattice sums are:

$$\begin{aligned} S_9^{(2)} &= 0.5460, & S_5^{(1,1)} &= -0.232, \\ S_5^{(0)} &= 2.9995, & S_7^{(2)} &= 1.441, \\ S_1^{(0)} &= 1.748, & S_9^{(2,1)} &= -0.115, \\ S_3^{(0)} &= 3.239, & S_9^{(1,1,1)} &= 0.0459, \\ S_5^{(2)} &= 1.046, & S_9^{(3)} &= 1.661. \end{aligned} \quad (24)$$

This completes stage one of the calculation.

## V. STAGE TWO

It is now necessary to remove certain redundant terms included in the energy density  $U$ . Although an expression for  $U$  in the stage one approximation was not given in Sec. IV, it may be easily constructed from Eqs. (18), (19), and (20). In stage one  $U$  was calculated by multipole interactions and nearest-neighbor repulsions. In DO it is shown that the interaction of the exchange charge between nearest-neighbor ions with these ions is in fact responsible for their repulsion. To include the exchange-charge Coulomb interactions and the repulsion is for near neighbors redundant. The analysis in DO was carried through only for a single pair of ions. In an actual NaCl structure alkali halide each ion has six nearest neighbors. In removing redundant terms from  $U$  we make the following assumptions.

(a) The Coulomb interactions with one another of exchange charges which have an adjacent ion in common have already been included in the repulsive energy and hence must be removed from the stage one energy density expression (exchange-exchange redundancy).

(b) An ion monopole interaction with an exchange charge adjacent to a nearest neighbor to this ion is to be removed as redundant (exchange-monopole redundancy).

(c) In the stage one calculation the monopoles have the charges given by Eq. (3). In addition the positive ions have exchange charges lumped with them so that the both positive and negative ions have monopoles of



FIG. 2. A pair of second-nearest-neighbor positive ions with their associated exchange charges indicated by small filled circles. The interaction of exchange charges  $\alpha$  and  $\beta$  with the monopole and quadrupole of ion  $A$  must be removed according to criteria (a) and (b). The modified charge on  $B$  must also be altered.

absolute magnitude  $e'$  given in Eqs. (6), (7), and (8). For ions not too far apart there are exchange charges which are to be removed from the model according to the above criteria (a) and (b). We suppose, to be consistent with DO, that those exchange charges which are not to be considered explicitly are returned to their two adjacent ions, one-half the exchange charge going to each. This alters the monopole-monopole interaction of near neighbors from the stage one value of  $\pm(e')^2/r$ , and the correction can be expressed as terms to be removed from  $U$  of stage one (monopole-monopole redundancy).

We now list the redundancies and exclude them systematically. Consider a positive ion and its six associated exchange charges to be located at and about the origin and consider the interaction of this monopole and quadrupole (referred to as "central") with successively distant neighbors.

(1) First nearest-neighbor (negative) ions. There are six such ions. The interaction of the central monopole and quadrupole with the modified monopole of these ions has been included in stage one. According to (b) and (c) above the central quadrupole-modified monopole interaction should be removed and the central monopole-modified monopole interaction  $-(e')^2/r$  should be replaced by  $-e^2/r$ . In doing this the strained ion separations must be taken into account so that strain cases I, II, and III must be considered separately.

(2) Second nearest-neighbor (positive) ions. There are 12 such ions one of which is shown in Fig. 2. According to criteria (a) and (b) the interaction of the central monopole and quadrupole of ion  $A$  with the exchange charges marked  $\alpha$  and  $\beta$  are to be removed. Further, according to (c), the interaction of the central monopole and quadrupole with the monopole at  $B$  should not be with a monopole  $e' = (e - \frac{1}{2}\sum q_i) + \sum q_i$  but, rather, with  $e' - \frac{1}{2}\alpha - \frac{1}{2}\beta$ , a differently modified monopole. Each of

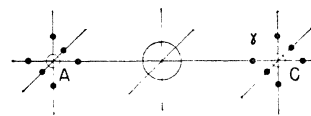


FIG. 3. A pair of fourth-nearest neighbors with associated exchange charges indicated by filled circles. The interaction of the exchange charge  $\gamma$  the monopole and quadrupole of ion  $A$  must be removed according to criteria (a) and (b). The modified charge on  $C$  must also be altered.

<sup>18</sup> M. H. Cohen and F. Keffer, Phys. Rev. **99**, 1128 (1955).

TABLE I. Redundant terms to be removed from  $U$ , Strain Case II. Energy density units  $e^2/a_0^4$ .  $e_{xx} \equiv \xi$ ;  $e_{yy} \equiv \eta$ .

