Dielectric parameters of alkali halides

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An *ab initio* calculation is presented for the refractive indices and Szigeti charge of 12 alkali halide solids. The polarizabilities of the anions and cations are calculated separately, and the refractive indices are obtained from the Clausius-Mosotti relation. The Szigeti charge is obtained by a calculation of the deformation dipole parameters. Both the polarizabilities and deformation dipole parameters are calculated with use of the local-density approximation. The parameters are found for each ion where the crystalline environment is simulated by a cage of pseudopotentials. The results agree well with experimental data.

I. INTRODUCTION

The Born-Mayer model provided one of the earliest theories of alkali halide crystals. This model assumed that the ions were spherical, polarizable, and interacted with only central forces. This model gave a good account of the cohesive energy and the compressibility but was not very successful in describing lattice dynamics. Later came refinements of the theory such as the deformation dipole theory,[1] various shell models,[2-4] and ion deformability.[5] These theories provided a better model of lattice dynamics. There also arose competing theories such as the ionicity theory,[6,7] where significant charge transfer is assumed—contrary to the Born-Mayer model.

These various theories contain a variety of parameters which are fitted to the experimental data. Very seldom are these parameters calculated from first principles. The present paper is somewhat of a milestone in that we report first-principles *ab initio* calculations of many of the important parameters which characterize the dielectric and vibrational properties of alkali halides.

Our basic premise is that the Born-Mayer model is valid except for the addition of polarization forces. The ions are each assumed to be spherical, although they slightly interpenetrate. The validity of this viewpoint was shown by Jennison and Kunz.[8] After finishing their self-consistent band-structure calculations, they found that the Coulomb potential at each nucleus was equal to the ideal Madelung potential. Thus their charge distributions are spherical. They concluded that the ionicity theories are wrong, and that there is no appreciable charge transfer.

Several years ago we developed a method of calculating the ionic polarizabilities of ions in solids.[9,10] The polarizability is found for a central ion. The neighboring ions are represented as a lattice of pseudopotentials which are spherically averaged. These calculations made several new predictions regarding the polarizability of ions in solids: (i) the polarizability of the cations is a constant α^+ independent of the solid; (ii) the polarizability of the anion α^- changed with each alkali halide, depending mainly on lattice constant. We also showed that the experimental data, where $\alpha^+ + \alpha^-$ is found from the Clausius-Mosotti relation

$$\alpha^+ + \alpha^- = (3V_0/4\pi)(\epsilon_\infty - 1)/(\epsilon_\infty + 2) , \qquad (1)$$

support the hypothesis that α^- varies with lattice constant. These findings contradict the old and established view of Tessman, Kahn, and Schockley[11] that the polarizability of each ion is fixed. Instead, we find that the anions are quite compressible and change their volume, hence their polarizability in each alkali halide. This prediction was confirmed by Colella and collaborators,[12] whose x-ray density maps support the view that the anions remain spherical but compressed in the alkali halides.

Part of the present results are new values for the polarizability of ions in solids. The earlier calculations were among the first to find static response functions using the local-density approximation (LDA). Since then, much has been learned about the calculational technology. The present method differs from the earlier ones in three respects: (i) there is a better choice of correlation energy, (ii) there is no self-interaction correction, and (iii) they employ the self-consistent field (SCF). The results are also much more accurate than our earlier results. The agreement with experiment is quite good; the results are within 1–2 % of the data, except for the sodium halides where we are about 6% high.

The basic method is explained further in Sec. II. A perturbation such as $\delta V = e\mathscr{E}z$ on the central ion causes a charge distortion $\delta n = L \, \delta V$ where L is an operator linear in the field $\mathscr{E}$ but not in z. The dipole polarizability α is given as the average of ez:

$$p = \alpha\mathscr{E} = \langle ez \, \delta n \rangle, \quad \alpha = e^2 \langle zLz \rangle . \qquad (2)$$

Recently, we collaborated[13] in showing that the polarization of a central ion causes indirect ionic interactions (I^3) between its first neighbors. This process can be calculated by the same computer code which finds the polarizability. Now the perturbation has the form of $\delta V = \mathbf{Q} \cdot \mathbf{F}$ where $\mathbf{Q}$ is the infinitesimal displacement of the neighboring ion,

and $F(r)$ is the force on the electrons of the central ion due to this displacement. Second-order perturbation theory shows that there is an energy term due to pairs of displacements for two neighbors of the central ion:

$$\Delta E = \sum_{i,j} Q_{i\mu} Q_{j\nu} \langle F_\nu L F_\mu \rangle .$$

The bracket $\langle FLF \rangle$ provides a force tensor between pairs of displacements.

