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Theory of dielectric properties of ionic crystals under hydrostatic pressure

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The dielectric behavior of typical ionic crystals, viz. alkali halides under hydrostatic pressure has been studied employing the shell model and the exchange-charge-polarization model originally formulated by Dick and Overhauser. It is observed that the simple shell model is not capable of explaining the dielectric properties of alkali halides. The effect of the exchange-charge polarization has been incorporated into the shell model, and the exchange-charge shell model thus developed is employed to evaluate the strain derivatives of dielectric constants. The volume dependence of the effective-charge parameter has been discussed within the framework of various dielectric models. The calculations presented in this paper reveal the necessity of considering the effect of exchange-charge polarization. A comparison of theoretical and experimental values of the strain derivatives of the Szigeti effective-charge parameters has been presented.

I. INTRODUCTION

The shell model for ions in alkali halides was originally formulated by Dick and Overhauser[1] (DO) to explain the dielectric behavior and was later suitably reformulated by Woods *et al.*[2] to study the lattice dynamics of ionic crystals. More recently various modifications have been incorporated into the original shell model.[3-5] These modified versions of the shell model have been widely used to study the dielectric, elastic, thermal, optical, and lattice-dynamical properties, not only of highly ionic insulating crystals, but also of partially covalent tetrahedrally coordinated semiconducting crystals.[6,7]

In the shell model, the ions are considered as being composed of cores and shells. The outer electrons far from the nucleus are loosely bound electrons. These electrons form the shell, as they are more profoundly affected by the application of an electric field. The core consists of the nucleus plus tightly bound inner electrons. The shell in its original formulation is considered to be spherical, massless, and isotropically coupled with the core. Thus, only the two parameters representing the shell charge and the spring constant coupling the shell and the core are sufficient to describe the shell model. The charge on the core can be predicted from the condition that the shell charge plus the core charge is equal to the ionic charge. In the present paper, we make a comprehensive investigation of the dielectric behavior of the NaCl-structure alkali halides. Although the shell model was initially motivated to explain the dielectric properties of alkali halides,[1,8] at first, the dielectric data, particularly on the pressure dependence of dielectric constants, were scanty. Reliable experimental data on the dielectric behavior of alkali halides have recently been reported in the literature.[9,10] It is therefore desirable to re-examine the suitability of the existing dielectric models in the light of recent and detailed experimental data. Studies on the pressure dependence of dielectric constants will, of course, provide a crucial test of any theoretical model since the strain derivative of the dielectric constant is more sensitive to the details of the model than the dielectric constant itself. The plan of the paper is as follows. In Sec. II, we present the formulation of the shell model and derive the expressions for the volume dependence of the dielectric constants. Numerical results based on the shell model are also compared with experimental data in Sec. II. It is revealed by this comparison that the simple shell model does not yield agreement with experiment. In Sec. III we have incorporated the effect of the exchange-charge polarization within the framework of the shell model and then the dielectric constants have been calculated. The dielectric behavior of crystals under hydrostatic pressure, on the basis of the exchange-charge shell model, is investigated in Sec. IV. In Sec. IV, we will also discuss the variation of the effective-charge parameter with changing volume. General conclusions are summarized in Sec. V.

II. SHELL-MODEL ANALYSIS

Havinga[8] has derived the expressions for the dielectric constants from the equations of motion of shells and cores of the ions. Following the formulation presented by him, we can write

$$\frac{\epsilon_0-1}{\epsilon_0+2}\,\frac{3V}{4\pi}=\alpha_0=\frac{(n_+ + Z)^2e^2}{k_+}+\frac{(n_- - Z)^2e^2}{k_-}+\frac{Z^2e^2}{A}\ , \tag{1}$$

