tween the observed properties of krypton and some calculations, but systematic agreement in detail for all thermal properties is lacking. For krypton, the situation can be considered good, however, when comparison is made to that for other classes of solids. For the latter, anharmonic effects being smaller are easier to approximate, and largely phenomenological theories with many adjustable parameters are generally employed.

APPENDIX

Complete lattice-thermal-expansion data for two different specimens of solid krypton are given in Table VI.

TABLE VI. X-ray lattice-parameter thermal-expansion data from specimens Nos. 1 and 2. $a_0 = 5.64587 \pm 0.00010$ Å*.

T, °K	$10^4\Delta a/a_0$	T, °K	$10^4\Delta a/a_0$	T, °K	$10^4\Delta a/a_0$	T, °K	$10^4\Delta a/a_0$	T, °K	$10^4\Delta a/a_0$	T, °K	$10^4\Delta a/a_0$
		Specimen No. 1						Specimen No. 2			
4.30	0.04[a]	35.92	45.77	76.01	163.84	2.5	0.01[d]	32.98	38.79	86.02	200.86
4.30	0.05	39.85	55.22	80.00	178.14	3.2	−0.01	35.98	45.57	90.00	216.20
4.30	0.03	39.87	55.50	83.98	192.73	4.25	0.04	38.99	53.28	94.04	232.75
8.45	0.95	43.97	65.92	88.01	208.48	4.25	0.04	42.01	60.85	94.15	233.00[e]
9.95	1.78	48.23	77.40	92.13	224.69	5.93	0.20	45.00	68.59	98.02	249.44
12.28	3.36	52.00	87.73	96.02	241.02	8.68	0.95	47.98	76.96	102.00	266.54
14.61	5.43	55.97	99.24	100.02	257.81	9.86	1.46	51.98	87.97	106.00	285.25
19.44	12.10	59.99	111.24	104.14	276.30	12.28	3.10	56.00	99.49	107.01	290.38
19.45	12.12	59.99	111.40[b]	108.05	295.52	15.14	6.13	59.97	111.46	107.07	290.60
24.28	20.23	59.99	111.49	111.98	315.31	18.00	9.63	63.99	123.33	108.87[c]	299.46
28.05	27.85	63.99	123.74	113.97	325.99	21.16	13.70	69.98	143.44	109.99[c]	305.38
31.97	36.26	67.99	136.72	···	···	24.02	19.03	74.00	156.90	110.03	305.39
35.92[c]	45.60	71.98	149.95	···	···	26.95	24.88	78.03	171.17	112.00	315.45
						29.96	31.93	82.00	185.73	114.04	326.34

[a] Ni $K\alpha_1$ radiation (1.657910 Å*) and (622) planes used on this and on succeeding data points, until otherwise specified.
[b] Co $K\alpha_1$ radiation (1.788965 Å*) and (620) planes used, as in Ref. a; refraction correction 0.00007 Å*.
[c] Measurement made after cooling.
[d] Cu $K\alpha_1$ radiation (1.540562 Å*) and (640) planes used, as above.
[e] Fe $K\alpha_1$ radiation (1.936042 Å*) and (531) planes used, as above; refraction correction 0.00008 Å*.

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Pressure Derivatives of Second-Order Elastic Constants of MgO*

S. Y. LA AND G. R. BARSCH
Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania

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The deviations of the second-order elastic constants from the Cauchy relation for some representative alkali halides were successfully accounted for by Löwdin's theory of many-body forces of quantum-mechanical origin. In the present paper, this theory is extended to include second-nearest-neighbor (nearest anion-anion) interaction in MgO for the calculation of the pressure derivatives of the second-order elastic constants. The calculated values, $\partial c_{12}^*/\partial p = 1.4$ and $\partial c_{44}^*/\partial p = 0.5$, are compared with the empirical results. While the qualitative agreement tends to support the theory that the many-body character of interionic interactions is indeed responsible for the particularly large deviations observed in MgO, better quantitative agreement would require a more elaborate calculation.

I. INTRODUCTION

THE elastic constants of crystals and their dependence on pressure are of considerable interest because of the information on the interatomic forces which they provide. In particular, deviations from the Cauchy relations in ionic crystals indicate in certain cases the presence of many-body forces of quantum mechanical (QM) origin.

For cubic crystals under hydrostatic pressure p the six Cauchy relations reduce to the equation[1] $c_{12} - c_{44} = 2p$, where c_{12} and c_{44} are the effective elastic constants of the compressed crystal that determine, for example, ultrasonic wave propagation. It is well established theoretically that the Cauchy relations hold for centrosymmetric crystal structures in the absence of thermal-

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and zero-point motion with no initial stresses present, if the cohesive forces are two-body central forces.[2] The role of many-body forces in destroying the Cauchy relation was first pointed out by Löwdin[3,4] in a comprehensive QM treatment of the cohesive properties of alkali halides. In this theory a Heitler-London–type wave function for the electrons in the crystal is constructed from the Hartree-Fock (HF) functions of the free ions. The theoretical results for the elastic constants and for the deviation from the Cauchy relation agree reasonably well with the experimental data, confirming the QM origin of the departures from the Cauchy relations. Remaining discrepancies are partly due to experimental error and to the uncertainty arising from subtracting the effect of thermal- and zero-point motion from the experimental data. In addition, a series of simplifying assumptions was made in the theory which reduce its accuracy.

The effect of thermal and zero-point motion was investigated by Leibfried and Hahn.[2,5] These authors showed that in crystals with central forces thermal motion causes deviations from the Cauchy relations which are only small and opposite to those found in the alkali halides, except in lithium halides. Thus the departures from the Cauchy relations in these alkali halides become larger if the vibrational contribution is subtracted and must for the static lattice be ascribed entirely to QM many-body forces.

Another mechanism for explaining departures from the Cauchy relations was proposed by Herpin.[6] It arises from the electrostatic interaction of quadrupole moments which are induced due to the loss of cubic symmetry in the strained crystal. Dick[7] has designed a simple model for estimating the effect arising from QM exchange charges which arise in the region of overlapping wave functions of neighboring ions. Recently, Haussühl[8] has discussed the empirical data for a large variety of materials and has proposed qualitative rules for the deviations from the Cauchy relations.

The pupose of the present paper is to investigate the failure of the Cauchy relations in MgO by means of the theory of Löwdin. Because the overlap of the wave functions of adjacent oxygen ions was found to be large it was necessary to extend Löwdin's formalism so as to include next-nearest-neighbor (NNN) anion-anion interaction. The choice of MgO was motivated by the fact that for this material the deviation from the Cauchy relation is much larger than for any alkali halide. In addition, the elastic constants of oxide compounds and their dependence on pressure are of great importance in connection with the problem of the constitution of the earth, and of all oxides MgO has the simplest possible electronic and crystal structure. The pressure dependence of the elastic constants is of theoretical interest in itself because one would expect that the deviations from the Cauchy relations increase with increasing overlap of the electronic wave functions, or with increasing pressure. Therefore, attention will be focused in this paper on the pressure dependence of the elastic constants.