		Constant terms	Linear terms*	Quadratic terms
First-nearest neighbors	$MM'$	$-9\kappa(2+3\kappa)$	$-3\kappa(3\kappa+2x-6\kappa x)(\xi+\eta)$	$-\left[\kappa(4-4x+3x^2)+6\kappa^2(1-3x+2x^2)\right](\xi^2+\eta^2)$ $+ [4\kappa(1-x)+6\kappa^2(1-x^2)]\xi\eta$
	$QM'$	0	0	$6(1+3\kappa)Q(3-x)(\xi^2+\eta^2-\xi\eta)$
Second-nearest neighbors	$MM'$	$3\sqrt{2}\kappa(1+3\kappa)$	$\sqrt{2}\kappa(3\kappa-x-6\kappa x)(\xi+\eta)$	$2^{-1/2}\kappa(x^2-x-\frac{1}{2}-\frac{1}{2}3\kappa-11\kappa x+8\kappa x^2)(\xi^2+\eta^2)$ $+ 2^{-1/2}\kappa(\frac{1}{2}+\frac{1}{2}3\kappa+x-\kappa x+4\kappa x^2)\xi\eta$
	$MD'$	$3\sqrt{2}\kappa r(1+3\kappa)$	$\sqrt{2}\kappa r(3\kappa-x-6\kappa x)(\xi+\eta)$	$2^{-1/2}\kappa r(x^2-3x-\frac{3}{2}-\frac{1}{2}9\kappa-17\kappa x+8\kappa x^2)(\xi^2+\eta^2)$ $+ 2^{-1/2}\kappa(-\frac{3}{2}+3x-4\kappa x+4\kappa x^2)\xi\eta$
	$MQ'$	$\frac{3}{4}\sqrt{2}Q(1+3\kappa)$	$\frac{1}{4}\sqrt{2}Q(3\kappa-x-6\kappa x)(\xi+\eta)$	$2^{-1/2}Q(x^2-9x+\frac{1}{2}37+\frac{1}{2}99\kappa-26\kappa x+5\kappa x^2)(\xi^2+\eta^2)$ $+ 2^{-1/2}Q(-\frac{1}{2}39-\frac{1}{2}117\kappa+9x+23\kappa x+4\kappa x^2)\xi\eta$
	$QM'$	0	0	$2^{-1}Q\kappa(4-x)(3-x)(\xi^2+\eta^2-\xi\eta)$
	$QD'$	0	0	$2^{-1}Q\kappa r(3-x)(2+x)(\xi^2+\eta^2-\xi\eta)$
	$QQ'$	0	0	$2^{-3/2}Q^2(13x^2-83x+132)(\xi^2+\eta^2-\xi\eta)$
Fourth-nearest neighbors	$MM'$	$\frac{3}{4}\kappa(1+3\kappa)$	$\frac{1}{4}\kappa(3\kappa-x-6\kappa x)(\xi+\eta)$	$\frac{1}{4}\kappa(\frac{1}{2}x^2-4\kappa x+4\kappa x^2)(\xi^2+\eta^2)-\frac{1}{2}\kappa^2 x(1-x)\xi\eta$
	$MD'$	$\frac{3}{4}\kappa r(1+3\kappa)$	$\frac{1}{4}\kappa r(3\kappa-x-6\kappa x)(\xi+\eta)$	$\frac{1}{4}\kappa r(\frac{1}{2}x^2-2\kappa x+3\kappa x^2)(\xi^2+\eta^2)-\frac{1}{2}\kappa^2 r x(1-x)\xi\eta$
	$MQ'$	$\frac{3}{8}Q(1+3\kappa)$	$\frac{1}{8}Q(3\kappa-x-6\kappa x)(\xi+\eta)$	$\frac{1}{8}Q(\frac{1}{2}x^2-2\kappa x+3\kappa x^2)(\xi^2+\eta^2)-\frac{1}{4}Q\kappa x(1-x)\xi\eta$
	$QM'$	0	0	$-\frac{1}{8}\kappa Q(2+x)(3-x)(\xi^2+\eta^2-\xi\eta)$
	$QD'$	0	0	$-\frac{3}{8}\kappa Q(2+x)(3-x)(\xi^2+\eta^2-\xi\eta)$
	$QQ'$	0	0	$-\frac{3}{8}Q^2(2+x)(3-x)(\xi^2+\eta^2-\xi\eta)$

\* The sum of the linear terms vanishes because of the equilibrium condition (27).

the twelve second-nearest neighbors will be at a different position and have different  $\alpha$  and  $\beta$  charges to be removed. The Coulomb interactions to be removed could easily be written down exactly and subtracted from  $U$ . However, this procedure would calculate the redundant interactions to a higher degree of accuracy than they were given when originally included in stage one. To be consistent the interaction of the central multipoles with the removed charges should be calculated by considering the multipole components of  $\alpha$  and  $\beta$  about the second-nearest neighbor sites. These include monopole ( $M$ ), dipole ( $D$ ), and quadrupole ( $Q$ ) components. The terms to be removed are designated by  $MM'$ ,  $MD'$ ,  $MQ'$ ,  $QM'$ ,  $QD'$ , and  $QQ'$  where the unprimed letter refers to the multipole of the central ion and the primed letter to that of the neighbor under consideration.