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\,\frac{3V}{4\pi} = \alpha_\infty = \frac{(n_+ e)^2}{k_+} + \frac{(n_- e)^2}{k_-} - \frac{(n_+ e/k_+ - n_- e/k_-)^2}{(A^{-1} + k_+^{-1} + k_-^{-1})}\;, \qquad (2)$$

$$(e^*/e - 1) = (n_+/k_+ - n_-/k_-)/(Z/A + Z/k_+ + Z/k_-)\;, \qquad (3)$$

where the suffixes + and – stand for cations and anions, respectively. n and k are the shell-model parameters representing, respectively, the shell charge and the spring constant coupling the shell of the ion with its core. Z is the valence of ions and is equal to 1 for alkali and halogen ions. A is the short-range force constant between the shells of the nearest-neighbor ions. V is the volume per ion pair. ϵ_0 and ϵ_∞ are, respectively, the low-frequency or static dielectric constant and high-frequency or electronic dielectric constant. Similarly, α_0 and α_∞ are the static and the electronic polarizabilities, respectively. e^*/e is the effective-charge parameter introduced by Szigeti.[11] For analyzing the dielectric behavior of crystals under hydrostatic pressure, one can find the expressions for the strain derivatives of ϵ_0, ϵ_∞, and e^*/e by differentiating Eqs. (1)–(3) with respect to V. Thus we obtain

$$\frac{9V}{4\pi}\,\frac{1}{(\epsilon_0 + 2)^2}\,\frac{d\epsilon_0}{dV} + \frac{\epsilon_0 - 1}{\epsilon_0 + 2}\,\frac{3}{4\pi} = \frac{d\alpha_0}{dV} = -\frac{e^2}{A^2}\,\frac{dA}{dV}\;, \qquad (4)$$

$$\frac{9V}{4\pi}\,\frac{1}{(\epsilon_\infty + 2)^2}\,\frac{d\epsilon_\infty}{dV} + \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\,\frac{3}{4\pi} = \frac{d\alpha_\infty}{dV} = -\frac{(n_+ e/k_+ - n_- e/k_-)}{(A^{-1} + k_+^{-1} + k_-^{-1})^2}\,\frac{1}{A^2}\,\frac{dA}{dV}\;, \qquad (5)$$

and

$$\frac{1}{e}\left(\frac{de^*}{dV}\right) = \frac{(n_+/k_+ - n_-/k_-)}{(A^{-1} + k_+^{-1} + k_-^{-1})^2}\,\frac{1}{A^2}\,\frac{dA}{dV}\,. \qquad (6)$$

In deriving Eqs. (4)–(6), it has been assumed that the shell-model parameters n and k do not vary with change in volume. An argument in support of this assumption can be made on the basis of the fact that n and k are determined from the free-ion polarizabilities[1] and thus are expected to remain constant under the effect of pressure.[8]

We have evaluated the dielectric constants and their strain derivatives employing the shell-model equation derived above. Values of the shell-model parameters n and k for alkali and halogen ions were reported by DO. In estimating n and k, DO made an inadvertent error which was later rectified by Dick,[12] who has listed the correct values for these parameters. Values of the force constant A and its volume derivative can be calculated from the Born-Mayer theory of ionic crystals[13] according to which

$$A = 2[\phi''(R) + (2/R)\phi'(R)]\;, \qquad (7)$$

where $\phi'(R)$ and $\phi''(R)$ are, respectively, the first and second derivatives of the short-range repulsive potential $\phi(R)$ with respect to interionic separation R. Using the exponential law

$$\phi(R) = B\exp(-R/\rho)\;,$$

we find that

$$\frac{dA}{dV} = \frac{1}{6R^2}\,\frac{dA}{dR} = \frac{B\exp(-R/\rho)}{3R^2\rho}\,(2/R\rho + 2/R^2 - 1/\rho)\,. \qquad (8)$$

TABLE I. Values of input parameters (in cgs units).