The effective charge e^* was originally conceived by Szigeti.[14] Its explanation in terms of deformation dipole was suggested by Hardy and Karo[1] and is well described in standard treatments on lattice dynamics.[15-17] Here one calculates the induced dipole moment on a central ion caused by the displacement of a neighbor. This quantity is just the cross term between the above two interactions:

$$p = \langle ezL F \cdot Q \rangle = e\gamma Q, \quad \gamma_{\mu\nu} = \langle r_\mu L F_\nu \rangle ,$$

We have introduced the dimensionless tensor γ which gives the magnitude of the induced moment caused by a neighboring displacement. The Szigeti charge is just

$$e^* = e(1-\Gamma), \quad \Gamma = 2(\gamma_l + 2\gamma_t) , \tag{3}$$

where $\gamma_{l,t}$ are the longitudinal and transverse components of the tensor.

Here we present calculations of the correlations $\langle zLz \rangle$ and $\langle zLF \rangle$. Results for $\langle FLF \rangle$ are presented elsewhere. Together they provide the parameters needed for the theory of ϵ_0, ϵ_∞, e^*, and the lattice dynamics.

II. NUMERICAL METHODS

The numerical quantities calculated in this paper can be expressed as the elements of some tensors. The tensors usually have a small number of nonzero components. Here we describe the method used to calculate them. The general method is similar to that used earlier for the ionic polarizabilities.[9,10] The Mth polarizability α_M is the response of the ion to an external perturbation of the form $\epsilon_M r^M P_M(\Theta)$ where ϵ_M is infinitesimal. The present calculations also find the response to more complicated functions of r: the force on an electron from the motion of a neighboring ion.

As discussed in Sec. I, the electron states are calculated using LDA for a central ion. A first neighbor whose center is at R_β causes a perturbation $V(\mathbf{r}-\mathbf{R}_\beta)$. The central ion in an alkali halide has six such neighbors which are spherically averaged to emulate the crystal potential in the immediate locality of the central ion. $V(\mathbf{r}-\mathbf{R}_\beta)$ can be expanded in spherical harmonics:

$$V(\mathbf{r}-\mathbf{R}_\beta) = \sum_l v_l(r,R) P_l(\Theta_\beta) . \tag{4}$$

The crystal potential is approximated as $V_c(r) = 6v_0(r,R)$. Earlier it was shown that this makes a square well potential which confines the electrons in negative ions and tends to make the halides contract in the solid. The standard LDA procedure is to first solve an effective Schrödinger-type equation for all of the ground-state eigenvalues ϵ_j and eigenfunctions ψ_j which are solutions of the self-consistent equations

$$(-\nabla^2 - 2Z/r + V_H + V_c + V_{xc} - \epsilon_j)\psi_j = 0 ,$$
$$n(r) = \Sigma_j |\psi_j|^2 , \tag{5}$$

where V_H is the Hartree potential for electron-electron interactions, V_{xc} is the exchange-correlation energy of Gunnarsson and Lundqvist,[18] and V_c is the crystal potential.