(3) Third-nearest-neighbor (negative) ions. There are 8 such ions. The exchange charges adjacent to third-nearest neighbors do not share an adjacent ion with any of the exchange charges associated with the central positive ion and so no redundancies occur in the interaction of the third-nearest neighbors with the central ion.

(4) Fourth-nearest neighbor (positive) ions. There are six such neighbors. In Fig. 3 it is seen that the exchange charge marked  $\gamma$  shares an adjacent ion with exchange charges on ion  $A$ . Just as with second nearest neighbors there will be  $MM'$ ,  $MD'$ ,  $MQ'$ ,  $QM'$ ,  $QD'$ , and  $QQ'$  removals.

(5) Fifth nearest and all more distant neighbors involve no redundancies.

In Table I and II the terms which must be subtracted from  $U$  to remove the redundancies are listed for the

TABLE II. Redundant terms to be removed from  $U$ , Strain Case III. Energy density in units  $e^2/a^4$ .  $\frac{1}{2}e_{xy} = \delta$ .

		Constant terms	Quadratic terms
First-nearest neighbors	$MM'$	$-9\kappa(2+3\kappa)$	$-3\kappa(3\kappa+2x-6\kappa x)\delta^2$
	$QM'$	0	$12Q(1+3\kappa)\delta^2$
Second-nearest neighbors	$MM'$	$3\sqrt{2}\kappa(1+3\kappa)$	$2^{-1/2}\kappa(3+15\kappa-2x-12\kappa x)\delta^2$
	$MD'$	$3\sqrt{2}\kappa r(1+3\kappa)$	$2^{-1/2}\kappa r(11+39\kappa-2x-12\kappa x)\delta^2$
	$MQ'$	$\frac{3}{4}\sqrt{2}Q(1+3\kappa)$	$-2^{-5/2}Q(21+57\kappa+2x+12\kappa x)\delta^2$
	$QM'$	0	$-3\sqrt{2}Q\kappa\delta^2$
	$QD'$	0	$-9\sqrt{2}Q\kappa r\delta^2$
	$QQ'$	0	$\frac{1}{2}93(2^{-1/2})Q^2\delta^2$
Fourth-nearest neighbors	$MM'$	$\frac{3}{4}\kappa(1+3\kappa)$	$\frac{1}{4}\kappa(3\kappa-x-6\kappa x)\delta^2$
	$MD'$	$\frac{3}{4}\kappa r(1+3\kappa)$	$-\frac{1}{4}\kappa r(4+9\kappa+x+6\kappa x)\delta^2$
	$MQ'$	$\frac{3}{8}Q(1+3\kappa)$	$-\frac{1}{8}Q(12+33\kappa+x+6\kappa x)\delta^2$
	$QM'$	0	$\frac{1}{2}3\kappa Q\delta^2$
	$QD'$	0	$\frac{1}{2}15Q\kappa r\delta^2$
	$QQ'$	0	$\frac{1}{2}21Q^2\delta^2$

Strain Cases II and III. The calculations are long and tedious. For convenience the strain parameters  $e_{xx}$ ,  $e_{yy}$ , and  $\frac{1}{2}e_{xy}$  have been denoted by  $\xi$ ,  $\eta$ , and  $\delta$ , respectively, in these tables.

Notice first the constant terms in Tables I and II. They are, of course, the same in both tables. They are terms which must be removed from the energy density of the unstrained crystal as calculated in stage one. These constant terms may be used to find the new equilibrium condition appropriate to stage two of the calculation. The equilibrium condition expresses the fact that the derivative with respect to  $a$  of the energy per ion pair is zero. The constant terms of Table I or II times  $2e^2/\rho x$  give the energy per ion pair which is to be subtracted from the energy per ion pair calculated in stage one. Differentiation of these correction terms with respect to  $x$  and combination of these terms with Eq. (16) gives the stage-two equilibrium condition

$$6Bxe^{-x} - (1+3\kappa)S_1^{(0)}(1-3\kappa+6\kappa x) + 6\{3\kappa(6\kappa x+2x-3\kappa) + (3\kappa-x-6\kappa x) \times [(\sqrt{2}+\frac{1}{2})\kappa(1+r) + \frac{1}{4}(\sqrt{2}+\frac{1}{2})Q]\} = 0. \quad (16')$$

Use of Eq. (16') eliminates all terms in  $U$  (stage two) which are linear in the strain components.