Crystal	n_+	n_-	$10^{-7}k_+$	$10^{-7}k_-$	$10^{-4}A$	$10^{-28}\frac{dA}{dV}$
LiF	1.12	2.40	1.00	0.13	8.18	–1.09
LiCl	1.12	4.35	1.00	0.12	4.62	–0.34
LiBr	1.12	4.95	1.00	0.12	3.93	–0.24
NaF	2.40	2.40	0.74	0.13	6.46	–0.66
NaCl	2.40	4.35	0.74	0.12	4.01	–0.25
NaBr	2.40	4.95	0.74	0.12	3.55	–0.20
NaI	2.40	5.65	0.74	0.10	2.94	–0.13
KF	4.35	2.40	0.53	0.13	4.84	–0.37
KCl	4.35	4.35	0.53	0.12	3.27	–0.16
KBr	4.35	4.95	0.53	0.12	2.95	–0.13
KI	4.35	5.65	0.53	0.10	2.46	–0.09
RbF	4.95	2.40	0.29	0.13	4.47	–0.30
RbCl	4.95	4.35	0.29	0.12	3.08	–0.14
RbBr	4.95	4.95	0.29	0.12	2.66	–0.11
RbI	4.95	5.65	0.29	0.10	2.33	–0.08

A and dA/dV can be calculated from Eqs. (7) and (8) taking the Born repulsive parameters B and ρ from Tosi.[14] Values of input parameters n, k, A, and dA/dV are listed in Table I. Calculated values of ϵ_0, α_0, $\epsilon_\infty, \alpha_\infty$, and e^*/e for 16 alkali halides from the shell-model equations (1)–(3) are given in Table II and are compared with experimental values. In Table III we have reported the values of $V(d\epsilon_0/dV)$ and $V(d\epsilon_\infty/dV)$ calculated from Eqs. (4) and (5), respectively. From Tables II and III we observe that the results obtained on the basis of the shell-model analysis show remarkable deviations from the experimental values. This clearly demonstrates the inadequacy of the simple shell model. We seek an explanation for this discrepancy in terms of the exchange-charge polarization.

III. EFFECT OF EXCHANGE-CHARGE POLARIZATION

In crystals, the ionic overlap causes the charge redistribution in the overlap region. As a result of this charge redistribution, the exchange charges are created between ionic sites. The dipole moment associated with these exchange charges is known as the exchange-charge polarization. The effect of the exchange-charge polarization on the dielectric properties has been worked out by DO. The inclusion of exchange-charge polarization in the shell model formalism modifies the Eqs. (1)–(3) as follows[1]:

$$\frac{\epsilon_0-1}{\epsilon_0+2}\left(\frac{3V}{4\pi}\right)=\alpha_0=(e+D)^2\left(\frac{1}{A}+\frac{1}{k_+}+\frac{1}{k_-}\right)+2(e+D)\left(\frac{n_+e-D}{k_+}-\frac{n_-e+D}{k_-}\right)+\frac{(n_+e-D)^2}{k_+}+\frac{(n_-e+D)^2}{k_-}, \tag{9}$$

$$\frac{\epsilon_\infty-1}{\epsilon_\infty+2}\left(\frac{3V}{4\pi}\right)=\alpha_\infty=\frac{(n_+e-D)^2}{k_+}+\frac{(n_-e+D)^2}{k_-}-\left(\frac{n_+e-D}{k_+}-\frac{n_-e+D}{k_-}\right)^2\left(\frac{1}{A}+\frac{1}{k_+}+\frac{1}{k_-}\right)^{-1}, \tag{10}$$

and

$$\frac{e^*}{e}-1=\frac{D}{e}+\frac{1}{e}\left(\frac{n_+e-D}{k_+}-\frac{n_-e+D}{k_-}\right)\left(\frac{1}{A}+\frac{1}{k_+}+\frac{1}{k_-}\right)^{-1}, \tag{11}$$