While the present work was being completed, Calais *et al.*[9] have reported calculations of the cohesive properties and the elastic constants of MgO on the basis of Löwdin's theory; however only nearest-neighbor (NN) interaction is taken into account for the elastic constants c_{12} and c_{44}, and only the zero-pressure values of the elastic constants are calculated.

Experimental data on the elastic constants of MgO and their dependence on temperature and pressure are available from several investigators.[10–15] The room-temperature values and the pressure derivatives obtained by different investigators are substantially in agreement. Marked differences in the temperature variation exist, however, and will be discussed in connection with the evaluation of the thermal contribution in Sec. II.

II. DEPENDENCE OF ELASTIC CONSTANTS ON PRESSURE AND TEMPERATURE

The isentropic second-order elastic coustants of a crystal at arbitrary pressure p and temperature T can in the quasiharmonic approximation be represented as the sum of two terms[2]:

$$C_{ijkl}{}^{S}(p,T)=C_{ijkl}{}^{*}(p)+B_{ijkl}(p,T). \qquad (1)$$

The first term represents the elastic constants of the static lattice. The second term contains the effect of thermal and zero-point motion and is usually much smaller than the first term. The first term consists of a contribution from the cohesive forces of the crystal and a second term which arises from the mechanical work of the surface forces against the pressure[2]:

$$C_{ijkl}{}^{*}(p)=\frac{1}{V}\left(\frac{\partial^2 E}{\partial e_{ij}\partial e_{kl}}\right)_{e=0}+pD_{ijkl}, \qquad (2)$$

where

$$D_{ijkl}=\delta_{ij}\delta_{kl}-\delta_{ik}\delta_{jl}-\delta_{il}\delta_{jk} \qquad (3)$$

and E is the cohesive energy of the crystal per mole at

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a state corresponding to the compression caused by the pressure upon which a deformation described by the strain tensor $\mathbf{e}=(e_{ij})$ is superimposed. V is the molar volume of the crystal at the pressure p, and δ_{ij} denotes the Kronecker symbol. The quantities defined in (2) are called effective elastic constants. For crystals of cubic symmetry the first term in (2) depends only on the NN distance a. Therefore the first and second pressure deviatives of the effective second-order elastic constants can be written in the form

$$\left(\frac{\partial C_{ijkl}^*}{\partial p}\right)_0 = -\frac{a_0}{3B_0}\left(\frac{\partial C_{ijkl}}{\partial a}\right)_0 + D_{ijkl}, \tag{4a}$$

$$\left(\frac{\partial^2 C_{ijkl}^*}{\partial p^2}\right)_0 = \left(\frac{a_0}{3B_0}\right)^2 \left(\frac{\partial^2 C_{ijkl}}{\partial a^2}\right)_0 - \frac{1}{3B_0}(1+3B_0') \times\left[\left(\frac{\partial C_{ijkl}^*}{\partial p}\right)_0 - D_{ijkl}\right]. \tag{4b}$$

Here B_0 and B_0' are the zero-pressure values of the bulk modulus and its first pressure derivative, respectively, and the index 0 always refers to the static lattice at zero pressure. The quantity

$$C_{ijkl}(a) = \frac{1}{V}\left(\frac{\partial^2 E}{\partial e_{ij}\partial e_{kl}}\right)_{\mathbf{e}=0} \tag{5}$$

is the contribution from the cohesive forces and will be calculated in Sec. III as a function of the interionic distance, and the first two pressure derivatives of the effective elastic constants of the static lattice will be evaluated according to (4).

The second term in (1) contains the temperature dependence of the adiabatic elastic constants for any given pressure. It is approximately proportional to the vibrational energy and therefore for temperatures above the Debye temperature directly proportional to the temperature. This is the justification for the widely used procedure (first suggested by Leibfried and Hahn[5]) to determine the elastic constants of the static lattice by extrapolating the experimental data from the high-temperature region linearly to $T=0$°K. The same procedure must be used to determine the lattice constant of the static lattice from measurements at high temperature.

The zero-pressure values of the elastic constants of the static lattice as determined from the experimental data of different investigators are for MgO listed in Table I. The data of Anderson and Andreatch[14] could not be used for this purpose since they cover only the range from 79°K to room temperature. Although at the lowest temperature measured the data for c_{11} and c_{12} of these authors are, rexpectively, 1 and 3% higher than the data of Chung,[15] there is very good agreement at room temperature. The room-temperature values for c_{11} and c_{12} of both authors fall almost exactly between those of Durand[10] and of Susse,[12] the deviations being 1 and 5%, respectively. The room-temperature values of c_{44} of three investigators agree, but those of Susse are 1% higher. Since the slopes at high temperatures are also slightly different the discrepancies for the extrapolated values of the static lattice are larger. The discrepancy is particularly striking for c_{12}, where the value obtained in Ref. 2 from Durand's data is 20% smaller than the value obtained from Susse. This is due to the fact that Durand's measurements covered only the range 80–560°K, whereas those of Susse and Chung are extended to 1480 and 1250°K, respectively. Since the Debye temperature of MgO is[16] about 950°K it may be expected that the temperature dependence of the elastic constants becomes linear at or above this temperature. The measurements of all three authors show that the linear range of c_{11} starts at about 500°K and that of c_{44} at about 700°K. According to Susse and Chung, c_{12} decreases linearly above 800°K; however, Durand finds a constant positive slope between 90 and 560°K. The other two investigators[14,15] that have extended their measurements to low temperature confirm the positive temperature coefficient of c_{12} below room temperature. It must be concluded, therefore, that c_{12} passes through a maximum which occurs according to Chung at about 300°K. Thus the static value of c_{12} obtained from Durand's data is too low and incorrect because it is not based on the correct high-temperature slope. All three static elastic constants as determined from the data of Susse and of Chung agree quite well. After a careful consideration of all factors involved it was decided to choose the data of Chung for further use in this paper.

TABLE I. Static elastic constants of MgO (in 10^{11} dyn cm^{-2}). (From linear extrapolation of high-temperature data to 0°K.)

c_{11}^0	c_{12}^0	c_{44}^0	B^0	Ref.
34.80	8.57	16.78	17.31	10, 2
32.27	10.80	16.38	17.96	12
31.88	10.00	16.24	17.29	15

In order to obtain the pressure derivatives of the elastic constants of the static lattice the same method of extrapolation of the data taken at high temperature has to be used. Unfortunately, the only available experimental data[13,14] for the pressure derivatives refer to 300 and 79°K. Since in this temperature range the thermal contribution may not be expected to be proportional to temperature, there is no direct way of determining the static values from the experimental data. In the absence of experimental data at or above the Debye temperature one could perform a lattice-dynamical calculation, but this is beyond the scope of the present paper. Therefore the unreduced experimental data will be used for the comparison with the theoretical results.