With the aid of the second-order terms of Tables I and II correction terms which must be subtracted from the stage-one elastic constants, Eqs. (18), (19), and (20), may be found. Expressions for  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$ , and  $\Lambda$  in which the redundancies have been removed may all be written in the same form

$$X = c_1 + c_2Be^{-x} + c_3Be^{-x^2} + \kappa(c_4 + c_5x + c_6x^2) + \kappa^2(c_7 + c_8x + c_9x^2) + \kappa r(c_{10} + c_{11}x + c_{12}x^2) + \kappa^2 r(c_{13} + c_{14}x + c_{15}x^2) + Q(c_{16} + c_{17}x + c_{18}x^2) + Q\kappa(c_{19} + c_{20}x + c_{21}x^2) + Q\kappa r(c_{22} + c_{23} + c_{24}x^2) + Q^2(c_{25} + c_{26}x + c_{26}x^2). \quad (25)$$

$X$  may be  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$ , or  $\Lambda$  depending on the values of the  $c$ 's. Numerical values of the constants  $c_1$  to  $c_{27}$  which are characteristic of the NaCl structure but independent of lattice constant are given in Table III for these cases. The elastic constants calculated from Eq. (25) are in units of  $e^2/a_0^4$ .

Just as Eq. (20) for  $c_{44}$  could be greatly simplified by use of the equilibrium condition Eq. (16) the Stage-Two version of  $c_{44}$  has been similarly simplified by use of the Stage-Two equilibrium condition Eq. (16'). The coefficients,  $c_i$ , for  $c_{44}$  which appear in Table III are those for the  $c_{44}$  which has been simplified in this way. Whether or not  $c_{44}$  is treated in this way makes no difference, of course, so long as the equilibrium condition Eq. (16') is satisfied. As is seen in Sec. VI, our choice of parameters does not satisfy Eq. (16') exactly. Such a choice of parameters corresponds to a crystal in which violation of Eq. (16') is maintained by the application of a pressure. This pressure, in units of  $e^2/a_0^4$ , is given by one-sixth the negative of the

 TABLE III.  $c_i$  coefficients for Eq. (25).

$X$ $i$	$c_{11}$	$c_{12}$	$c_{44}$	$\Lambda$	$P$
1	-1.278	0.348	0.348	0	0.291
2	0	0	0	0	-1.000
3	1.000	0	0	0	0
4	2.206	-1.101	1.027	-2.128	0
5	-4.255	2.128	0	2.128	-2.588
6	2.588	0	0	0	0
7	4.370	-2.181	-0.050	-2.131	1.385
8	-7.956	1.207	0	1.207	-2.771
9	3.694	0.924	0	0.924	0
10	2.121	1.061	-3.389	4.450	0
11	4.243	-2.121	0	-2.121	1.664
12	-1.664	0	0	0	0
13	6.364	0	-10.17	10.17	-4.826
14	25.042	3.328	0	3.328	-9.985
15	-12.814	-3.328	0	-3.328	0
16	-24.693	12.523	9.730	2.793	0
17	9.233	-4.616	0	-4.616	0.479
18	-0.479	0	0	0	0
19	-150.945	41.063	29.812	11.251	-1.436
20	33.045	-15.492	0	-15.492	2.496
21	-3.475	-0.478	0	-0.478	0
22	-8.228	4.114	2.614	1.500	0
23	-1.371	0.686	0	0.686	0
24	1.371	-0.686	0	-0.686	0
25	-90.973	45.486	-21.690	67.176	0
26	61.747	-30.873	0	-30.873	0
27	-10.474	5.237	0	5.237	0

left-hand side of Eq. (16'). This pressure,  $P$ , is calculated in Sec. VI; coefficients for Eq. (25) when  $X=P$  are also tabulated in Table III.

## VI. NUMERICAL RESULTS

The quantities  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$ ,  $\Lambda$ , and  $P$  have been calculated from Eq. (25) and Tables III and IV. In principle one might attempt to evaluate  $x$ ,  $B$ ,  $r$ ,  $\kappa$  from the equilibrium condition and  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$ . One could then calculate the binding energy of the crystal for comparison with the experimental value. This

TABLE IV. Choices of parameters defined in Eq. (15).