where D is the exchange-charge polarization parameter defined as

$$D=[(r_+-r_-)(R-4\rho)/\rho\lambda e]B\exp(-R/\rho) \tag{12}$$

where B, ρ, and λ are constants. Equation (12) was derived by DO making use of the theory of overlap integrals[15] in their phenomenological scheme of exchange-charge polarizations. The evaluation of D sensitively depends upon the ionic radii and overlap parameter λ which are not accurately known. In particular the factor (r_+-r_-), which arises from the assumption concerning the location of the exchange charges, is quite uncertain. For example in NaCl, $r_+-r_-=-0.83$ Å if one uses Zachariasen's radii following the suggestion of DO, whereas the corresponding value from the recent sets of ionic radii[16] is -0.23 Å. Thus the choice of ionic radii can drastically alter the magnitudes of D. In order to avoid the uncertainty, we have evaluated D from Eq. (11) taking experimental values of e^*/e reported by Lowndes and Martin.[9] This method for determining D has earlier been suggested by Dick.[17] Values of D/e thus calculated are included in Table II. We now estimate ϵ_0, α_0, ϵ_∞, and α_∞ from Eqs. (9) and (10) and report in Table II. It is observed from Table II that the dielectric constants obtained from the exchange-charge shell model are closer to the experimental values than the corresponding values obtained from the simple shell model. The improvement is remarkable, particularly for static dielectric constant ϵ_0 and static polarizability α_0.

IV. STRAIN DERIVATIVES OF DIELECTRIC CONSTANTS AND EFFECTIVE-CHARGE PARAMETER

When the crystal is subjected to hydrostatic pressure, the interionic separation or the volume of the crystal is changed. Within the framework of the exchange-charge shell model, the expressions for the strain derivatives of the dielectric constants and the effective charge parameter can be obtained by differentiating Eqs. (9)–(11) with respect to V. Thus we find

$$\frac{9V}{4\pi}\frac{1}{(\epsilon_0+2)^2}\frac{d\epsilon_0}{dV}+\frac{\epsilon_0-1}{\epsilon_0+2}\frac{3}{4\pi}=\frac{d\alpha_0}{dV}=\frac{e+D}{A^2}\left(2A\frac{dD}{dV}-(e+D)\frac{dA}{dV}\right), \tag{13}$$

$$\frac{9V}{4\pi}\frac{1}{(\epsilon_\infty+2)^2}\frac{d\epsilon_\infty}{dV}+\frac{\epsilon_\infty-1}{\epsilon_\infty+2}\frac{3}{4\pi}=\frac{d\alpha_\infty}{dV}=-\frac{2}{A}\left(\frac{dD}{dV}\right)[(e^*-e)-D]-[(e^*-e)-D]^2\frac{1}{A^2}\left(\frac{dA}{dV}\right), \tag{14}$$

and

$$\frac{1}{e}\left(\frac{de^*}{dV}\right)=\frac{1}{e}\left(\frac{dD}{dV}\right)-\frac{1}{e}\left(\frac{dD}{dV}\right)\left(\frac{1}{k_+}+\frac{1}{k_-}\right)\left(\frac{1}{A}+\frac{1}{k_+}+\frac{1}{k_-}\right)^{-1}+\frac{1}{e}[(e^*-e)-D]\left(\frac{1}{A}+\frac{1}{k_+}+\frac{1}{k_-}\right)^{-1}\frac{1}{A^2}\left(\frac{dA}{dV}\right). \tag{15}$$

TABLE II. Values of dielectric constants and polarizabilities. (a) Based on the shell-model calculations. (b) Based on the exchange-charge shell-model calculations. (c) Experimental values (Ref. 9).

