

Self-consistent tight-binding theory of elasticity in ionic solids

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Intra-atomic and interatomic Coulomb contributions to the total energy are added to the tight-binding theory of bonding in simple ionic solids. They are found to remove the principal discrepancies with experiment found earlier for the bulk modulus and Grüneisen constant for the alkali halides and alkaline-earth chalcogenides. The analysis is extended also to predict the full elastic tensor for these systems and the pressure dependence of that tensor, in good accord with experiment where it exists.

I. INTRODUCTION

An earlier publication gave¹ an elementary tight-binding theory of cohesion and the bulk modulus in ionic solids in the rocksalt structure. It was based upon s states from the metallic atoms (e.g., Na) and p states from the nonmetallic atoms (e.g., Cl) with nearest-neighbor coupling given in terms of the internuclear distance d by the general form

$$V_{sp\sigma} = 1.42\hbar^2/md^2. \quad (1)$$

The virial theorem suggested a repulsive overlap interaction between ions of the form

$$V_0 = \eta_0 |\epsilon_{IG}| [\hbar^2/(m\epsilon_{IG}d^2)]^4, \quad (2)$$

where ϵ_{IG} is the p state term value for the inert gas in the row of the Periodic Table from which the constituent atoms come; if they come from different rows, the geometric mean of the two values is used. The motivation for the exact form is given in Ref. 1; the principal feature is the dependence upon $1/d^8$. Exactly this form was used, and is used here, both for the interaction between nearest-neighbor metallic and nonmetallic ions (separated by d) and between nearest-neighbor nonmetallic ions (separated by $d\sqrt{2}$). The coupling between states on nearest-neighbor metallic ions did not enter the total energy since the corresponding states are not occupied. The coefficient η_0 was fit for each anion row to give the correct spacing for the potassium halide. Then, using Hartree-Fock free-atom term values, all parameters were known which were needed to predict the equilibrium spacing, cohesion, bulk modulus, and Grüneisen constant for all alkali-metal halides and alkaline-earth chalcogenides. The first two properties were well given, but the bulk modulus and Grüneisen constant were in error by factors of order 2. We subsequently added d states in order to extend this analysis to the transition-metal compounds in the rocksalt structure² with similar successes and discrepancies.

In these analyses no account was taken of Coulomb corrections to the term values in the solid, not because the effective charges Z^* of constituent ions were small, but because the intra-atomic shift Z^*U of the levels due

to excess charge on the ion is very nearly equal and opposite to the Madelung shift $\alpha Z^*e^2/d$. Thus, for example, the observed band gaps in alkali-metal halides are very nearly equal to the difference in the free-atom p -state energy of the halogen and the free-atom s -state energy of the cation. Note, however, that only the Madelung term depends upon internuclear distance so that significant interatomic forces could arise from the Coulomb term even if the two energies cancel at the observed spacing. Indeed, a more intricate tight-binding analysis of sp -bonded systems by Majewski and Vogl³ did include Coulomb effects and gave a good account of the bulk modulus as well as structural stabilities. It was not clear from that paper whether the improvement came principally from the additional parameters in the theory or from the Coulomb effects. We shall see here that, in fact, our omission of Coulomb effects was responsible for the principal discrepancies which we found for the bulk modulus and Grüneisen constant.

Coulomb interactions were added in Ref. 4 for these systems and values given for the intra-atomic Coulomb repulsion U , but this was not formulated for, nor applied to, the volume dependence of the energy. That is one subject of the present study. The other is the analysis of the elastic shear constants.

II. THE TOTAL ENERGY

A. Without Coulomb effects

We first restate the tight-binding theory of the total energy, under the assumption that the atoms remain neutral in the solid. Then there are no Coulomb corrections and the relative energy of different atomic arrangements (including the difference between the solid and dispersed free atoms) can be obtained as the difference between the sum of the one-electron energy eigenvalues for the occupied states, as in Refs. 1 and 2. This can be simplified for the solid using the Baldereschi point method^{5,6} in which the average over a band is replaced by a value at a specially selected wave number \mathbf{k}^* . For sp bands in the rocksalt structure¹ two p bands are independent of wave number at the p state energy ϵ_p and the coupling between the s -like Bloch sum and the remaining p -like Bloch sum

at the Baldereschi point is given by $V_2 = \sqrt{6}V_{sp\sigma}$. For analysis of the total energy it is convenient to write the band energies in terms of the coefficients u_s and u_p of the two Bloch sums making up the state:

$$\epsilon_{k*} = u_s^2 \epsilon_s + 2u_s u_p V_2 + u_p^2 \epsilon_p. \quad (3)$$