	$\kappa \times 10^{-2}$ <sup>a</sup>	$Q \times 10^{-3}$ <sup>b</sup>	$x^c$	$r^d$	$(e^2/a^4) \times 10^{-12}$ <sup>e</sup>	$Be^{-x} \times 10^2$ <sup>e</sup>
LiF	0.837	1.917	8.25	0.338	1.413	3.530
LiCl	0.889	1.243	7.75	0.264	0.5270	3.747
LiBr	0.879	1.078	7.88	0.248	0.4062	3.690
LiI	0.862	0.894	8.02	0.227	0.2847	3.629
NaF	2.578	9.288	8.03	0.424	0.8099	3.626
NaCl	2.397	5.838	8.57	0.348	0.3678	3.392
NaBr	2.320	5.015	8.95	0.329	0.2920	3.257
NaI	2.328	4.269	8.90	0.303	0.2116	3.262
KF	2.351	11.699	8.82	0.499	0.4572	3.293
KCl	2.134	7.646	9.71	0.424	0.2372	3.000
KBr	2.107	6.875	9.85	0.404	0.1961	2.956
KI	2.057	5.862	10.10	0.377	0.1492	2.890
RbF	2.345	12.955	8.85	0.526	0.3673	3.296
RbCl	2.141	8.764	9.70	0.453	0.2017	3.006
RbBr	2.120	7.890	9.77	0.432	0.1672	2.972
RbI	1.997	6.518	10.40	0.404	0.1281	2.796

<sup>a</sup> From Dick and Overhauser, reference 12.

<sup>b</sup>  $Q = \kappa r^2$ .

<sup>c</sup> From Born and Huang, reference 1.

<sup>d</sup> Zachariasen radii from Kittel, reference 13.

TABLE V. Experimental and calculated elastic constants. All elastic constants and  $P$  are in units of  $10^{11}$  dyn/cm<sup>2</sup>.

	Exp <sup>a</sup>	$c_{11}$ Theory	$c_{11}^*$ Theory <sup>b</sup>	Exp <sup>a</sup>	$c_{12}$ Theory	Exp <sup>a</sup>	$c_{44}$ Theory	Exp <sup>a</sup>	$\Lambda$ Theory	$P$ Theory
LiF	11.35	29.68	14.29	4.80	5.50	6.35	5.17	-1.24 -2.18	0.326	-1.86
LiCl	4.94	10.06	4.25	2.26	2.21	2.49	1.90	-0.11 -0.35	0.309	-0.750
LiBr	3.94	8.05	3.39	1.88	1.73	1.91	1.46	0.07 -0.13	0.269	-0.593
LiI	2.85	5.85	2.43	1.40	1.23	1.35	1.02	0.13 -0.03	0.212	-0.425
NaF	9.71	30.08	7.81	2.43	2.67	2.80	3.49	-0.24 -0.50	-0.813	-2.77
NaCl	4.93	15.45	3.40	1.31	1.64	1.275	1.48	0.12 -0.34	0.154	-1.41
NaBr	4.02	13.28	2.89	1.15	1.38	0.99	1.16	0.24 -0.02	0.225	-1.16
NaI	3.035	9.6	1.90	0.90	1.08	0.72	0.826	0.23 0.13	0.253	-0.87
KF	6.58	18.68	6.66	1.49	0.868	1.28	2.05	0.28 0.13	-1.18	-1.36
KCl	4.08	11.51	3.52	0.69	0.753	0.635	0.985	0.095 -0.064	-0.233	-0.821
KBr	3.49	9.78	2.91	0.58	0.684	0.51	0.803	0.105 0.04	-0.118	-0.699
KI	2.775	7.82	2.23	0.47	0.584	0.38	0.599	0.11 0.009	-0.014	-0.556
RbF	5.7	14.92	5.68	1.25	0.511	0.91	1.69	0.40 0.28	-1.18	-1.04
RbCl	3.645	9.62	3.17	0.61	0.535	0.475	0.856	0.165 0.105	-0.321	-0.663
RbBr	3.185	8.11	2.57	0.48	0.505	0.385	0.698	0.115 0.075	-0.193	-0.567
RbI	2.585	6.86	2.12	0.375	0.443	0.281	0.520	0.114 0.074	-0.077	-0.457

<sup>a</sup> Spangenberg and Haussühl, reference 19. Estimated errors  $c_{11} < 0.35\%$ ,  $c_{12} < 5\%$ ,  $c_{44} < 0.4\%$ .

<sup>b</sup>  $c_{11}^*$  is calculated by eliminating  $Be^{-z}$  from Eq. (25) for  $c_{11}$  by use of the equilibrium condition Eq. (16').

<sup>c</sup> The two values given are extreme values of  $\Lambda$  from room-temperature and 0°K extrapolated data of several investigators.

would put the exchange charge model to the same test which the BM model passes so well. Our present concern, however, is in learning to what extent the exchange charge model can help explain the violation of the Cauchy relation. Consequently we have chosen reasonable values for the parameters  $\kappa$ ,  $r$ ,  $x$ ,  $B$ , and  $Q(=\kappa r^2)$ . These choices are tabulated in Table IV.  $B$  and  $x$ , Eq. (5), have been taken from the tabulation of Born and Huang<sup>1</sup>.  $\kappa$ , Eqs. (2) and (5), has been evaluated from these same Born-Huang data and the values of the parameter  $\gamma$  estimated in DO.  $Q$  and  $r$  have been calculated from the above data and the Zacharisen radii tabulated in Kittel.<sup>16</sup> It should be emphasized that all of these parameters have been estimated in advance; none were adjusted to the purposes of the present theory.