Crystal	ϵ_0			ϵ_∞			$\alpha_0(\text{Å}^3)$			$\alpha_\infty(\text{Å}^3)$			e^*/e		D/e Calculated from Eq. (11)
	a	b	c	a	b	c	a	b	c	a	b	c	a	c	
LiF	16.65	9.45	8.50	2.06	1.96	1.93	3.27	2.88	2.79	1.02	0.95	0.92	0.87	0.80	−0.07
LiCl	26.46	13.23	10.83	3.35	3.19	2.79	7.25	6.50	6.21	3.56	3.42	3.03	0.84	0.77	−0.08
LiBr	28.93	10.93	11.23	3.65	3.37	3.16	8.98	7.63	7.69	4.66	4.38	4.16	0.85	0.73	−0.12
NaF	8.75	5.79	4.73	1.75	1.69	1.75	4.28	3.66	3.29	1.19	1.11	1.19	0.91	0.82	−0.09
NaCl	11.15	6.67	5.45	2.61	2.49	2.35	8.27	7.00	6.40	3.74	3.55	3.32	0.87	0.76	−0.12
NaBr	11.26	6.26	5.78	2.83	2.66	2.64	9.87	8.13	7.83	4.84	4.54	4.51	0.87	0.73	−0.14
NaI	14.18	7.55	6.62	3.34	3.30	3.08	13.19	11.11	10.56	7.09	7.02	6.63	0.85	0.71	−0.14
KF	7.75	5.90	5.11	1.77	1.74	1.86	6.36	5.66	5.28	1.86	1.80	2.03	0.95	0.88	−0.08
KCl	8.08	5.34	4.49	2.27	2.20	2.20	10.45	8.80	8.00	4.43	4.25	4.25	0.91	0.79	−0.13
KBr	8.14	4.98	4.52	2.43	2.32	2.39	12.06	9.76	9.24	5.53	5.23	5.42	0.91	0.75	−0.16
KI	9.64	5.58	4.68	2.77	2.73	2.68	15.63	12.72	11.60	7.80	7.70	7.56	0.89	0.72	−0.17
RbF	12.14	8.31	5.99	2.19	2.16	1.94	8.33	7.55	6.67	3.02	2.97	2.54	0.99	0.92	−0.08
RbCl	9.22	5.54	4.53	2.48	2.41	2.20	12.47	10.25	9.20	5.61	5.44	4.86	0.94	0.81	−0.14
RbBr	9.62	5.67	4.51	2.58	2.48	2.36	14.48	11.89	10.52	6.72	6.46	6.09	0.94	0.78	−0.16
RbI	9.94	5.79	4.55	2.85	2.82	2.61	17.69	14.52	12.80	8.99	8.93	8.25	0.91	0.74	−0.18

It should be noted that Eqs. (13)–(15) reduce to (4)–(6), respectively, if the effect of exchange-charge polarization is neglected, i.e., $D = dD/dV = 0$. It can be seen from Table III that the strain derivatives of the dielectric constants obtained from Eqs. (4) and (5), which take $dD/dV = 0$, are not in agreement with the corresponding experimental values. The values of dD/dV which are obtained from Eqs. (13) and (14) using experimental values of $V(d\epsilon_0/dV)$ and $V(d\epsilon_\infty/dV)$ are given in Table IV. It is found that dD/dV obtained from Eqs. (13) and (14) are different. This implies that the variation in the exchange-charge polarization under the effect of pressure is not the same for the static and the electronic dielectric constants. In fact the values of dD/dV obtained in the aforementioned way are empirical as they are determined, thus making the theory compatible with experiment. The theoretical values of dD/dV, on the other hand, can be estimated from Eq. (12). We make a plausible assumption that the ionic radii, under compressive stress, change such that $(r_+ - r_-)$ is not altered. In that case Eq. (12) yields

$$\frac{dD}{dV} = \frac{D(5\rho - R)}{6R^2\rho(R - 4\rho)} \; . \tag{16}$$

Values of dD/dV corresponding to Eq. (16) have been compared with the empirical values in Table IV.

An analysis of the variation of the Szigeti effective-charge parameter under hydrostatic pressure can be performed within the framework of the exchange-charge shell model. We have calculated $(V/e^*)(de^*/dV)$ for alkali halides from Eq. (15) using D/e from Table II and various sets of dD/dV given in Table IV. The values of $(V/e^*) \times (de^*/dV)$ listed in second and third columns of Table V are those which reproduce the experimental data on $V(d\epsilon_0/dV)$ and $V(d\epsilon_\infty/dV)$ respectively. In column 4 of Table V, we have reported $(V/e^*)(de^*/dV)$ derived from the theory of exchange-charge model [Eq. (16)]. Values of $(V/e^*)(de^*/dV)$ calculated from the shell-model theory (Eq. 6), neglecting the effect of the exchange-charge polarization, are given in column 5 of Table V.

An alternative theoretical approach which has been often used by earlier investigators[18,19] for evaluating $(V/e^*)(de^*/dV)$ is that based on the deformation dipole model (DDM) of Hardy[20] and Mitskevitch.[21] Following DDM, one can express the deviation of effective charge from its nominal value as

$$e^* - e = 2m'(R) + 4m(R)/R \; , \tag{17}$$

where $m(R)$ is the deformation dipole moment due to an ion pair and $m'(R)$ is its derivative with respect to ionic separation R. It has been sug-

TABLE III. Values of the strain derivatives of dielectric constants.