In fact, it will be more convenient to write the band energies in terms of a parameter S^* which will be equal to the effective charge Z^* for the alkali-metal halides. We write $u_s^2 = (1 - S^*)/2$; then by normalization we know $u_p^2 = (1 + S^*)/2$. Since V_2 is positive, the lowest-energy state will have $u_s = -u_p$. Note that the two electrons per atom pair occupying this band place $1 - S^*$ electrons on an alkali-metal atom, which yields a net positive ion charge of Z^*e equal to S^*e . We, however, are using S^* here as a variational parameter. Substituting for u_s and u_p in Eq. (3), and multiplying by 2, we obtain the energy per ion pair, relative to the energy with one electron in each atomic state, as

$$E_{sp \text{ bond}} = -S^*(\epsilon_s - \epsilon_p) - 2V_2(1 - S^{*2})^{1/2}. \quad (4)$$

In the absence of Coulomb effects we could simply minimize this with respect to S^* to obtain $S^* = V_3/(V_2^2 + V_3^2)^{1/2}$ with the polar energy V_3 defined by $V_3 = (\epsilon_s - \epsilon_p)/2$. We could then substitute this S^* back in Eq. (4) to obtain the bonding energy and add an overlap repulsion to obtain the total energy as a function of spacing d .

B. Adding Coulomb effects

We return to an isolated atom and write the total energy of the atom in terms of the difference Z between the number of electrons on the atom and the number for the neutral atom as a Taylor expansion:

$$E(Z) = E(0) + E'Z + \frac{1}{2}E''Z^2 + \dots \quad (5)$$

For the free atom Z will be an integer, but it will become continuous in the solid. We next wish to identify the parameters E' and E'' in terms of free-atom parameters, dropping terms in Eq. (5) of higher order than Z^2 . We identify the free-atom term value as the energy $\epsilon = E(0) - E(-1) = E' - E''/2$ (the negative of the energy required to take an electron from the neutral atom and carry it to zero energy at infinite distance). The Coulomb energy U is defined (and obtained in Ref. 3) as the difference between the ionization energy $-\epsilon$ and the electron affinity. Thus the negative of the electron affinity is $\epsilon + U = E(1) - E(0) = E' + E''/2$. Substituting back for E' and E'' yields

$$E(Z) - E(0) = (\epsilon + U/2)Z + UZ^2/2. \quad (6)$$

Having dropped higher-order terms, we would obtain the second ionization energy as $E(-2) - E(1) = -\epsilon + U$, larger than the first ionization energy by U . This is in reasonable accord with experiment as may be seen, for example, from the CRC handbook.⁷ For ϵ we use the Hartree-Fock term value, which is a good approximation to the first ionization potential. We use U^s from Ref. 3 as the intra-atomic Coulomb repulsion for the metal and U^p

as the intra-atomic Coulomb repulsion for the nonmetal.

As we return to the compound, we use this same expression for the energy per atom, with Z given by the number of electrons on the atom ($1 - S^*$ for the metallic atom) minus the number on the neutral atom (1 for the alkali metal). The energy for the metallic atom, $E(S^*) - E(0) = -S^*\epsilon_s - S^*U^s/2 + S^{*2}U^s/2$ for alkali-metal halides, is added to that, $S^*\epsilon_p + S^*U^p/2 + S^{*2}U^p/2$, for the nonmetallic atom. We note also that the effective charge on the ions is S^*e for the alkali-metal halides so that we should add a Madelung energy $-\alpha S^{*2}e^2/d$ with $\alpha = 1.75$. There are also six nearest-neighbor and six second-neighbor-halide interatomic repulsions per ion pair,^{1,2} which we write collectively as E_{overlap} . The energy per ion pair for the alkali-metal halides becomes

$$\begin{aligned} E_{sp \text{ bond}} = & -S^*(\epsilon_s - \epsilon_p) - 2V_2(1 - S^{*2})^{1/2} \\ & + \frac{1}{2}S^*(U^p - U^s) + \frac{1}{2}(U^p + U^s)S^{*2} \\ & - \alpha e^2 S^{*2}/d + E_{\text{overlap}}. \end{aligned} \quad (7)$$