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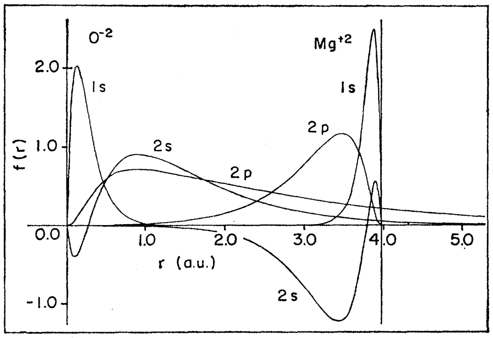

FIG. 1. The radial wave functions for O^{-2} and Mg^{+2} in MgO. Functions for O^{-2} and Mg$^{+2}(2p)$ are Hartree-Fock solutions. Mg$^{+2}(1s)$ and Mg$^{+2}(2s)$ are obtained by a variation principle.

III. QUANTUM-THEORETICAL CALCULATION

In this section the theoretical method developed by Löwdin[3,4] and applied by him to alkali halides will be adapted to evaluate for MgO the elastic constants and their pressure dependence for the static lattice.

Although alkali halides and divalent oxides such as MgO have in common the ionic bond and the rocksalt structure, there are several important differences.

In alkali halides, only NN interactions have to be taken into account, because the overlapping of wave functions between other than NN ions is usually small. Also, the deformation of the ions due to the effect of the crystal field and that arising from direct interactions with neighboring ions may be omitted. Hence the use of HF functions of the free ion represents a good approximation to the "true" electronic wave functions of the ions in the crystal. These assumptions are obviously much less valid, if valid at all, in MgO. As shown in Figs. 1 and 2, the overlap between nearest oxygen pairs of ions is by no means small, as expected, because the outer electrons of the negative ion are more loosely bound to its nucleus. This, in turn, leads one to expect large deformations of the negative ions. It is also likely that in a divalent crystal, the effect of the crystal field upon the electronic wave functions, perhaps mostly those of the outer electrons, would be considerably greater than in alkali halides. To incorporate these additional conditions, the contribution from the many-body-force interaction of nearest oxygen pairs of ions is estimated. Any rigorous attempt to obtain the perturbed wave functions would require much too great an effort to be practicable, at least for our purpose. Consequently, a more feasible approach appears to be a semiempirical method. Therefore it is assumed that, due to the Coulomb repulsion arising from the effective negative charge of the neighboring anions, the electrons of the negative ion tend to localize toward the center at its nucleus along the lines joining the NN anions; in a similar manner, the electrons tend to diffuse outward along the lines joining the nearest cations for the same reason. As for a cation as a center, the same effect occurs, except that the directions of localization and diffusion are reversed. In order to take this effect approximately into account, two "scaling" parameters λ_+ and λ_- for evaluating the overlap integrals are introduced and defined by the following condition:

$$\lambda_-\lambda_-\sum_i\sum_j\langle i_H,Sj_H\rangle=\sum_i\sum_j\langle i_T,Sj_T\rangle,$$

$$\lambda_-\lambda_+\sum_m\sum_n\langle m_H,Sn_H\rangle=\sum_m\sum_n\langle m_T,Sn_T\rangle. \qquad (6)$$

The brackets denote matrix elements of an operator S between two electronic states that do not belong to the same ion, and i_H, j_H are the HF functions of the free ions associated with ith and jth states of NN pairs of anions. The quantities i_T, j_T are hypothetical true wave functions of the corresponding states in the crystal. Similarly, m_H, n_H, m_T, and n_T have the same meaning as the corresponding i_H, j_H, i_T, and j_T except that they refer to nearest cation-anion pairs. The factors λ_+ and λ_- may either be real or complex. In the case of $S=1$ the quantities in Eq. (6) become the overlap integrals between two states, and the only restriction on the possible values of λ_s is that the absolute values are upper bounded by the fact that the greatest possible values of the right sides of Eq. (6) are integers representing the sums of the overlapping states considered. However, in view of the reasoning for introducing them, meaningful values should be within the range of $|\lambda_-|<1.0$, $|\lambda_+|>1.0$, and $|\lambda_-\lambda_+|\cong 1.0$.

To derive an expression for the QM contribution to the elastic constants c_{12} and c_{44} from the many-body force of NNN interactions, a rectangular coordinate is fixed at one of the anion sites as origin and with its axis coinciding with the edges of the unstrained lattice. If a distance between two points, say, from a fixed point as origin to an arbitrary point occupied by the gth ion, is given by a coordinate (an_1, an_2, an_3), where n_s are integers and a an interionic distance, then the distance r in the homogeneously strained lattice can be written as

$$r=aD_g\,, \qquad (7a)$$

where

$$D_g=[\mathbf{N}^\dagger\mathbf{J}^\dagger\mathbf{J}\mathbf{N}]^{1/2}. \qquad (7b)$$

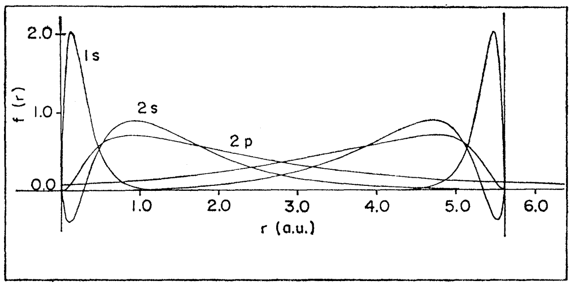

FIG. 2. Overlap between radial wave functions of nearest oxygen pair of ions in MgO. All functions are Hartree-Fock solutions by Watson (Ref. 20).

Here $\mathbf{N}$ is considered as a column vector with components (n_1,n_2,n_3), and $\mathbf{J}$ is the deformation gradient tensor which is related to the strain tensor $\mathbf{e}$ according to

$$(\mathbf{J}^\dagger\mathbf{J})_{ij}=2e_{ij}+\delta_{ij}. \tag{8}$$

The daggered quantities in (7) and (8) denote the transpose of a matrix.