The six first neighbors form a shell around the central ion. An infinitesimal motion of one of these neighbors causes a distortion in the central ion. This distortion is calculated by considering the effects of an infinitesimal perturbation

$$\delta V = \mathbf{Q} \cdot \mathbf{F}, \quad \mathbf{F} = -\nabla V , \tag{6}$$

where $\mathbf{Q}$ is the infinitesimal displacement. From first-order perturbation theory, one can show that this induces a change in the wave function ψ_j' which obeys an equation

$$(H_0 - \epsilon_j)\psi_j' = (-V_{SCF} + \epsilon_j')\psi_j ,$$
$$V_{SCF} = \delta V + 2 \int d^3 r' \frac{\delta n(r')}{|r-r'|} + \delta n(r) \frac{\delta V_{xc}}{\delta n} , \tag{7}$$
$$\delta n = 2 \sum_j \psi_j^* \psi_j' ,$$

where V_{SCF} is the self-consistent-field potential, ϵ_j' is the first-order change in the energy, and δn is the first-order change in the density. Using V_{SCF} instead of δV is what makes the L operator nonlinear in Sec. I. After finding δn, its integral is taken with $\mathbf{F}_\mu(r)$ to find the tensor for the indirect force between neighbors and with ez to find the parameter γ which determines the Szigeti charge.

Both (5) and (7) are differential equations with spherically symmetric potentials. Their solutions can be expanded in terms of radial functions and spherical harmonics. Only the radial function needs to be solved numerically. Standard techniques are used for solving the eigenvalue equation for the ground state. The techniques are less well known for solving the inhomogeneous differential equation for the first-order changes ψ'. The angular momentum theorem for closed shells limits the number of radial functions.

The solutions can be classified into two general types. (i) The angular momentum l of ψ is not equal to the angular momentum l' of ψ'. Then the radial equation is solved by introducing two parameters A and B which are determined by two constraints. The parameters A and B are the slope of the radial function at the origin and at the last end point: both initial and final values are set to zero. Numerov's method is used to iterate the solution outward from the origin and inward from the far point. The two constraints are that these two solutions have the same value and slope at some predetermined match point.

The other case is when $l = l'$, which can happen when δV has even angular momentum. Then the inhomogeneous differential equation (7) also has a solution to the homogeneous equation, so that ψ' has a random mixture of ψ. Usually one wants $\langle \psi | \psi' \rangle = 0$ so that this admixture is zero. This can be imposed as a third constraint, but that introduces the need for a third variational parameter. After much trial and error, we discovered that it is the first-order energy ϵ'. This quantity is zero unless

$l = l'$, and then it should be

$$\varepsilon_j' = \langle \psi_j \mid \delta V \mid \psi_j' \rangle \ .$$

When ε' is allowed to vary, it chooses a value which is identical to the calculated one within four or five significant digits. However, the small difference is needed to eliminate the unwanted homogeneous solution to the differential equation.

Earlier we gave the angular momentum decomposition of s, p, and d shells perturbed by a δV of the form $r^M P_M(\Theta)$. Exactly the same formulas are found for general functions of r: for potentials of the form $f(r)P_M(\Theta)$. We have generalized these results to show that the same formulas for $\delta n(r)$ are found for an angular perturbation of the form $f(r)P_M^m(\Theta)\exp(im\phi)$.

After the perturbed density $\delta n(r)$ has been found self-consistently, one can calculate the correlation of this perturbation with any other function $\Xi(r)$ of r

$$\langle \Xi \mid \delta V \rangle = \int d^3r\, \Xi(r)\delta n(r) \ .$$

The symbol $\langle \Xi \mid \delta V \rangle$ means to correlate Ξ with the density change caused by δV. Of course, one could also calculate $\langle \delta V \mid \Xi \rangle$, which is the correlation of δV with the density change caused by the perturbation $\Xi(r)$. Without SCF one finds that $\langle \Xi \mid \delta V \rangle = \langle \delta V \mid \Xi \rangle$. They are not equal when the fields are made self-consistent because the screening is different for each perturbation. Then one asks the question of which is correct since they are different. The answer is that if one is trying to correlate two different perturbations, the correct procedure is to average them:

$$(\Xi \mid \delta V) = \tfrac{1}{2}(\langle \Xi \mid \delta V \rangle + \langle \delta V \mid \Xi \rangle) \ . \qquad (8)$$

This identity is not based upon any mean value theorem. Instead, we wrote out the LDA equations for two perturbations, derived the equations (7) for ψ' from variational theory, and then evaluated the ground-state energy. The cross term linking two perturbations has the above form as the average of the two quantities.

