

Volume dependence of ion polarizabilities in alkali-halide crystals

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The volume dependence of the static, linear polarizabilities of alkali-halide crystals is computed in a local-density-approximation (LDA) scheme. The calculated polarizabilities are inserted into the Clausius-Mossotti relation in order to obtain the high-frequency dielectric constant and its volume dependence. The theoretical values agree well with direct experimental values, as well as those inferred from photoelastic coefficients. A perfect linear relationship between the change in the refraction index and the volume strain is obtained all the way to the phase transition in RbCl in agreement with experiment. These results lend support to the LDA and the use of the spherical-averaging approximation for these crystals.

I. INTRODUCTION

The static linear polarizabilities, α^+ and α^- , of the individual ions in an alkali-halide crystal cannot be measured directly, but they can be related to the high-frequency dielectric constant, ϵ_∞ , through the Clausius-Mossotti relation,

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi}{3v_a}(\alpha^+ + \alpha^-), \quad (1)$$

where v_a is the volume of the unit cell. Several sets of ion polarizabilities have been derived¹⁻³ by assuming that an ion has the same polarizability regardless of which crystal it is located in and then fitting Eq. (1) to experimental data of the dielectric constants for all the alkali halides.

However, first-principles calculations⁴⁻⁶ show that it is only the cations that retain the same polarizability in all crystal environments while the polarizability of the anions varies among the crystals. The first-principles calculations agree well with experiment.

A simple relation for the volume dependence of the dielectric constant can be derived from Eq. (1) by assuming that the polarizabilities are independent of volume, but it has been shown^{7,8} that such an approach does not agree very well with experimental data and the conclusion has been drawn that the change in polarizabilities with volume is significant.

The volume dependences of the polarizabilities are needed to understand how the dielectric constant depends on the lattice constant, but our work is also applicable in lattice-dynamical calculations since calculations of the phonon dispersion relations in the alkali-halide crystals require, among other things, the polarizabilities of the individual ions.⁹ Knowing how the phonon energies depend on volume makes it then possible to calculate

the pressure dependence of properties such as the thermal conductivity¹⁰ and the heat capacity.

From Eq. (1) we get

$$\frac{R}{\epsilon_\infty} \frac{d\epsilon_\infty}{dR} = -\frac{\epsilon_\infty + 2}{\epsilon_\infty} \left[\epsilon_\infty - 1 - \frac{2\pi(\epsilon_\infty + 2)}{9R^2} \left(\frac{d\alpha^+}{dR} + \frac{d\alpha^-}{dR} \right) \right], \quad (2)$$

where R is the nearest-neighbor distance. The volume derivative of the dielectric constant is also related to the elasto-optic coefficients, p_{1n} .¹¹ These are defined as

$$\Delta \left(\frac{1}{\epsilon_1} \right) = p_{1n} \tau_n, \quad (3)$$

where τ_n is the strain tensor in the standard contracted notation. For the NaCl structure the number of elasto-optic constants reduces exactly as the corresponding elastic constants, which is not true for all cubic crystal systems.¹¹ In the same way as the bulk modulus is obtained from the elastic constants in cubic crystals, we obtain

$$\frac{R}{\epsilon_\infty} \frac{d\epsilon_\infty}{dR} = -\epsilon_\infty(p_{11} + 2p_{12}). \quad (4)$$

Previous theoretical work^{7,12,13} on the photoelastic effect in the alkali halides has been based on phenomenological assumptions, whereas we will present results from first-principles calculations.

We have calculated the polarizabilities for sixteen alkali halides for a range of different values of the lattice constant in each crystal. Since details of the calculational procedure have been given elsewhere,^{6,5} we will just briefly mention the main steps. In view of the closed-shell configurations of the ions, the calculations are per-

formed for individual ions, with the effect of the crystalline environment included as an external potential in an approximate way. The justification for this approach has been given earlier.⁶ The first step is to compute the Kohn-Sham eigenvalues, E_j , and the orbitals, ψ_j , of the ground state for a particular lattice constant. We use the exchange-correlation energy of Ceperley and Alder.^{14,15} The crystal potential is obtained as the spherical average of a sum over pseudopotentials,⁶ representing the interactions with the other ions. The spherical averaging simplifies the calculation so that only the radial part of the Schrödinger equation needs to be solved numerically.