	$V\left(\frac{d\epsilon_0}{dV}\right)$		$V\left(\frac{d\epsilon_\infty}{dV}\right)$	
Crystal	Calculated from shell model [Eq. (4)]	Experimental values	Calculated from the shell model [Eq. (5)]	Experimental values
LiF	84.70	30.00[a]	−1.40	−0.37[b]
LiCl	170.81	30.36[c]	−3.84	...
LiBr	198.73	40.37[c]	−4.60	...
NaF	31.34	12.70[a]	−0.87	...
NaCl	43.09	14.50[a]	−2.30	−0.74[b]
NaBr	42.65	15.90[a]	−2.75	...
NaI	56.81	16.55[c]	−3.84	...
KF	25.80	12.75[c]	−0.95	...
KCl	26.41	9.11[a]	−1.74	−0.68[b]
KBr	25.69	8.92[a]	−2.02	−1.08[b]
KI	32.96	8.16[c]	−2.66	−1.40[b]
RbF	45.68	14.46[c]	−1.66	...
RbCl	30.49	7.79[c]	−2.17	−1.01[d]
RbBr	32.86	7.46[c]	−2.36	−1.24[d]
RbI	32.78	6.94[c]	−2.89	−1.41[d]

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gested[19,20] that $m(R)$ varies exponentially with R in the following manner

$$m(R)=m_0\exp(-R/\rho)\,. \tag{18}$$

Equations (17) and (18) yield

$$\frac{V}{e^*}\left(\frac{de^*}{dV}\right)=\frac{1}{3}\left[\frac{R}{\rho}-\frac{2\rho}{(R-2\rho)}\right]\left(\frac{e}{e^*}-1\right)\,. \tag{19}$$

Values of $(V/e^*)\,(de^*/dV)$ estimated from Eq. (19) are reported in column 6 of Table V.

Recently Lawaetz[22] has investigated a correlation between Szigeti effective-charge parameter e^*/e and the electronegativity difference. According to this correlation one can write to a good approximation

$$e^*/e=C/\hbar\omega_p\,, \tag{20}$$

where C is the electronegativity parameter.[23] The plasma energy $\hbar\omega_p$ is defined in terms of the plasma frequency $\omega_p^2=4\pi Ne^2/m$ and it is a measure of the total oscillator strength of the N electrons per unit volume. Differentiation of Eq. (20) with respect to V yields

$$\frac{V}{e^*}\left(\frac{de^*}{dV}\right)=\frac{1}{3}\,\frac{R}{e^*}\left(\frac{de^*}{dR}\right)=\frac{1}{3}\,\frac{R}{C}\left(\frac{dC}{dR}\right)+0.5\,. \tag{21}$$

The strain derivatives of the electronegativity parameter i.e., $R/C\,(dC/dR)$ can be evaluated from the Phillips–Van Vechten (PVV) theory of the electronic dielectric constant.[23] According to PVV theory we have[24]

$$\epsilon_\infty=1+[(\hbar\omega_p)^2/E_g^2]\,G \tag{22}$$

with

$$G=1-B+\tfrac{1}{3}B^2\,, \tag{23}$$

and

$$E_g^2=E_h^2+C^2\,, \tag{24}$$

TABLE IV. Values of the strain derivatives of the exchange charge polarization parameter dD/dV (10^{14} cgs).

	Empirical values deduced from		Theoretical values obtained from
Crystal	Eq. (13)	Eq. (14)	Eq. (16)
LiF	0.039	0.22	0.032
LiCl	0.003	...	0.021
LiBr	0.032	...	0.029
NaF	0.023	...	0.035
NaCl	0.022	0.14	0.029
NaBr	0.031	...	0.032
NaI	0.021	...	0.036
KF	−0.004	...	0.023
KCl	0.005	0.15	0.026
KBr	0.012	0.11	0.029
KI	0.006	0.08	0.026
RbF	0.007	...	0.021
RbCl	0.004	0.16	0.027
RbBr	0.003	0.13	0.027
RbI	0.004	0.10	0.026

TABLE V. Values of the strain derivatives of the Szigeti effective-charge parameter $V/e^* \, (de^*/dV)$. (a) Derived from the empirical values of dD/dV given in column 2 of Table IV. (b) Derived from the empirical values of dD/dV given in column 3 of Table IV.