From Eq. (7) it is easily seen that among the 12 possible pairs of ionic distances between nearest anions of the strained lattice, only six of them are distinct and are given by

$$\begin{aligned}a(1)&=a[2(1+e_2+e_3+e_4)]^{1/2},\\ a(2)&=a[2(1+e_2+e_3-e_4)]^{1/2},\\ a(3)&=a[2(1+e_1+e_3+e_5)]^{1/2},\\ a(4)&=a[2(1+e_1+e_3-e_5)]^{1/2},\\ a(5)&=a[2(1+e_1+e_2+e_6)]^{1/2},\\ a(6)&=a[2(1+e_1+e_2-e_6)]^{1/2}.\end{aligned} \tag{9}$$

They are obtained by letting $n_2=1$, $n_3=1$, $n_1=0$; $n_2=1$, $n_3=-1$, $n_1=0$; $n_1=1$, $n_3=1$, $n_2=0$; $n_1=1$, $n_3=-1$, $n_2=0$; $n_1=1$, $n_2=1$, $n_3=0$; $n_1=1$, $n_2=-1$, $n_3=0$ into Eq. (7). In Eq. (9), the contracted notation of the strain components e_{ij} is used; $e_{ij}=\frac{1}{2}(1+\delta_{ij})e_\mu$, where $ij\rightarrow\mu$ is related to $11\rightarrow1$, $22\rightarrow2$, $33\rightarrow3$, $23\rightarrow4$, $13\rightarrow5$ and $12\rightarrow6$.

The interaction energy arising from many-body forces between the ions is given by[3] (e in the following expression is the electronic charge)

$$\epsilon=2e^2\sum_i\sum_j\langle\phi_i(\mathbf{r}_1),\phi_j(\mathbf{r}_1)\rangle\langle\phi_j(\mathbf{r}_1)|\sum_g{}' v_g/r_{1g}|\phi_i(\mathbf{r}_1)\rangle, \tag{10}$$

where the brackets have the usual meaning as in evaluating integrals of matrix elements. ϕ_s are HF electronic wave functions associated with different ions (ϕ_i and ϕ_j in the above expression have the same coordinate $\mathbf{r}_1$ because one of them can always be expanded with respect to the other), v_g denotes the valency of the ions, and r_{1g} is the distance from a point $\mathbf{r}_1$ to an arbitrary point occupied by the gth ion. The summation of i and j runs over all electronic states of the ions considered. The prime in the summation over g indicates to exclude the ion with respect to which the summation is to be performed. As in the case of alkali halides, it will be assumed in carrying out the integration in Eq. (10) that most of the contributions come from the region where $r\leqq a$. This is justified because the wave function diminishes rapidly beyond this region. Analogously to Löwdin's calculation, one of the ϕ functions is expanded in terms of the α functions, and $1/r_{1g}$ in terms of spherical harmonics. Then the energy per unit volume E for NNN interaction having n sets of M_k equivalent neighbors can be written as

$$E=\frac{1}{4a^3}\sum_k^n M_k\epsilon_k, \tag{11a}$$

where the following notations are used:

$$\epsilon_k=2e^2\sum_h^\infty(1/a^{h+1})A_h(k)B_h, \tag{11b}$$

$$A_h(k)=2\pi\lambda_-{}^2\sum_i\sum_j\langle\phi_i(\mathbf{r}_1),\phi_j(\mathbf{r}_1)\rangle U(k)_{ji,h}, \tag{11c}$$

$$B_h=\sum_g{}'\frac{v_g}{r_{1g}}P_h(\cos\theta g), \tag{11d}$$

$$\begin{aligned}U(k)_{ji,h}=\lambda_-{}^2\sum_{t=|M|}^\infty K_{lm}{}^{LM}\langle P_h(x),P_t{}^M(x)P_l{}^M(x)\rangle&\\ \times\langle\alpha_t[\text{NLM}: a_{ij}(k),r],\ r^{h-1}f_{nl}(r)\rangle,&\end{aligned} \tag{11e}$$

$$\begin{aligned}K_{lm}{}^{LM}=[(2l+1)(2L+1)(l-m)!(L-M)!/&\\ 16\pi(l+m)!(L+M)!]^{1/2},&\end{aligned} \tag{11f}$$

$$\begin{aligned}\alpha_t[\text{NLM}: a_{ij}(k),r]=\frac{2t+1}{2ar}\frac{(t-M)!}{(t+M)!}\int_{|a-r|}^{a+r}f_{NL}(r)&\\ \times P_L{}^M(z_1)P_t{}^M(z_2)dR,&\end{aligned} \tag{11g}$$

$$z_1=(r^2-a^2-R^2)/2aR, \tag{11h}$$

$$z_2=(r^2+a^2-R^2)/2aR. \tag{11i}$$

$P_L{}^M(x)$ is Legendre's associated function and NLM, nlm refer to the usual quantum numbers associated with each wave function. $f_{nl}(r)$ represents the radial wave functions multiplied by the radial distance r. R is a radial distance measured from the center of the neighbor ion. θ_g in B_h is the angle between the line extending from the origin to a nearest cation and the line joining the origin with an arbitrary gth ion. Since in the actual computation the α functions play a central role, all α functions used are listed in Appendix A.

According to Eqs. (5) and (11) and by noting that according to (9) there are six distinct ionic distances between nearest anion pairs in the strained lattice, the expression for $c_{\mu\nu}''$, the QM part of the elastic constant $c_{\mu\nu}$ due to NNN interactions, takes the form

$$\begin{aligned}c_{\mu\nu}''=\frac{e^2}{2a^4}\sum_h\frac{1}{a^h}\bigg\{\frac{\partial^2}{\partial e_\mu\partial e_\nu}\big[(A_h(1)+A_h(2))(B_h(2)+B_h(3))&\\ +(A_h(3)+A_h(4))(B_h(1)+B_h(3))&\\ +(A_h(5)+A_h(6))(B_h(1)+B_h(2))\big]_{\mathrm{e}=0}\bigg\}.&\end{aligned} \tag{12}$$

Here $B_h(n)$ with $n=1$, 2, 3 represents lattice sums [Eq. (11d) carried out with respect to three possible z axes, namely, $\mathrm{z}(1)=a(1+2e_1)^{1/2}$, $\mathrm{z}(2)=a(1+2e_2)^{1/2}$, and $\mathrm{z}(3)=a(1+2e_3)^{1/2}$]. Since for each $A_h(k)$, there are two corresponding $B_h(n)$, Eq. (12) follows. Observing that while all of $B_h(n)$ are functions of all six strain components, each $A_h(k)$ depends only on three of the six components, Eq. (12) can be differentiated directly

TABLE II. Lattice sums in Eqs. (13) and (14).