The polarizability, α , is given in atomic units by

$$\alpha = -2 \int d^3r \delta n(\mathbf{r}) r \cos \theta, \quad (5)$$

where δn is the density distortion induced by a perturbing electric field. The density distortion is obtained from the modified Sternheimer equation,⁶ which takes account of the self-consistent, screened perturbing potential.

II. RESULTS

The calculated polarizabilities for the lattice constant corresponding to the volume at ambient pressure are given in Table I together with values for their volume derivatives. As has been noted before,⁶ the anions have a larger polarizability than the cations since the anions are larger and the electrons are more loosely bound. The dif-

ferences between $d\alpha^+/dR$ and $d\alpha^-/dR$ are even greater than the differences in polarizabilities. The electrons on the cation are so tightly bound that the polarizability does not change when the lattice constant is altered. This is consistent with the fact that the cations have approximately the same polarizability in all crystal environments. The anions, on the other hand, show a large dependence on volume. To a very good approximation we can say that changes in the polarizability of these crystals are due totally to changes in the anion polarizability.

Since individual polarizabilities cannot be measured, we can only make an indirect comparison of our calculation with experiment. From Eq. (1) we calculate theoretical values for the dielectric constant, which is obtained as a function of the lattice constant. In Table I we also give theoretical and experimental values of $(R/\epsilon_\infty)d\epsilon_\infty/dR$. We have found experimental values of $(R/\epsilon_\infty)d\epsilon_\infty/dR$ for only six alkali halides. Therefore, in the last column in Table I we have listed values derived from Eq. (4) and tabulated experimental values of p_{11} and p_{12} from Ref. 20. We have put the values for the rubidium salts in parentheses since the elasto-optic constants given in Ref. 20 are not strict experimental values as explained in Ref. 21.

The calculated values for $(R/\epsilon_\infty)d\epsilon_\infty/dR$ agree well with experiment. The differences between values obtained in different experiments are almost as large as the differences between theory and experiment. There appears to be no systematic deviation between theory and

TABLE I. Calculated static linear polarizabilities, their strain derivatives and values for $(R/\epsilon_\infty)d\epsilon_\infty/dR$ for sixteen alkali-halide crystals. Two sets of experimental data for $(R/\epsilon_\infty)d\epsilon_\infty/dR$ are given. The first set is reported values for $(R/\epsilon_\infty)d\epsilon_\infty/dR$ obtained from hydrostatic pressure measurements. The second set of experimental values are obtained from Eq. (4) and values for elasto-optic constants given in Ref. 20 .

Crystal	α^+ (\AA^3)	α^- (\AA^3)	$\frac{d\alpha^+}{dR}$ (\AA^2)	$\frac{d\alpha^-}{dR}$ (\AA^2)	$\left(\frac{R}{\epsilon_\infty} \frac{d\epsilon_\infty}{dR}\right)_{\text{theory}}$	$\left(\frac{R}{\epsilon_\infty} \frac{d\epsilon_\infty}{dR}\right)_{\text{expt}}$	$\left(\frac{R}{\epsilon_\infty} \frac{d\epsilon_\infty}{dR}\right)_{\text{Eq.(4)}}$
LiF	0.032	0.848	0.001	0.96	-0.47	-0.57 ^a	-0.55
LiCl	0.032	2.81	0.001	2.05	-1.09		
LiBr	0.032	3.86	0.001	2.63	-1.23		
LiI	0.032	5.67	0.001	3.40	-1.53		
NaF	0.158	1.13	0.006	1.07	-0.62		-0.84
NaCl	0.158	3.26	0.008	2.04	-1.13	-0.95 ^b	-0.98
NaBr	0.158	4.40	0.006	2.57	-1.28		-1.35
NaI	0.159	6.37	0.006	3.29	-1.53		
KF	0.839	1.28	0.031	1.08	-0.99		-1.22
KCl	0.838	3.50	0.029	1.98	-1.21	-0.93 ^b	-1.09
KBr	0.838	4.66	0.030	2.41	-1.33	-1.42 ^c	-1.29
KI	0.838	6.68	0.030	3.10	-1.49	-1.60 ^c	-1.47
RbF	1.39	1.38	0.063	1.09	-1.27		
RbCl	1.39	3.68	0.050	1.90	-1.38	-1.44 ^d	(-1.38)
RbBr	1.39	4.89	0.051	2.38	-1.44		(-1.54)
RbI	1.38	6.95	0.054	3.00	-1.59		(-1.57)