In Table V are listed experimental values and calculated values for  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$ ,  $\Lambda$ , and  $P$  the pressure which indicates the degree of failure of Eq. (16'). For convenience, these results are shown graphically in Figs. 4-7.

The experimental values in Table V are taken from the room-temperature data of Spangenberg and Haussühl<sup>19</sup> except for  $\Lambda$ . In finding extreme values for  $\Lambda$ , values for  $c_{12}$  and  $c_{44}$  from Spangenberg and Haussühl

and the compilations of Huntington<sup>20</sup> and Lothe<sup>9</sup> were used. Some of these are extrapolated to 0°K and some are not. In ascribing extreme values to  $\Lambda$ , the extremes of  $c_{12}$  and  $c_{44}$  among these experimental data have been used. It should be pointed out that our calculation is only for 0°K while most of the data are taken at room temperature. Huntington<sup>10</sup> has pointed out that  $\Lambda$  may increase with decreasing temperature.

## VII. DISCUSSION

The most important results are the calculated values of  $\Lambda$ . In those cases where the method of calculation is expected to be valid, this difference should be more accurate than the separate values of  $c_{12}$  and  $c_{44}$ . Neglected central force contributions (second-nearest-neighbor repulsions, van der Waals interactions), should tend to cancel in the difference. As mentioned in Secs. II and III, the method of calculation is expected to be valid when

(1) The positive-ion radius is small compared with the negative-ion radius; for then the multipole expansions should be rapidly convergent.

(2) The positive ion is still not so small as to cause the negative ions to overlap.

<sup>19</sup> K. Spangenberg and S. Haussühl, Z. Krist. **109**, 4 (1957).

<sup>20</sup> H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 7.



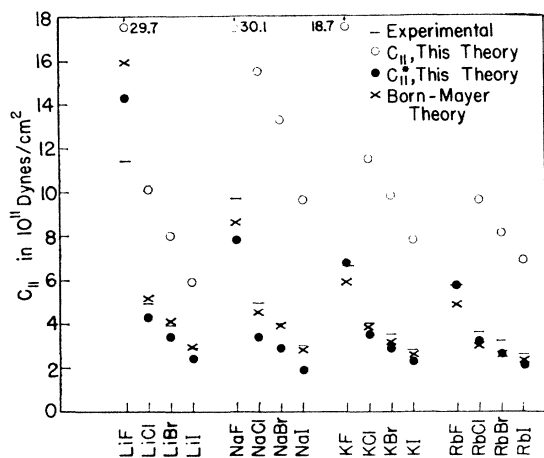


FIG. 4. Experimental and theoretical values of  $c_{11}$ . The experimental values are those of Spangenberg and Haussühl reference 19 (room temperature). The theoretical values  $c_{11}^*$  differ from  $c_{11}$  in that the parameter  $B$  has been adjusted to satisfy the equilibrium condition Eq. (16') in calculating  $c_{11}^*$ , while the Born-Mayer value of  $B$  from reference 1 has been used for  $c_{11}$ . The Born-Mayer values are calculated from Eq. (27) and Table IV.

According to these criteria it can be anticipated that the present calculation will yield poor results for the lithium halides because of the failure of (2) and for KF and RbF because of the failure of (1).<sup>21</sup> The calculated values of  $\Lambda$  for the K and Rb salts should improve as one follows the sequence chloride, bromide, iodide because of the consequent improvement in satisfying criterion (1). The whole method of calculation fails where criterion (1) is not met, but the failure of criterion (2) could be remedied within the method of calculation by relocating the exchange charges between the negative ions. This has not been done here.

Table V shows that these expectations are born out

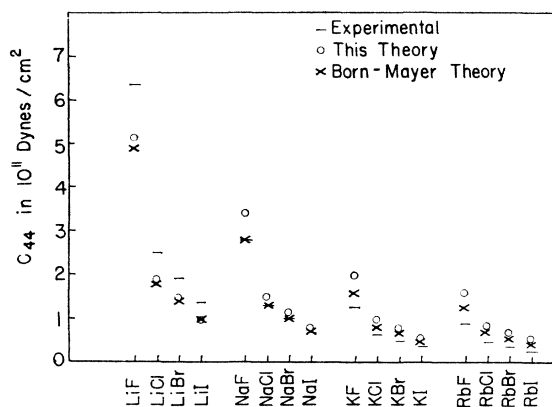


FIG. 5. Experimental and theoretical values of  $c_{44}$ . The experimental values are those of Spangenberg and Haussühl reference 19 (room temperature). Born-Mayer values are calculated from Eq. (27) and Table IV.