III. RESULTS AND DISCUSSION

Numerical calculations were done for the 12 alkali halides of flourine, chlorine, and bromine, with lithium, sodium, potassium, and rubidium. Iodine and cesium are omitted because our codes are not relativistic. We also confined our calculations to the rocksalt structure. The alkali pseudopotential is taken from our earlier compilation.[9]

Table I shows low-temperature results for the polarizabilities. The first column lists the solid. The second and third columns list our calculated values for α^+ and α^-. The sum $\alpha^+ + \alpha^-$ is listed in the next column. The last column lists the experimental value of $\alpha^+ + \alpha^-$ derived from the Clausius-Mosotti relation. The data are taken from Lowndes and Martin.[19] Our results for the sodium halides are too high by 5%, but the agreement is within 2% for the other cases. We think the agreement is quite good since there are no adjustable parameters in the theory. We believe this is the easiest and most successful

method for calculating the polarizabilities and refractive index.

The alkali polarizabilities shown in Table I are smaller than the ones we published earlier for free ions. The difference occurs because these alkali ions are slightly compressed in the solid. When run for free ions, the same computer code reproduces our earlier results. It is interesting that the alkali polarizabilities are nearly the same for all of the halides. This confirms our previous findings that the cation polarizability is independent of halide salt.

Table II shows our calculated values for the quadrupole and octupole polarizabilities of the halide ions in the alkali halide solid. Again we regard these values as more accurate than our earlier ones.

Table III shows our calculated values of the Szigeti charge. The top entry is for the halide ion, while the bottom entry is for the alkali. The lithium ion was not evaluated since one expects the answer to be small, and LDA is not accurate for two electron atoms. The experimental data are again taken from Lowndes and Martin. If R is the vector between the central ion and its neighbor, and Q is the displacement of the neighbor, then γ_l is for $Q||R$ and γ_t is for $Q \perp R$. In both cases the induced moment is in the direction of Q. These values are best ap-

TABLE I. Ionic polarizabilities (Å^3).

Salt	ab initio			Data[a]
	α^+	α^-	$\alpha^+ + \alpha^-$	$\alpha^+ + \alpha^-$
LiF	0.032	0.85	0.88	0.91
NaF	0.136	1.11	1.25	1.17
KF	0.69	1.26	1.95	1.98
RbF	1.08	1.36	2.44	2.49
LiCl	0.032	2.86	2.89	2.94
NaCl	0.136	3.29	3.43	3.24
KCl	0.68	3.48	4.16	4.15
RbCl	1.08	3.65	4.73	4.78
LiBr	0.032	3.97	4.00	4.09
NaBr	0.135	4.46	4.60	4.38
KBr	0.68	4.64	5.32	5.29
RbBr	1.08	4.85	5.93	5.96

[a]Reference 19.

TABLE II. Quadrupole and octupole polarizabilities.

	Alkali	F$^-$	Cl$^-$	Br$^-$
		Quadrupole (Å^5)		
Li$^+$		0.89	4.83	7.84
Na$^+$	0.057	1.34	6.08	9.48
K$^+$	0.50	1.62	6.70	10.2
Rb$^+$	1.02	1.84	7.26	11.0
		Octupole (Å^7)		
Li$^+$		1.84	16.8	32.4
Na$^+$	0.042	3.25	23.2	42.28
K$^+$	0.73	4.35	27.0	47.1
Rb$^+$	1.90	5.22	30.3	52.5

TABLE III. Szigeti charge. $e^* = e(1-\Gamma)$, $\Gamma = 2(\gamma_l + 2\gamma_t)$. Top entry: halide; lower entry: alkali.