$\frac{\partial^2 Q_0}{\partial e_1 \partial e_2} = -4.1730$	$\frac{\partial B_0(2)}{\partial e_1} = \frac{\partial B_0(1)}{\partial e_2} = -1.1653$
$\frac{\partial^2 Q_2}{\partial e_1 \partial e_2} = 0.0$	$\frac{\partial B_2(2)}{\partial e_1} = \frac{\partial B_2(1)}{\partial e_2} = 5.9490$
$\frac{\partial Q_0}{\partial e_1} = \frac{\partial Q_0}{\partial e_2} = -3.4960$	$B_0(1) = B_0(2) = B_0(3) = 3.496$
$\frac{\partial Q_2}{\partial e_1} = \frac{\partial Q_2}{\partial e_2} = 16.2166$	$B_2(1) = B_2(2) = B_2(3) = 0.0$
$\frac{\partial^2 Q_0}{\partial e_4^2} = -4.1730$	$\frac{\partial^2 Q_2}{\partial e_4^2} = 23.7960$

with respect to the strain components to obtain the expressions for c_{12}'' and c_{44}'' in the following form:

$$c_{12}'' = \frac{2e^2}{a^4} \sum_h (1/a^h) \left\{ A_h \left(\frac{\partial^2 Q_h}{\partial e_1 \partial e_2} \right)_0 + \frac{a}{4} \frac{\partial A_h}{\partial a} \times \left[\frac{\partial Q_h}{2e_1} + \frac{\partial Q_h}{\partial e_1} + \frac{\partial B_h(2)}{\partial e_1} + \frac{\partial B_h(1)}{\partial e_2} \right]_0 + \left[a^2 \frac{\partial^2 A_h}{2a^2} - a \frac{\partial A_h}{\partial a} \right] (Q_h/12)_0 \right\}, \quad (13)$$

$$c_{44}'' = \frac{2e^2}{a^4} \sum_h (1/a^h) \left\{ A_h \left(\frac{\partial^2 Q_h}{\partial e_4^2} \right)_0 + \left[a^2 \frac{\partial^2 A_h}{\partial a^2} - a \frac{\partial A_h}{\partial a} \right] (Q_h/12)_0 \right\}, \quad (14)$$

where $Q_h = B_h(1) + B_h(2) + B_h(3)$.

Some of the lattice sums appearing in the above expressions are identical except for sign differences with those computed by Löwdin by means of the Evjen method. Others can be easily derived as linear combinations of already known lattice sums. Values thus determined are listed in Table II. Substitution of these values into Eqs. (13) and (14), together with the approximation that the series converge sufficiently fast as to allow truncation at $h=2$, gives for the final expressions

$$c_{12}'' = (e^2 v/2a^4)[-8.346A_0 - 6.4093a(dA_0/da) + 22.1656(1/a)(dA_2/da) + 1.748a^2(d^2A_0/da^2)], \quad (15)$$

$$c_{44}'' = (e^2 v/2a^4)[-8.346A_0 + 47.592(1/a^2)A_2 - 1.748a(dA_0/da) + 1.748a^2(d^2A_0/da^2)]. \quad (16)$$

Here $v = |v_g|$.

TABLE III. Exponents and normalization coefficients in analytic HF adapted functions as given in Eq. (17).

	$i =$	1	$i =$	1	2	3
$O^{-2}(2s)$	a_i	7.700	b_i	1.490	2.802	1.776
	A_i	−10.3813	B_i	−0.13332	−6.21035	−2.9479
$O^{-2}(2p)$			b_i	0.714	3.412	1.384
			B_i	0.11617	8.74998	1.49205
[a]$Mg^{+2}(1s)$	a_i	11.6586				
	A_i	79.6158				
[a]$Mg^{+2}(2s)$	a_i	10.3251	b_i	3.8100		
	A_i	19.23955	B_i	34.56014		
$Mg^{+2}(2p)$			b_i	2.7226	4.4808	7.9907
			B_i	7.0360	22.795	21.348

[a] These functions were obtained by a variational method by Morse-Young-Haurwitz (Ref. 21) and subsequently corrected by Tubis (Ref. 22).

TABLE IV. Elastic constants c_{12} and c_{44} of NaCl (in 10^{11} dyn cm^{-2}) for zero pressure from tabulated (Löwdin) and analytical HF wave functions. ($a = 5.20$ a.u. was used for the ionic distance in both cases.)

	Electrostatic part	QM part	Theoretical value
c_{12}(Löwdin)	1.399	−0.417	0.982
c_{12}(analytic)	1.399	−0.388	1.011
c_{44}(Löwdin)	1.399	0.126	1.525
c_{44}(analytic)	1.399	0.118	1.517

All calculations in Lödwin's work were carried out by means of numerical integration. This was necessary because most of HF functions are given in tabulated form. However, in many calculations of atomic and molecular properties, analytic solutions are often more convenient. For this reason, we have used HF adapted analytic wave functions of exponential type.

Slater[17] first developed analytic forms of HF wave functions by fitting the tabulated functions with hydrogen-like exponentials employing the method of successive approximation. This method has subsequently been generalized as well as refined by Löwdin[18,19] and applied to many light and intermediate atoms including Na^+, Cl^-, $Mg^{+2}(2p)$. As for the O^{-2} ion, Watson[20] has carried out an analytic solution of the HF equation for O^{-2} in solids using a "stabilizing" sphere of $+1$ charge having a width equal to the radius of the ion, 2.66 a.u. The effect of such a well is to preserve the "correct" potential within the sphere while destroying the repulsive potential due to the net charge of -1 outside the ion boundary. For the $1s$ and $2s$ functions of Mg^{+2}, Morse *et al.*[21] have given similar functious obtained by a variation method. Their calculations were later corrected by Tubis.[22] We have

Table V. Scaling factors λ_+ and λ_- for MgO determined from the static elastic constants c_{12} and c_{44} of Table I (Ref. 15).

λ_+	λ_-
2.355	0.470

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[17] J. C. Slater, Phys. Rev. **42**, 33 (1932).

[18] P. O. Löwdin, Phys. Rev. **90**, 120 (1952).

[19] P. O. Löwdin, Phys. Rev. **163**, 1746 (1956).

[20] R. E. Watson, Phys. Rev. **111**, 1108 (1958).

[21] P. M. Morse, L. A. Young, and E. S. Haurwitz, Phys. Rev. **48**, 948 (1935).

[22] A. Tubis, Phys. Rev. **102**, 1049 (1956).

TABLE VI. Electrostatic and QM contribution to c_{12} from NN and NNN interactions (in 10^{11} dyn/cm^2). c_{12} denotes the sum of c_{12}', c_{12}'' and the electrostatic part (ES).

a(a.u.)	ES	NN(c_{12}')	NNN(c_{12}'')	c_{12}
3.9680	16.5000	−4.9977	−1.5023	10.0000
3.9630	16.5840	−5.0518	−1.5064	10.0258
3.9580	16.6680	−5.1047	−1.5105	10.0528
3.9530	16.7530	−5.1601	−1.5146	10.0783
3.9480	16.8380	−5.2142	−1.5188	10.1050
3.9380	17.0090	−5.3262	−1.5272	10.1556

checked that even the $2p$ function of Mg^+ obtained from the variation principle is almost identical with that of the corresponding HF solution.