<sup>21</sup> These features are immediately apparent in Fig. 45-2 of L. Pauling, *The Nature of The Chemical Bond* (Cornell University Press, Ithaca, New York, 1945), 2nd ed., p. 353.

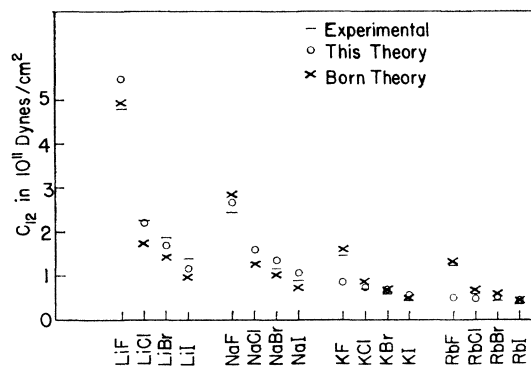


FIG. 6. Experimental and theoretical values of  $c_{44}$ . The experimental values are those of Spangenberg and Haussühl, reference 19 (room temperature). Born-Mayer values are calculated from Eq. (27) and Table IV.

by the results of the calculation. The chief justification for carrying out the calculations for the lithium salts, KF, and RbF is to be assured of their expected failure. In the remaining cases where there is some hope of success it is seen, as expected, that the sodium salts offer the best agreement with experiment. The  $\Lambda$  calculated for K and Rb chlorides, bromides, and iodides although coming closer to the experimental values in the expected order are incorrect in sign. Also included in Fig. 1 are points giving the theoretical values for  $\Lambda$  of Lowdin,<sup>3</sup> Lundqvist,<sup>8</sup> Lothe,<sup>9</sup> and estimates of that part of  $\Lambda$ ,  $\Lambda_H$ , arising from Herpin's mechanism. This latter is estimated from Lothe's recalculated version of Herpin's formula

$$\Lambda_H = 2.37(\alpha_+^2 E_+ + \alpha_-^2 E_-) / (1/a^9) \quad (26)$$

in which the  $\alpha$ 's are ion polarizabilities, and  $E_+$  and  $E_-$  are the positive-ion first ionization potential and

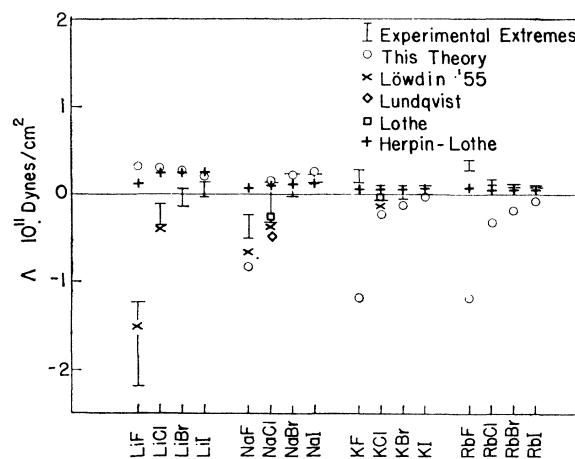


FIG. 7. Experimental and theoretical values of  $\Lambda = c_{12} - c_{44}$ . Experimental extremes are from the data of references 19, 20, and 9. The present theory values are those of Table V. Other theoretical values due to Löwdin reference 3 ("multiplier technique"), Lundqvist (reference 8), Lothe (reference 9), and Herpin's mechanism as recalculated by Lothe (reference 9) are also shown.

negative-ion affinity. In using Eq. (26) the Tessman, Kahn, and Shockley<sup>22</sup> polarizabilities and the electron affinities from the tabulation of Born and Huang<sup>1</sup> were used.

Turning now to  $c_{11}$ , it is noticed that the calculated values of this elastic constant that appear in the second column of Table V are in very poor agreement with experiment. In Fig. 4 it is seen, in fact, that the BM theory which gives

$$\begin{aligned} c_{11} &= (e^2/a_0^4)[Be^{-x}x^2 + \frac{1}{6}S_0^{(0)} - \frac{3}{2}S_5^{(2)}], \\ c_{12} = c_{44} &= (e^2/a_0^4)[-\frac{3}{2}S_5^{(1,1)}], \end{aligned} \quad (27)$$