Salt	γ_l	γ_t	Γ	Theory e^*/e	Data[a] e^*/e
LiF	0.044	0.069	0.365	0.64	0.81
NaF	−0.016	0.067	0.236	0.77	0.83
	−0.025	0.011	−0.006		
KF	0.004	0.049	0.204	0.82	0.88
	−0.085	0.037	−0.022		
RbF	−0.003	0.046	0.177	0.85	0.92
	−0.117	0.050	−0.034		
LiCl	−0.086	0.138	0.380	0.62	0.77
NaCl	−0.110	0.124	0.276	0.75	0.76
	−0.024	0.007	−0.021		
KCl	−0.067	0.093	0.239	0.83	0.79
	−0.082	0.024	−0.066		
RbCl	−0.065	0.086	0.216	0.86	0.85
	−0.108	0.034	−0.081		
LiBr	−0.102	0.159	0.432	0.57	0.66
NaBr	−0.136	0.143	0.300	0.73	0.73
	−0.024	0.006	−0.025		
KBr	−0.091	0.110	0.259	0.82	0.76
	−0.082	0.022	−0.077		
RbBr	−0.87	0.101	0.230	0.88	0.83
	−0.118	0.030	−0.114		

[a]Reference 19.

preciated by comparing them to the classical prediction of the dipole-induced-dipole model

$$\gamma_l \rightarrow -2\alpha/R^3, \quad \gamma_t \rightarrow \alpha/R^3 ,$$

where α is the polarizability of the central ion. The classical prediction is that $\gamma_l = -2\gamma_t$ so that Γ equals zero.

Our computed results for the halides do not come close to agreeing with this classical prediction. The magnitude of γ_l is smaller than γ_t in every case. For some florines γ_l is positive rather than negative. The alkali ions behave more classically and come closer to satisfying the classical identity $\gamma_l = -2\gamma_t$. It is interesting that Γ is always positive for the halides and negative for the alkalis.

Our agreement is poor for the lithium salts. The agreement with experiment is good for the other nine cases. Since these *ab initio* calculations have no adjustable parameters, we regard the agreement as satisfactory. Cer-

tainly these results show that the deformation dipole model can explain the origins of the deviation of e^*/e from unity.

The method was also used to calculate the force constants between two neighbors of the central ion, as found from the correlation $\langle FLF \rangle$. These values are reported elsewhere.[13]

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[1]J. R. Hardy, Philos. Mag. 7, 315 (1962); A. M. Karo and J. M. Hardy, Phys. Rev. 129, 2024 (1963).

[2]U. Schroder, Solid State Commun. 4, 347 (1966).

[3]M. J. L. Sangster, J. Phys. Chem. Solids 34, 355 (1967).

[4]W. Cochran, CRC Rev. Solid State Sci. 2, 1 (1971).

[5]K. Fischer, H. Bilz, R. Haberkorn, and W. Weber, Phys. Status Solidi B 54, 285 (1972).

[6]J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).

[7]B. F. Levine, J. Chem. Phys. 59, 1463 (1973).

[8]D. R. Jennison and A. B. Kunz, Phys. Rev. B 13, 5597 (1976).

[9]G. D. Mahan, Solid State Ionics 1, 29 (1980).

[10]G. D. Mahan, Phys. Rev. A 22, 1780 (1980).

[11]J. R. Tessman, A. H. Kahn, and W. Schockley, Phys. Rev. 92, 890 (1953).

[12]D. R. Yoder and R. Colella, Phys. Rev. B 25, 2545 (1982); M.

C. Schmidt, R. Colella, and D. R. Yoder-Short, Acta Crystallogr. A **41**, 171 (1985).

[13]G. D. Mahan and M. Mostoller, Phys. Rev. B (to be published).

[14]B. Szigeti, Proc. R. Soc. London, Ser. A **204**, 52 (1950).

[15]M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).

[16]A. A. Maradudin, E. W. Montroll, G. H. Weiss, and I. P. Ipa-
tova, *The Theory of Lattice Dynamics in the Harmonic Approximation* (Academic, New York, 1971).

[17]J. R. Hardy and A. M. Karo, *The Lattice Dynamics and Statics of Alkali Halide Crystals* (Plenum, New York, 1979).

[18]O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[19]R. P. Lowndes and D. H. Martin, Proc. R. Soc. London, Ser. A **308**, 473 (1969).