^aReference 16.

^bReference 17.

^cReference 18.

^dReference 19.

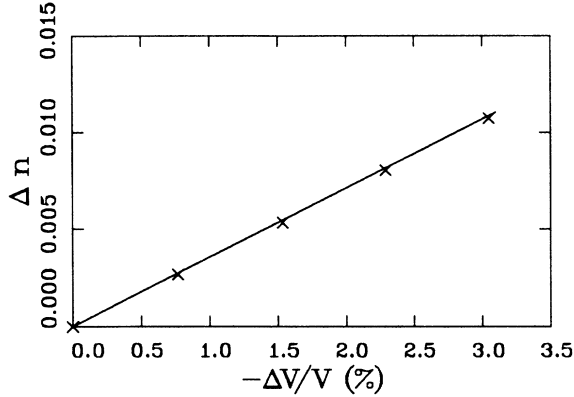


FIG. 1. The change in the refractive index as a function of volume strain for RbCl. The crosses are theoretical values and the straight line is drawn with the slope that was obtained in experiment (Ref. 19). RbCl transforms from the rock-salt structure to the CsCl structure at a volume strain of 3.05%.

experiment.

It has been shown in experiment that the refractive index varies linearly with volume strain in KBr, KI,¹⁸ and RbCl.¹⁹ We have calculated the refractive index for RbCl as a function of volume strain all the way to the volume at which a phase transition to the CsCl structure is known to occur. Our calculations give a perfect linear relationship between the change in the refractive index and the volume strain which is shown in Fig. 1 (crosses). The straight line in Fig. 1 is drawn with the slope that was obtained from experiment.¹⁹ We see that there is a very good agreement between theory and experiment. The perfect linear relationship that is obtained in our calculations lends support to the validity of the Hohenberg-Kohn-Sham local-density approximation (LDA) and the spherical-averaging approximation in calculations of the polarizability and its volume dependence.

We will make some comparisons with the phenomenological theory used by Sharma *et al.*⁷ They calculated the derivatives of the polarizabilities from a theory developed by Ruffa,²² in which the cation polarizability scales with the Madelung energy according to

$$\frac{\alpha^+(R)}{\alpha_f^+} = \left(\frac{E_f}{E_f - V_M(R)} \right)^2, \quad (6)$$

TABLE II. Theoretical values for the volume dependences of the polarizabilities and of the high-frequency dielectric constant, $(R/\epsilon_\infty)d\epsilon_\infty/dR$. A comparison between values obtained from the present first-principles calculation and values obtained with the phenomenological theory of Ref. 7.

Crystal	This work			Ref. 7		
	$\frac{d\alpha^+}{dR}$ (\AA^2)	$\frac{d\alpha^-}{dR}$ (\AA^2)	$\frac{R}{\epsilon_\infty} \frac{d\epsilon_\infty}{dR}$	$\frac{d\alpha^+}{dR}$ (\AA^2)	$\frac{d\alpha^-}{dR}$ (\AA^2)	$\frac{R}{\epsilon_\infty} \frac{d\epsilon_\infty}{dR}$
LiF	0.001	0.96	-0.47	-0.007	0.68	-0.57
NaCl	0.008	2.04	-1.13	-0.021	1.78	-0.91
KCl	0.029	1.98	-1.21	-0.153	1.98	-1.09
RbF	0.063	1.09	-1.27	-0.299	0.93	-1.74

where α_f^+ is the free state polarizability, E_f is an empirical free state energy parameter, and $V_M(R)$ is the Madelung potential.