For the alkaline-earth chalcogenides it becomes

$$\begin{aligned} E_{sp \text{ bond}} = & -(S^* + 1)(\epsilon_s - \epsilon_p) - 2V_2(1 - S^{*2})^{1/2} \\ & + \frac{1}{2}(S^* + 1)(U^p - U^s) + \frac{1}{2}(U^p + U^s)(S^* + 1)^2 \\ & - \alpha e^2 (S^* + 1)^2/d + E_{\text{overlap}}. \end{aligned} \quad (8)$$

The evaluation of the energy for any translationally symmetric (so all ions of the same type are in equivalent environments) arrangement of ions is now straightforward. We are to minimize Eq. (7) or (8) with respect to S^* and all parameters have been specified. We shall do this for the potassium halides and fit η_0 for the corresponding row to obtain the observed d . Then we evaluate the energy from Eq. (7) or (8) for each other compound to predict the spacing d from the minimum, the cohesion from the energy at the minimum, the bulk modulus from the curvature at the minimum, and the Grüneisen constant from the third derivative. We shall also shear the lattice and recompute the energy in order to predict the shear elastic constants.

C. The relation to density-functional theory

We first relate the atomic energy, Eq. (6), to density-functional theory. In that theory the direct Coulomb energy of the charge distribution corresponding to the $Z + 1$ electrons on an alkali-metal atom is $(Z + 1)^2 U^s/2$, greater than the free-atom value ($Z = 0$) of $U^s/2$ by $ZU^s + Z^2 U^s/2$. There is also an exchange interaction, the largest effect of which is to cancel the direct interaction of each electron with itself, a correction of $-U^s/2$ for each electron times the number $Z + 1$ of electrons. We subtract from this correction the value $-U^s/2$ from $E(0)$ in Eq. (6) giving a net correction of $-ZU^s/2$. This reduces the excess Coulomb interaction to the $ZU^s/2 + Z^2 U^s/2$ given by Eq. (6) so the approaches are consistent. The same analysis applies to the nonmetallic p state. The density-functional eigenvalue is the derivative of Eq. (6) with respect to occupation, $\epsilon + U/2 + ZU$.

We may also see the relation between the energy of the solid and a density-functional band calculation. In particular, the maximum of the valence band and the minimum of the conduction band come at $\mathbf{k}=\mathbf{0}$ where the coupling between s -like and p -like Bloch sums is zero. Thus the eigenvalue for each is simply the free-atom eigenvalue ($\epsilon + U/2 + ZU$) shifted also by the Madelung potential. For the alkali metal in an alkali-metal halide $Z = -Z^*$ and this is $\epsilon_s + U^s/2 - Z^*U^s + \alpha Z^*e^2/d$. For the halogen it is $\epsilon_p + Up/2 + Z^*U^p - \alpha Z^*e^2/d$. The gap becomes

$$E_g = \epsilon_s - \epsilon_p + (U^s - U^p)/2 - Z^*(U^s + U^p - 2\alpha e^2/d). \quad (9)$$

The same expression obtains for divalent compounds, but then of course $Z^* = 1 + S^*$ rather than simply S^* .

The final term in Eq. (9) is very small because the average U is nearly equal to the Madelung energy, $\alpha e^2/d$. However, the term $(U^s - U^p)/2$ reduces the gap considerably below the observed values, which are near $\epsilon_s - \epsilon_p$. In fact, the density-functional gap is expected to be smaller than the observed gap by the correlation energy, $(U^s + U^p)/2$ divided by the static dielectric constant.^{4,8,9} It was noted in Ref. 4 that this correction was in good accord with the observed enhancement of the gap in comparison with other density-functional-theory values.¹⁰ However, correcting tight-binding gaps (then taken as $\epsilon_s - \epsilon_p$) gave gaps too large. That discrepancy is now removed.