All of the HF adapted functions used in the present calculation can be written in the following forms:

$$f_{1s}(r)=r\sum_i A_i \exp(-a_i r)\,,$$

$$f_{2s}(r)=r\sum_i A_i \exp(-a_i r)-r^2\sum_i B_i \exp(-b_i r)\,, \quad (17)$$

$$f_{2p}(r)=r^2\sum_i B_i \exp(-b_i r)\,,$$

where the parameters A_i, a_i, B_i, and b_i are listed in Table III. With these functions, together with the α functions shown in Appendix A, the quantities A_0 and A_2 in Eqs. (15) and (16) and their derivatives with respect to ionic distance can be calculated analytically. The most extensively used integral formulae for this computation are shown in Appendix B.

In order to see how much the results obtained by the two methods differ, we first repeated the calculation of c_{12} and c_{44} for NaCl and compared with the results of Löwdin (Table IV).

We now proceed to determine the scaling factors λ_+ and λ_- for MgO introduced in the overlap integrals which occur in all of the quantities A_h. Since the pressure derivatives of the elastic constants refer to the rate at which the elastic constants vary with changes in ionic distance, they depend primarily on the rate at which the overlap of the wave functions varies with ionic distance. Therefore, they are almost independent of the initial (zero-pressure) values of the elastic constants. To make use of this fact, let d_{12} and d_{44} represent the QM parts of the empirical values of c_{12} and c_{44}, respectively, which can be obtained by simply subtracting the electrostatic contribution from the empirical values. Then the solution of the following simultaneous linear equations determines the values of λ_+ and λ_-:

$$c_{12}'+c_{12}''=d_{12}\,,$$
$$c_{44}'+c_{44}''=d_{44}\,. \quad (18)$$

TABLE VII. Electrostatic and QM contribution to c_{44} from NN and NNN interactions (in 10^{11} dyn/cm^2). c_{44} denotes the sum of c_{44}', c_{44}'' and electrostatic part (ES).

a(a.u.)	ES	NN(c_{44}')	NNN(c_{44}'')	c_{44}
3.9680	16.5000	2.1654	−2.4354	16.2300
3.9630	16.5840	2.1913	−2.4481	16.3272
3.9580	16.6680	2.2183	−2.4607	16.4256
3.9530	16.7530	2.2454	−2.4736	16.5248
3.9480	16.8380	2.2737	−2.4866	16.6251
3.9380	17.0090	2.3291	−2.5128	16.8253

TABLE VIII. Derivatives of the cohesive contribution to the elastic constants c_{12} and c_{44} with respect to interionic distance (in 10^{11} dyn/cm^2).

$a_0\left(\dfrac{\partial c_{12}}{\partial a}\right)_0$	$a_0\left(\dfrac{\partial c_{44}}{\partial a}\right)_0$	$a_0^2\left(\dfrac{\partial^2 c_{44}}{\partial a^2}\right)_0$	$a_0^2\left(\dfrac{\partial^2 c_{44}}{\partial a^2}\right)_0$
−20.5	−77.1	77	74

The single and double primes denote QM contributions from NN and NNN interactions, respectively. c_{12}' and c_{44}' are calculated exactly in the same manner as for the alkali halides. For the determination of the non-Coulomb contributions d_{12} and d_{44} the static elastic constants c_{12} and c_{44} of Chung[15] as given in Table I and the NN distance $a_0=2.096$ Å which follows from the thermal-expansion data of Skinner[23] were used. The results of these computations are shown in Tables V–VII.

From the data in the last columns of Tables VI and VII the first and second derivatives of the static elastic constants with respect to interionic distance were determined. The results are shown in Table VIII. Finally, the pressure derivatives of the effective elastic constants are calculated from these data according to Eqs. (4) by using the static bulk modulus of Table I, Ref. 15. The results are listed in Table IX together with the available experimental data. Since it is apparent from Tables VI and VII that the second derivatives of the elastic constants with respect to the interionic distance are much less accurate than the first derivatives, the second pressure derivatives are also much less accurate than the first pressure derivatives

TABLE IX. Calculated pressure derivatives of elastic constants (from quantum theory) and of bulk modulus (from Born-Mayer theory) and experimental data.

	$\mu\nu$	12	44	B
$\left(\dfrac{\partial c_{\mu\nu}^*}{\partial p}\right)_0$	Theory	1.39	0.48	3.40
	Expt.[a,b] (300°K)	1.78	1.20	4.16
	Expt.[c,d] (300°K)	1.84	1.06	4.50
	Expt.[c,d] (78°K)	1.51	1.14	4.74
$\left(\dfrac{\partial^2 c_{\mu\nu}^*}{\partial p^2}\right)_0$	Theory	0.18[e]	−0.11[e]	−0.20
(10^{-11} dyn^{-1} cm^2)		0.08[f]	−0.30[f]	

[a] Rererence 13.
[b] Reference 24.
[c] Reference 14.
[d] Reference 25.
[e] Purely QM calculation.
[f] Experimental first pressure derivative of Ref. 24 used in Eq. (4b).

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[23] B. J. Skinner, Am. Mineral. 42, 39 (1957).

and therefore, at best, only estimates. It may be seen, however, from Eq. (4b) and the numerical data of Table VIII that the second pressure derivatives are the difference of two positive terms, and that the second term in (4b) depends only on the first pressure derivatives and may be several times larger than the first term. Since it is necessary to determine this term more accurately, the second pressure derivatives were also calculated by using the experimental room-temperature values of the first pressure derivatives of Ref. 24. These data are purely isothermal quantities and were calculated from the third-order elastic constants of Ref. 14.[25]

For the sake of completeness the first and second pressure derivative of the bulk modulus were calculated from the classical model of ionic crystals based on Coulomb interaction and exponential two-body central force repulsion between first nearest neighbors[26] and are included in Table IX. Actually, the expression for the pressure dependence of the bulk modulus does not change if second NN repulsion is included, as long as the repulsive exponents for first and second nearest interaction are the same. Since the repulsive exponent is determined from the experimental bulk modulus the second NN interaction is included approximately in the theoretical data for the pressure derivatives.

It goes without saying that it is inconsistent to use the QM data and the results based on the point ion model alongside. On the other hand, it is well known that the simple classical model not only accounts satisfactorily for the cohesive energy of ionic crystals with cubic symmetry but also for the equation of state at high pressure.[27] This implies that the bulk modulus, its first and, perhaps, its second pressure derivative are correctly described in this model. In order to provide additional evidence, the pressure derivative of the Grüneisen constant is calculated in Appendix C from the second pressure derivative of the bulk modulus, and it is shown that the result is of the same order as the experimental value.