Crystal	Empirical values a	Empirical values b	Exchange-charge model	Shell model	Deformation dipole model	Lawaetz ionicity model	Experimental values
LiF	0.48	1.20	0.45	0.31	0.56	0.25	0.55
LiCl	0.49	...	0.66	0.44	0.79	...	...
LiBr	0.87	...	0.83	0.44	1.04	...	...
NaF	0.40	...	0.47	0.24	0.50	...	...
NaCl	0.70	2.06	0.79	0.40	0.96	0.32	0.63
NaBr	0.95	...	0.96	0.42	1.07	...	...
NaI	1.01	...	1.11	0.52	1.19	...	...
KF	0.10	...	0.34	0.14	0.36	...	...
KCl	0.40	2.75	0.73	0.29	0.82	0.31	0.52
KBr	0.62	2.54	0.93	0.32	1.09	0.42	1.03
KI	0.65	2.52	1.14	0.41	1.29	0.46	0.99
RbF	0.07	...	0.21	0.01	0.26	...	...
RbCl	0.21	3.06	0.68	0.19	0.81	0.46	0.47
RbBr	0.30	2.97	0.81	0.21	0.96	0.49	0.42
RbI	0.48	2.98	1.07	0.32	1.27	0.47	0.87

where $B = E_g/4E_F$, E_F being the Fermi energy. E_g is the energy gap between bonding and antibonding states. G is always approximately 1 because $|B|$ is much smaller than 1. Making the assumption that G remains constant under changing volume, we find[23]

$$\frac{V}{\epsilon_\infty}\left(\frac{d\epsilon_\infty}{dV}\right) = \frac{1}{3}\frac{R}{\epsilon_\infty}\left(\frac{d\epsilon_\infty}{dR}\right)$$

$$= \frac{2}{3}\frac{(\epsilon_\infty - 1)}{\epsilon_\infty}\left[\tfrac{1}{2}R\frac{dD'}{dR} + 2.48\frac{E_h^2}{E_g^2} - \frac{C^2}{E_g^2}\left(\frac{R}{C}\frac{dC}{dR}\right) - 1.5\right] . \quad (25)$$

It has been suggested by Van Vechten[23] that one can take $dD'/dR = 0$ for alkali halides. Values of $(R/C)\,(dC/dR)$ can be estimated from Eq. (25) using data on $(d\epsilon_\infty/dV)$, E_h, C, and E_g. As the experimental data on $(d\epsilon_\infty/dV)$ exist for eight alkali halides (Table III), we can evaluate $(R/C)\,(dC/dR)$ for these crystals only. Using $(R/C)\,(dC/dR)$ thus evaluated, we have calculated $(V/e^*)\,(de^*/dV)$ from Eq. (21) (listed in column 8 of Table V).

The foregoing analyses and the results obtained there from present an interesting comparison of the strain derivatives of the Szigeti effective-charge parameter obtained from various dielectric models. The theories employed and extended in the present study were, at the time of their inception, motivated to study the dielectric behavior of crystals under no external pressure. It is to be emphasized that the Szigeti effective-charge parameter has been an important and useful quantity in explaining the structural and dielectric properties of ionic crystals.[25] One should, of course, remember that the values of de^*/dV are much more affected by the short-range forces than the effective-charge parameter itself. This implies the sensitivity of the results to the model adapted.