III. RESULTS FOR THE VOLUME-DEPENDENT ENERGY

The evaluation of the energy as a function of volume from Eq. (7) is straightforward, leading to the properties given in Table I for the alkali-metal halides. We see that the accord with experiment is generally very good for the bulk modulus, as well as for the equilibrium spacing. This removal of discrepancies of the order of a factor of 4 has come from the inclusion of Coulomb interaction without the addition of any adjustable parameters.

There remain significant discrepancies for the fluorides. Such difficulties with systems from the carbon row of the Periodic Table are usual both for tight-binding and for pseudopotential theories. We note here that the discrepancies are qualitatively those that would arise if the overlap repulsion varied as a lower power of d , such as $1/d^6$, for the fluorides rather than as $1/d^8$. For example, replacing the V_0 of Eq. (2) by $\eta_0 \epsilon_{IG} |[\hbar^2/(m |\epsilon_{IG}| d^2)]^3$ (and η_0 readjusted for KF) leads to the fluoride properties listed in Table II. This makes considerable improvement in the predicted properties, except for the equilibrium spacings. We might note, however, that although the elastic constants (to be discussed in the next section) appear to be in good accord, the pure shear constant $\frac{1}{2}(c_{11} - c_{12})$ comes out too small by a factor of about 2; the contribution of the second neighbors turns out accidentally to be zero for a $1/d^6$ repulsion. We have no basic reason to make this change in the repulsion for the fluorides so such a change should be re-

garded as an empirical correction.

The direct application of Eq. (8) to the divalent compounds, with no additional adjustments, yields the values given in Table III. We see that the agreement with experiment is comparable to that obtained for the alkali-metal halides. Indeed, the larger discrepancies for the oxides would appear to be improved by the same change in overlap repulsion which was suggested above for the fluorides.

IV. THE ELASTIC CONSTANTS

The theory embodied in Eqs. (7) and (8) is also applicable to shearing of the lattice. In that case the Madelung constant α depends upon shear and E_{overlap} , consisting of first- and second-neighbor radial repulsions, and needs to be evaluated for the sheared geometry (using, however, exactly the same repulsions). Also, the $V_2 = \sqrt{6} V_{sp\sigma}$ came¹ from a sum over neighbors $[\sum_i V_{sp\sigma}(d_i)^2]^{1/2}$. In the sheared lattice that sum can be directly evaluated but no longer leads to $[6V_{sp\sigma}(d)^2]^{1/2}$.

A. Madelung contributions

The Madelung calculation uses the Ewald-Fuchs method as given by Wallace¹¹ to evaluate the stress-strain coefficients¹² B_{ij} for a system of point charges. The lattice sum formulas for B_{44} and $B_{11} - B_{12}$ may be factored into a form

$$\text{const} \times Z^* e^2 / 2d^4,$$

with the constant dependent only on the structure and independent of volume. The results for the pressure and elastic moduli in the rocksalt structure are

$$\begin{aligned} P_{\text{es}} &= -(\alpha/3)Z^*e^2/2d^4, \quad \alpha = 1.747565 \\ B_{\text{es}} &= -(4\alpha/9)Z^*e^2/2d^4, \\ (B_{11} - B_{12})_{\text{es}} &= \beta Z^*e^2/2d^4, \quad \beta = -2.66901 \\ B_{44\text{es}} &= \xi Z^*e^2/2d^4, \quad \xi = 1.27802 \end{aligned} \quad (10)$$

These Madelung contributions to the shear moduli are of the same order, but of opposite sign, as the corresponding contributions from E_{overlap} .

B. Comparison of elastic constants with experiment

The resulting elastic constants appear in the last three columns of Tables I and III. The agreement with experiment is comparable to that for the bulk modulus for the alkali-metal halides; the discrepancy discussed before for the fluorides shows up also in the other elastic constants. Agreement for the oxides is comparable to that for the fluorides. For the divalent sulphides, selenides, and tellurides we found no data with which to compare and these predictions may be useful because of that. The accuracy should be comparable to the agreement found for the monovalent compounds.