The derivative of the cation polarizability, $d\alpha^+/dR$, is easily obtained from Eq. (6) since, on the right-hand side, it is only the Madelung potential that depends on the lattice constant. In order to obtain the corresponding derivative for the anion, Sharma *et al.* assumed that the polarizability of an ion is proportional to its radius and that the sum of the ion radii, r_+ and r_- , is equal to the lattice constant. With these assumptions they derived

$$\frac{r_-}{\alpha^-} \frac{d\alpha^-}{dR} + \frac{r_+}{\alpha^+} \frac{d\alpha^+}{dR} = 1 \quad (7)$$

from which $d\alpha^-/dR$ can be obtained.

We compare in Table II our values for $d\alpha^+/dR$ and $d\alpha^-/dR$ with the values calculated by Sharma *et al.*⁷ The values obtained for $d\alpha^-/dR$ in the two calculations are of roughly the same size. The most noticeable difference between the present work and Ref. 7 is the sign of $d\alpha^+/dR$. The negative sign of $d\alpha^+/dR$ obtained in Ref. 7 indicates that the anion contracts while the cation expands when the crystal as a whole is compressed. We find from our first-principles calculations that both the cation and anion contract when the lattice constant decreases. This has been checked by calculating the root-mean-square radius of the ions.

Several authors^{7,22-24} have suggested that the cation radius increases when the free cation is placed in an alkali-halide crystal. The suggested increase of the cation radius is due to the Madelung energy at the cation site that raises the electronic energy levels, which would correspond to a more extended wave function. However, there is also the Pauli effect, which tends to expel the wave function from the regions with high electron density at the neighboring anions. The Pauli effect was neglected in Ruffa's theory.²²

To test the effect of the Madelung potential alone we have done a calculation for RbF with all surrounding ions represented as point charges, i.e., there is no overlap of the cation's electron cloud and the electron clouds of the neighboring ions. In this approximation we find that the cation does expand when the lattice constant decreases and we obtain $d\alpha^+/dR = -0.050 \text{ \AA}^2$. This is the same sign as was obtained in the phenomenological theory of

Ref. 7 but there is a factor of 6 difference in the magnitudes.

We do not believe that the cation expands in reality when the crystal as a whole is compressed. It should be remarked, however, that our calculations use pseudopotentials with fixed radii to represent the neighbors. Thus, our calculation does not take account of the compression of the neighbors while calculating the orbitals of the central ion. This is a second-order effect, and should be quite small. In any case, the difference between our calculation and Ref. 7 is not important from a practical point of view since $d\alpha^+/dR$ is generally very small.

The anion polarizabilities are not affected to any great extent by the use of cation pseudopotentials since the cation radius changes very little when the lattice becomes compressed. We expect the relative error in our values for $d\alpha^-/dR$, and hence in $(R/\epsilon_\infty)d\epsilon_\infty/dR$, due to the use of volume independent pseudopotentials to be very small.

III. SUMMARY

We have performed first-principles calculations of the polarizability as a function of lattice constant for the alkali halides with rock-salt structure. We have found that

the change in cation polarizability when the crystal is compressed is negligible. The changes in the polarizability of the crystal are due totally to changes in the anion polarizability. The calculations show good agreement with experimental data for the high-frequency dielectric constant and its volume dependence. Our calculations show that both the cation and anion get compressed when the lattice constant decreases contrary to the oft-cited claim that the cation would expand. We obtained a perfect linear relationship between the change in the refractive index and the volume strain in agreement with experiment. This lends support to the validity of LDA and the spherical-averaging approximation in calculations of the polarizability and its volume dependence.

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