IV. DISCUSSION AND CONCLUSION

It is apparent from Table VI that the QM contributions to c_{12} arising from first and second nearest neighbors are of opposite sign as the Coulomb term and reduce it by about 40%. The data in Table VII show that for c_{44} the QM NN, and NNN contributions are both as big as about 15% of the Coulomb term, but of opposite sign, so that the total elastic constant c_{44} is given to 98–99% by the Coulomb term. Note that two-body central forces between NN do not contribute to the elastic constants c_{12} or c_{44}.[28] Thus the large contributions contained in Tables VI and VII must arise from three-body forces of central type. The situation is the same as in the alkali halides[3,4] where NN three-body forces give a negative contribution to c_{12}, and a small positive one to c_{44}. The situation in MgO is different, however, insofar as the NN contribution to c_{12} is 13 times larger than in NaF (which is isoelectronic with MgO) and that to c_{44} is eight times larger than in NaF.[4] Also, the NN contribution to c_{44} is over-compensated in MgO by the NNN contribution (which consists of two- and three-body terms). Thus because of the large NNN term the non-Coulomb forces give in MgO a negative contribution to c_{44}, whereas it is positive in the alkali halides.[4]

Comparison between experimental and theoretical pressure derivatives in Table IX indicates that the agreement is satisfactory for c_{12}, but rather poor for c_{44}. This may be due to the fact that the non-Coulomb contribution is the difference of two terms of about equal magnitude, but opposite sign. Apparently the rate of change of this difference is underestimated in the present calculation, but it does have the right sign. This can be seen by comparing the present theoretical value with the value of 0.25 arising from the Coulomb contribution only.

The main source of error, however, must be ascribed to the use of the free ion HF functions which are modified here only through the isotropic scaling factors, which are assumed to be the same for all orbitals and independent of pressure. The true scaling factors which relate the wave function in the crystal to the free-ion HF function must be expected to be orientation-dependent. This then explains why the isotropic scaling factors apparently are a reasonable approximation for c_{12}, but not for c_{44}; whereas the deformation described by c_{12} is the Poisson contraction in which NN bond angles are preserved, c_{44} is a shear modulus which reflects the stiffness against bond angle changes.

In order to verify whether the departure from the Cauchy relation increases with pressure we consider, following Löwdin,[4] the expression $D=[c_{44}^*(p)-c_{12}^*(p)+2p]/[c_{12}^*(p)+c_{44}^*(p)]$, which is zero if the Cauchy relation is fulfilled. With the zero-pressure values from Tables VI and VII and the theoretical pressure derivatives from Tables VI and VII and the theoretical pressure derivatives from Table IX one obtains for $p=0$, $D=0.238$; and for $p=100$ kbar, $D=0.256$, hence a 15% increase in absolute magnitude.

Although the theoretical values of the second pressure derivatives of Table IX cannot be considered as more than rough estimates they are useful for estimating the pressure at which marked deviations from a linear pressure dependence of the elastic constants may be expected to occur. Using the experimental data for the

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[24] G. R. Barsch and Z. P. Chang, Phys. Status Solidi 19, 139 (1967).

[25] The data at 78°K of Ref. 14 have been revised [O. L. Anderson (private communication)].

[26] M. Born and M. Goeppert-Mayer, edited by H. Geiger and K. Scheel, *Handbuch der Physik* (Julius Springer, Berlin, 1933), Vol. 24, Part 2, p. 623.

[27] H. G. Drickamer, R. W. Lynch, R. L. Clendenen, and E. A. Perez-Albuerne, Solid State Phys. 19, 135 (1966).

[28] A. May, Phys. Rev. 52, 339 (1937).

zero-pressure values and the first pressure derivatives, and the theoretical second-pressure derivatives one finds that at 1 Mbar the bulk modulus deviates 15%, the shear modulus $c_s=\frac{1}{2}(c_{11}-c_{44})=\frac{3}{2}(B-c_{12})$ 60%, and the shear modulus c_{44} 20% from the values calculated from a linear relationship. This should have important implications in the analysis of seismic velocity versus depth profiles for the mantle of the earth. Since the NNN interaction is pronounced in all oxide compounds, one should expect similar deviations for other oxides too, if the pressure is measured in relative units and referred to the bulk modulus.

As far as the departures from the Cauchy relations in other oxides (of the rocksalt type) are concerned, one may expect a behavior similar to that in alkali halides, i.e., a decreasing deviation with increasing cation size for substances with identical anions. This tendency was attributed by Löwdin to the fact that the QM contributions are proportional to an inverse fourth power law of the NN distance. This situation is not changed if NNN interaction is included because according to Tables VI and VII the absolute magnitude of these effects decreases with increasing interionic distance. The same tendency as in alkali halides is in fact observed in the sequence MgO-CaO. The static elastic constants of CaO are[29] $c_{12}=6.65\times10^{11}$ dyn/cm^{-2} and $c_{44}=7.40\times10^{11}$ dyn cm^{-2}, corresponding to a comparatively small deviation from the Cauchy relation. The unusually large deviation occurring in MgO must therefore be ascribed to the small cation-anion radius ratio.

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APPENDIX A

The α functions used in the calculation are listed.

$$\alpha_0(300:a,r)=(1/2ar)\int f_{30}(R)dR\,,$$

$$\alpha_1(300:a,r)=\frac{3}{4}\left(\frac{1}{r^2}+\frac{1}{a^2}\right)\int f_{30}(R)dR-\frac{3}{4a^2r^2}\int f_{30}(R)R^2dR\,,$$

$$\alpha_2(300:a,r)=\frac{15}{16}\left(\frac{a}{r^3}+\frac{r}{a^3}+\frac{2}{3ar}\right)\int f_{30}(R)dR-\frac{30}{16}\left(\frac{1}{ar^3}+\frac{1}{a^3r}\right)\int f_{30}(R)R^2dR+\frac{15}{16a^3r^3}\int f_{30}(R)R^4dR\,,$$

$$a_3(300:a,r)=\frac{35}{32}\left(\frac{a^2}{r^4}+\frac{3}{5r^2}+\frac{3}{5a^2}+\frac{r^2}{a^4}\right)\int f_{30}(R)dR-\frac{105}{32}\left(\frac{1}{r^4}+\frac{6}{5a^2r^2}+\frac{1}{a^4}\right)\int f_{30}(R)R^2dR$$
$$+\frac{105}{32}\left(\frac{1}{a^2r^4}+\frac{1}{a^4r^2}+\frac{1}{a^4}\right)\int f_{30}(R)R^4dR-\frac{35}{32a^4r^4}\int f_{30}(R)R^6dR\,,$$

$$\alpha_0(310:a,r)=\frac{1}{4}\left(\frac{1}{r}-\frac{r}{a^2}\right)\int\frac{f_{31}(R)}{R}dR+\frac{1}{4a^2r}\int f_{31}(R)RdR\,,$$

$$\alpha_1(310:a,r)=\frac{3}{8}\left(\frac{a}{r^2}-\frac{r^2}{a^3}\right)\int\frac{f_{31}(R)}{R}dR+\frac{3}{4a^3}\int f_{31}(R)RdR-\frac{3}{8a^3r^2}\int f_{31}(R)R^3dR\,,$$

$$\alpha_2(310:a,r)=\frac{15}{32}\left(\frac{a^2}{r^3}-\frac{1}{3r}+\frac{r}{3a^2}-\frac{r^3}{a^4}\right)\int\frac{f_{31}(R)}{R}dR+\frac{15}{32}\left(-\frac{1}{r^3}+\frac{2}{3a^2r}+\frac{3r}{a^4}\right)\int f_{31}(R)RdR$$
$$-\frac{15}{32}\left(\frac{1}{a^2r^3}+\frac{3}{a^4r}\right)\int f_{31}(R)R^3dR+\frac{15}{32a^4r^3}\int f_{31}(R)R^5dR,$$