An interesting aspect of the results is that we predict in all cases a c_{44} somewhat less than c_{12} , whereas the experimental values are comparable and in some cases c_{44} is

TABLE I. The lattice spacing d , effective charge Z^* , cohesive energy E_{coh} , bulk modulus B , and second-order elastic constants for the alkali-metal halides. Experimental values are given in parentheses. Experimental values for d and E_{coh} are taken from the tabulations in Ref. 1. Experimental elastic moduli are from G. Simmons and H. Wang, *Single-Crystal Elastic Constants and Calculated Aggregate Properties*, 2nd ed. (MIT Press, Cambridge, 1971).

	d (Å)	Z^*	E_{coh} (eV)	B (eV/Å ³)	C_{11}^3 (eV/Å ³)	C_{12}^3 (eV/Å ³)	C_{44}^3 (eV/Å ³)
NaF	2.459 (2.32)	0.719	-10.81 (-7.9)	0.410 (0.290)	0.821 (0.605)	0.204 (0.152)	0.115 (0.175)
NaCl	2.872 (2.82)	0.762	-7.94 (-6.8)	0.200 (0.150)	0.366 (0.303)	0.117 (0.078)	0.079 (0.079)
NaBr	3.027 (2.99)	0.729	-6.73 (-6.1)	0.157 (0.124)	0.280 (0.248)	0.096 (0.066)	0.064 (0.062)
NaI	3.228 (3.24)	0.729	-5.82 (-5.2)	0.117 (0.094)	0.198 (0.189)	0.076 (0.056)	0.053 (0.046)
KF	2.648 (fit)	0.766	-10.52 (-7.6)	0.290 (0.190)	0.598 (0.410)	0.136 (0.091)	0.079 (0.078)
KCl	3.121 (fit)	0.814	-7.82 (-6.9)	0.137 (0.109)	0.267 (0.253)	0.072 (0.041)	0.049 (0.051)
KBr	3.296 (fit)	0.789	-6.62 (-6.2)	0.107 (0.092)	0.207 (0.216)	0.058 (0.035)	0.039 (0.032)
KI	3.519 (fit)	0.793	-5.77 (-5.4)	0.080 (0.079)	0.150 (0.172)	0.045 (0.028)	0.032 (0.023)
RbF	2.707 (2.80)	0.781	-10.42 (-7.4)	0.262 (0.164)	0.542 (0.345)	0.122 (0.087)	0.072 (0.058)
RbCl	3.200 (3.29)	0.831	-7.76 (-6.7)	0.123 (0.097)	0.242 (0.222)	0.063 (0.037)	0.044 (0.029)
RbBr	3.384 (3.42)	0.809	-6.56 (-6.1)	0.096 (0.081)	0.187 (0.196)	0.050 (0.030)	0.035 (0.024)
RbI	3.616 (3.64)	0.815	-5.72 (-5.4)	0.071 (0.066)	0.136 (0.160)	0.039 (0.022)	0.028 (0.017)

higher than c_{12} . This is of interest because the Cauchy relations, which follow if the system is in equilibrium under two-body radial forces only, are that $c_{12} = c_{44}$. We have found deviations because multibody forces can arise from the $V_2 = [\sum_i V_{sp\sigma}(d_i)^2]^{1/2}$; one can expand the square root and see that there are cross terms between different d_i . There may also be cross terms from Coulomb interactions for different d_i . The effects of these multibody radial forces are apparently small since we predict small deviations from the Cauchy relations.

Angular forces can also arise in tight-binding theory. The lowest-order (in $V_{sp\sigma}$) ones arise in fourth-order perturbation theory and are called the "chemical grip."⁶ These contribute to c_{44} but not to c_{12} . The change in energy arising from each metal-nonmetal-metal angle at a given nonmetal is $2[V_{pd\sigma}^4/(\epsilon_s - \epsilon_p)^2] \sum_{ij} \sin^2 \theta_{ij}$. This gives a contribution to c_{44} of

$$\delta c_{44} = 16V_{pd\sigma}^4 / (\epsilon_s - \epsilon_p)^3 d^3. \quad (11)$$