Now we proceed to determine $V/e^* \, (de^*/dV)$ directly from experimental data. Following Szigeti,[11] we have

$$\left(\frac{e^*}{e}\right)^2 = (9\mu\omega_{\mathrm{TO}}^2/4\pi N e^2)[(\epsilon_0 - \epsilon_\infty)/(\epsilon_\infty + 2)^2] , \quad (26)$$

where μ is the reduced mass per ion pair, ω_{TO} the transverse-optical mode frequency of lattice vibrations, and N is the number of ion pairs per unit volume. The experimental data on ϵ_0, ϵ_∞, and ω_{TO} for alkali halides have been reported by Lowndes and Martin.[9] Values of the Szigeti effective-charge parameter e^*/e derived from Eq. (26) using experimental data are given in Table II. These values of e^*/e are supposed to be accurate within ±1%. By differentiating Eq. (26) with respect to volume we find

$$\frac{V}{e^*}\left(\frac{de^*}{dV}\right) = 0.5 - \gamma_{\mathrm{TO}} - V\left(\frac{d\epsilon_\infty}{dV}\right)\left[\frac{1}{\epsilon_\infty + 2} + \frac{1}{2(\epsilon_0 - \epsilon_\infty)}\right] + \frac{1}{2}\frac{V}{(\epsilon_0 - \epsilon_\infty)}\left(\frac{d\epsilon_\infty}{dV}\right) , \quad (27)$$

where

$$\gamma_{\mathrm{TO}} = -\frac{V}{\omega_{\mathrm{TO}}}\left(\frac{d\omega_{\mathrm{TO}}}{dV}\right) \tag{28}$$

is known as the transverse-optical mode Grüneisen parameter. The experimental values of γ_{TO} have recently been published by Lowndes and Rastogi.[26] We can make an estimate of $(V/e^*)\,(de^*/dV)$ from Eq. (27) using experimental data for ϵ_0, ϵ_∞, $d\epsilon_0/dV$, $d\epsilon_\infty/dV$, and γ_{TO}. Values of $(V/e^*)\,(de^*/dV)$ for eight alkali halides obtained from Eq. (27) are given in the last column of Table V and are referred to as experimental.

V. CONCLUSIONS AND SUMMARY

Thus, we have made a comprehensive study of the dielectric behavior of rocksalt-structure alkali halides in the light of recent experimental data on dielectric constants and their strain derivatives. It has been found that the simple shell model is not adequate to describe the dielectric properties, particularly the static dielectric behavior of alkali halides. This situation has revealed the necessity of adopting a more sophisticated polarization mechanism. Following Dick and Overhauser,[1] we have incorporated the effect of the exchange-charge polarizations in the shell-model formulation. The exchange-charge shell model thus developed has been employed to calculate the static and the electronic dielectric constants. The inclusion of the exchange-charge polarization in the theory of the shell model brings the calculated values of the dielectric constants in closer agreement with experiment.

It has also been evident from the analysis of the dielectric behavior under hydrostatic pressure that the simple shell model is not capable of explaining the strain dependence of electronic and static dielectric constants. The exchange-charge shell model has, therefore, been adapted to analyse the strain derivatives of dielectric constants. It is found that the volume derivative of the exchange-charge polarization dD/dV necessary to account for the strain derivative of the electronic dielectric constant is substantially higher than dD/dV corresponding to the strain derivative of the static dielectric constant. This prediction deserves further attention. A theoretical analysis of dD/dV has also been made by extending the model of DO.

In our opinion, the most important contribution of the present work is the evaluation of the strain derivatives of the Szigeti effective-charge parameter $(V/e^*)\,(de^*/dV)$, employing the various dielectric models, viz. the shell model, the exchange-charge polarization model, the deformation dipole model, and the Phillips-Lawaetz ionicity model. A comparison of various sets of $(V/e^*)\times(de^*/dV)$, along with experimental values, is presented in Table V. The extent to which the values of $(V/e^*)\,(de^*/dV)$, obtained from different models, agree with each other and with experimental values, is remarkable, particularly in view of quite different origins of the models adopted for evaluating $(V/e^*)\,(de^*/dV)$. The common feature of the results obtained from different models is, however, that $(V/e^*)\,(de^*/dV)$ is positive without any exception. This implies, as expected, that the decrease in the crystal volume due to the effect of pressure increases the overlap and distortion of ions, thereby causing the decrease in the effective charge parameter e^*/e.

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