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[29] H. E. Hite, R. J. Kearney, J. Appl. Phys. 38, 5424 (1967).

$$\alpha_3(310:a,r)=\frac{35}{64}\left(\frac{a^3}{r^4}-\frac{2a}{5r^2}+\frac{2r^2}{5a^3}-\frac{r^4}{a^5}\right)\int\frac{f_{31}(R)}{R}dR+\frac{70}{64}\left(-\frac{a}{r^4}+\frac{3}{5a^3}+\frac{2r^2}{a^5}\right)\int f_{31}(R)RdR$$

$$-\frac{210}{64}\left(\frac{3}{5a^3r^2}+\frac{1}{a^5}\right)\int f_{31}(R)R^3dR+\frac{70}{64}\left(\frac{1}{a^3r^4}+\frac{2}{a^5r^2}\right)\int f_{31}(R)R^5dR-\frac{35}{64}\frac{1}{a^5r^4}\int f_{31}(R)R^7dR\,,$$

$$\alpha_1(311:a,r)=-\frac{3}{16}\left(\frac{a}{r^2}-\frac{2}{a}+\frac{r^2}{a^3}\right)\int\frac{f_{31}(R)}{R}dR+\frac{3}{8}\left(\frac{1}{ar^2}+\frac{1}{a^3}\right)\int f_{31}(R)dR-\frac{3}{16a^3r^2}\int f_{31}(R)R^3dR\,,$$

$$\alpha_3(311:a,r)=-\frac{105}{768}\left(\frac{a^3}{r^4}-\frac{4a}{5r^2}-\frac{2}{5a}-\frac{4r^2}{5a^3}+\frac{r^4}{a^5}\right)\int\frac{f_{31}(R)}{R}dR+\frac{105}{192}\left(\frac{a}{r^4}+\frac{3}{5ar^2}+\frac{3}{5a^3}+\frac{r^2}{a^5}\right)\int f_{31}(R)RdR$$

$$-\frac{315}{384}\left(\frac{1}{ar^4}+\frac{6}{5a^3r^2}+\frac{1}{a^5}\right)\int f_{31}(R)R^3dR+\frac{105}{192}\left(\frac{1}{a^3r^4}+\frac{1}{a^5r^2}\right)\int f_{31}(R)R^5dR-\frac{105}{768}\frac{1}{a^5r^4}\int f_{31}(R)R^7dR.$$

APPENDIX B

From Eq. (11), it is easily seen that for the evaluation of A_0 and A_2 and their derivatives with respect to ionic distance, the following general type of integration need be evaluated:

$$I=\int_0^a\int_q^p(R^{\mathrm{m}}e^{cR}dR)e^{b'r}r^ndr\,,\qquad\text{(B1)}$$

where $p=a+r$ and $q=a-r$. Equation (1) can be integrated into the form

$$I=I_A+I_{\mathrm{B}}\,,$$

$$I_A=\sum_{i=1}^{m+1}\sum_{j=0}^{n}M_{nij}[\exp(Ha)\sum_{s=1}^{k+1}2^{k-s+1}U_{\mathrm{s}}(1)a^f$$

$$-\exp(ca)\sum_{s=1}^{k+1}U_s(1)a^f],\qquad\text{(B2a)}$$

$$I_{\mathrm{B}}=(-1)^n\sum_{i=1}^{m+1}\sum_{j=0}^{n}M_{nij}[\exp(ab)a^jU_{k+1}(2)$$

$$-\exp(ca)\sum_{s=1}^{k+1}U_s(2)a^f],\qquad\text{(B2b)}$$

where

$$M_{nij}=(-1)^j\,{}_nC_jg_i\,,$$

$${}_nC_j=n!/[(n-j)!j!],$$

$$g_i=(-1)^{i+1}m!/[(m-i+1)!c^i],$$

$$U_s(t)=(-1)^{s+1}k!/[(k-s+1)!h^s(t)],\quad(t=1,2)$$

$$h(1)=c+b\,,$$

$$h(2)=c-b\,,$$

$$k=m+n-j-i+1\,,$$

$$f=k-s+j+1,$$

$$H=2c+b.$$

Derivative of I with respect to a is then given by

$$\frac{dI}{da}=\sum_{i=1}^{m+1}\sum_{j=0}^{n}M_{nij}\{\sum_{s=1}^{k+1}U_s(1)a^f[2^{k-s+1}e^{Ha}(H+f/a)$$

$$-e^{ca}(c+f/a)]-(-1)^n[a^je^{ab}(b+j/a)U_{k+1}(2)$$

$$-e^{ca}\sum_{s=1}^{k+1}U_s(2)a^f(c+f/a)]\}\,.\qquad\text{(B3)}$$

APPENDIX C

In order to verify the order of magnitude of the second pressure derivative of the bulk modulus as calculated from the Born-Mayer theory the pressure coefficient of the Grüneisen parameter will be estimated by using this value and compared with the experimental value.

The pressure coefficient of the Grüneisen parameter may be obtained by differentiating the Dugdale-McDonald relation in a form which is valid for arbitrary pressure.[30] The result is

$$\gamma'=\left(\frac{\partial\gamma}{\partial p}\right)_0=\tfrac{1}{2}B_0''+\frac{1}{6B_0}B_0'.$$

From the theoretical data of Table IX one obtains for MgO $\gamma'=-1.15$, which refers to the static lattice. The experimental value can be calculated by differentiating the defining relation $\gamma=B^s\beta/(\rho C_p)$ with respect to pressure and converting the pressure derivatives of the volume thermal expansion coefficient and the specific heat C_p into temperature derivatives of the bulk modulus and the thermal expansion coefficients, respectively.[31] Using the numerical data compiled in Ref. 24 one obtains at 300°K $\gamma'=-1.44$, in fair agreement with the above estimate for the static lattice.

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[30] J. S. Dugdale and D. K. C. McDonald, Phys. Rev. **89**, 832 (1953).

[31] W. C. Overton, Jr., J. Chem. Phys. **37**, 117 (1962).