Note that this correction varies as $1/d^{11}$ so it becomes much more important in the first-row systems. It was

evaluated using $\epsilon_s + U^s/2 - \epsilon_p - U^p/2$ in the denominator, as is appropriate for density-functional theory. This gives an increase in c_{44} of 0.011 eV/Å³ for NaF and 0.050 eV/Å³ for CaO. The corrections are considerably smaller for the heavier compounds, 0.006 eV/Å³ for NaCl. Thus

TABLE II. Fluoride compounds with the empirical adjustment of E_{overlap} . For each compound, the top entry is for $E_{\text{overlap}} \sim 1/d^8$, the second entry is for $E_{\text{overlap}} \sim 1/d^6$, and the last entry in parentheses is the experimental value.

	d (Å)	B (eV/Å ³)	C_{11}^3 (eV/Å ³)	C_{12}^3 (eV/Å ³)	C_{44}^3 (eV/Å ³)
NaF	2.459	0.410	0.821	0.204	0.115
	2.475	0.271	0.392	0.211	0.124
	(2.32)	(0.290)	(0.605)	(0.152)	(0.175)
KF	2.648	0.290	0.598	0.136	0.079
	2.651	0.198	0.301	0.146	0.089
	(fit)	(0.190)	(0.410)	(0.091)	(0.078)
RbF	2.707	0.262	0.542	0.122	0.072
	2.705	0.180	0.277	0.131	0.082
	(2.80)	(0.164)	(0.345)	(0.087)	(0.023)

we see that it accounts for some of the discrepancy in the predicted $c_{12} - c_{44}$ difference.

C. Pressure derivatives of the elastic constants

For the compounds NaCl, KCl, KBr, and KI, the pressure derivatives of the stress-strain coefficients,¹² denoted

by B_{ij} , have been determined experimentally and are compared with the present results in Table IV. The theoretical derivatives were calculated as numerical derivatives of the B_{ij} 's. Measurements were made of the velocities of acoustic pulses propagating in the [110] direction of single-crystal samples. The overall agreement with experiment is good both in terms of magnitude

TABLE III. The lattice spacing d , effective charge Z^* , cohesive energy E_{coh} , bulk modulus B , and second-order elastic constants for the divalent compounds in the rocksalt structure. Experimental values are given in parentheses. *Divalent compound references are as follows:* MgO, O. L. Anderson and P. Andreatch, J. Am. Ceram. Soc. **49**, 404 (1966). CaO,SrO, P. R. Son and R. A. Bartels, J. Phys. Chem. Solids **33**, 819 (1972). CaTe,SrTe, H. Zimmer, H. Wingen, and K. Syassen, Phys. Rev. B **32**, 4066 (1985). CaS, E. Perez-Albuerné and H. G. Drickhamer, J. Chem. Phys. **43**, 1381 (1965). BaTe, T. Bryzbowski and A. Ruoff, Phys. Rev. Lett. **53**, 489 (1984). BaO, V. Vetter and R. Bartels, J. Phys. Chem. Solids **34**, 1448 (1973). CaSe,SrSe,BaSe, O. Anderson and J. Nafe, J. Geophys. Res. **70**, 3951 (1965). BaS, S. Yamaoka, O. Shimomura, H. Nakazawa, and O. Fukuma, Solid State Commun. **33**, 87 (1980).