predicts a  $c_{11}$  closer to experiment than Eq. (25) does. [Setting  $\kappa=Q=0$  in Eqs. (18), (19), and (20) yields Eq. (27).] This fact is not surprising; it arises from the presence of the  $Be^{-x}x^2$  term in Eq. (25) for  $c_{11}$ . The  $B$  and  $x$  used in our calculation are those evaluated from the BM theory which gives<sup>1</sup>

$$6Be^{-x}x = S_1^{(0)}, \quad (28)$$

$$\mathfrak{B} = S_1^{(0)}(x-2)/18. \quad (29)$$

Equation (28) is the equilibrium condition and Eq. (29) relates the bulk modulus,  $\mathfrak{B}$ , in units  $e^2/a_0^4$  to the parameters of the BM theory. Both these equations must be augmented by additional terms if the exchange charge contributions to crystal energy density are included. For instance, Eq. (28) must be replaced by Eq. (16'). Let  $\delta$  and  $\epsilon$  represent these additional terms:

$$6Be^{-x}x = S_1^{(0)} + \delta, \quad (28')$$

$$\mathfrak{B} = S_1^{(0)}(x-2)/18 + \epsilon. \quad (29')$$

From Eqs. (28') and (29') it follows that

$$\begin{aligned} B &= \frac{1}{6}S_1^{(0)}(S_1^{(0)} + \delta)[18(\mathfrak{B} - \epsilon) + 2S_1^{(0)}]^{-1} \\ &\quad \times \exp[2 + (18/S_1^{(0)})(\mathfrak{B} - \epsilon)], \end{aligned} \quad (30)$$

so that  $B$  is very sensitive to  $\epsilon$  through the exponential and the BM value of  $B$  used is quite poor.

Since there are no  $Be^{-x}$  terms in  $c_{12}$  or  $c_{44}$  they are free from this source of error. That this analysis of the origin of error in the calculated values is essentially correct can be seen as follows. Let us satisfy the equilibrium condition by adjusting  $B$  until  $P=0$ . By the remark at the end of Sec. V

$$\begin{aligned} P &= \frac{1}{6}[-6Bxe^{-x} + E], \\ 0 &= \frac{1}{6}[-6B^*xe^{-x} + E], \end{aligned} \quad (31)$$

where  $E$  denotes the negative of all terms but the first on the left-hand side of Eq. (16') and  $B^*$  is the adjusted

value of  $B$ . From Eqs. (31)

$$B^*e^{-x}x = P + Be^{-x}x. \quad (32)$$

Denote by  $c_{11}^*$  the value of  $c_{11}$  calculated with the aid of Eq. (25) (for  $c_{11}$ ) with  $B$  replaced by  $B^*$ , then

$$c_{11}^* = c_{11} + xP, \quad (33)$$

where  $c_{11}$  and  $P$  are given by Eq. (25) using the BM value of  $B$ . This procedure is simply one of eliminating  $Be^{-x}$  from Eq. (25) for  $c_{11}$  by use of Eq. (16'). Values of  $c_{11}^*$  are listed in Table V and appear in Fig. 4. The considerable improvement over the calculated  $c_{11}$  which  $c_{11}^*$  exhibits supports the view that an erroneous value of  $B$  is in large part responsible for the poor agreement of  $c_{11}$  with experiment. This is not the whole story, however, for using Eq. (32) to evaluate  $B^*$  yields in many case negative values of  $B^*$  which are inadmissible. This means that other of the parameters must also be adjusted from their estimated values in a consistent theory which satisfies the equilibrium condition Eq. (16').

As mentioned in the introduction, exchange charges play a role in the dielectric theory. It is tempting to seek a relationship between the deviation from unity of Szigeti's<sup>10</sup>  $e^*/e$  and the deviation of  $\Lambda$  from zero. In DO it is shown that the exchange charges are at least in part responsible for the deviation of  $e^*/e$  from unity and we have just seen that they may be used to account in large part for the deviation of  $\Lambda$  from zero. If the exchange charge parameter  $\gamma$  in Eq. (2) be so chosen as to force the exchange charge polarization mechanism of DO to account alone and fully for the observed values of  $e^*/e$  and if these values of  $\gamma$  be used to calculate values of  $\kappa$  and  $Q$  for use in the elastic constant theory of this paper, then all agreement with experiment is lost. The resulting exchange charges are much too large. Although the theories of  $e^*$  and  $\Lambda$  share a mechanism they also separately invoke mechanisms in addition which they do not share so that there appears to be no simple relation between  $e^*$  and  $\Lambda$ .

## VIII. SUMMARY

Exchange charges arising from the requirements of the exclusion principle may be included in a Born-Mayer like model of ionic crystals. Their presence leads to many-body forces and resulting predicted deviations from the Cauchy relation. In those cases where the method of calculation is expected to be valid, the model has some success in quantitative prediction.

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<sup>22</sup> J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).