	d (Å)	Z^*	E_{coh} (eV)	B (eV/Å ³)	C_{11} (eV/Å ³)	C_{12} (eV/Å ³)	C_{44} (eV/Å ³)
MgO	2.188 (2.10)	1.599	-14.63 (-10.4)	1.551 (1.03)	2.843 (1.91)	0.905 (0.59)	0.824 (0.98)
MgS	2.526 (2.60)	1.742	-11.57 (-8.0)	0.918 (0.71)	1.436	0.659	0.621
MgSe	2.663 (2.73)	1.694	-9.21	0.697	1.075	0.507	0.496
MgTe	2.832	1.703	-7.82	0.534	0.776	0.412	0.412
CaO	2.327 (2.41)	1.663	-15.13 (-11.0)	1.243 (0.71)	2.393 (1.39)	0.667 (0.37)	0.606 (0.51)
CaS	2.704 (2.85)	1.802	-12.52 (-9.7)	0.722 (0.28)	1.263	0.452	0.421
CaSe	2.855 (2.96)	1.770	-10.17 (-7.3)	0.555 (0.32)	0.969	0.348	0.334
CaTe	3.037 (3.18)	1.786	-8.93	0.431 (0.26)	0.730	0.282	0.274
SrO	2.367 (2.58)	1.704	-15.58 (-10.4)	1.191 (0.55)	2.303 (1.08)	0.636 (0.28)	0.574 (0.35)
SrS	2.761 (3.10)	1.834	-13.14 (-9.3)	0.677	1.206	0.413	0.383
SrSe	2.916 (3.12)	1.811	-10.77	0.527 (0.29)	0.937	0.322	0.305
SrTe	3.104 (3.33)	1.828	-9.57	0.409 (0.25)	0.709	0.259	0.248
BaO	2.415 (2.76)	1.713	-15.80 (-10.3)	1.100 (0.38)	2.148 (0.70)	0.576 (0.22)	0.520 (0.21)
BaS	2.828 (3.19)	1.841	-13.41 (-9.4)	0.615 (0.56)	1.118	0.363	0.337
BaSe	2.990 (3.30)	1.819	-11.04 (-10.3)	0.477 (0.25)	0.868	0.281	0.266
BaTe	3.187 (3.49)	1.836	-9.87	0.369 (0.18)	0.658	0.224	0.214

TABLE IV. Pressure derivatives of B_{ij} and mode Grüneisen parameters. Experimental values of dB_{ij}/dP and $\gamma(B_{ij})$ are from Simmons and Wang [G. Simmons and H. Wang, *Single-Crystal Elastic Constants and Calculated Aggregate Properties*, 2nd ed. (MIT Press, Cambridge, 1971)], and from Bartels and Schule [R. A. Bartels, and D. R. Schule, *J. Phys. Chem. Solids* **26**, 537 (1965)] for $T=195$ K and are written here in parentheses.

	dB_T/dP	dB_{11}/dP	dB_{12}/dP	dB_{44}/dP	$\gamma(B_{11})$	$\gamma(B_{12})$	$\gamma(B_{44})$
NaCl	4.55 (5.13)	10.5 (11.5)	1.59 (1.95)	-0.07 (+0.32)	2.86 (2.59)	1.19	-0.26 (0.14)
KCl	4.43 (5.34)	10.7 (12.8)	1.31 (1.61)	-0.29 (-0.42)	2.58 (2.56)	1.08	-0.57 (-0.77)
KBr	4.48 (5.39)	10.7 (13.0)	1.37 (1.59)	-0.24 (-0.33)	2.61	1.11	-0.50
KI	4.51 (6.28)	10.6 (14.0)	1.47 (2.42)	-0.14 (-0.24)	2.66	1.14	-0.34

and trends for the potassium halides. The negative value of dB_{44}/dP is somewhat unusual and is not observed in cubic-structure metals. dB_{44}/dP is quite sensitive to the repulsive interaction; the excellent agreement for all of the potassium compounds and correct trend between NaCl and KCl indicates that our treatment of the overlap repulsion is appropriate.

The mode Grüneisen parameters γ_i can be determined from the pressure derivatives of the elastic constants. For a particular vibrational mode of frequency ω_i , the $\gamma_i = -d(\ln\omega_i)/d(\ln V)$. For the low-frequency acoustic modes this may be written as $\gamma_i = -\frac{1}{6} + (B_T/2B_{ij})(dB_{ij}/dP)$. This latter expression may be derived by

using $\omega_i = k_i v_i$, where k_i is the wave vector and v_i is the wave velocity of the mode. The experiment measures the elastic moduli in terms of the propagation velocity by $B_{ij} = \rho v_{ij}^2$. Using a bulk modulus $B_T = -\partial P/\partial \ln V$, we obtain the relation between γ_i and the pressure derivatives given above.

Calculated values of $\gamma(B_{11})$, $\gamma(B_{12})$, and $\gamma(B_{44})$ are listed in the last three columns of Table IV with experimental values at $T=195$ K given in parentheses. We note that $\gamma(B_{44})$ is predicted to be small and negative, in contrast to the other values, and in agreement with experiment for KCl, though not NaCl.

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