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The shell model for alkali halide crystals: do the equations adequately describe their dielectric behaviour?

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Abstract. For the theoretical calculation of low-frequency *in crystal* ion polarizabilities two independent approaches have been developed and shown to give rather similar results for the rock-salt structured oxides of the alkaline earths. The theory based on the lattice dynamical shell model for alkali halides is believed to have successfully provided values for individual ion polarizabilities in those crystals. The alternative theory which relies on known ionic radii, however, through a new prediction, reveals that the former provides a poor fit for fluorides with gradual improvement for chlorides, bromides and iodides in that order. It seems that the shell model is inadequate for describing the dielectric behaviour of the alkali halides. The observed discrepancies are attributed to the neglect of second-nearest neighbour interactions which have been shown to be important for the theory of their cohesion.

New values for the *in crystal* polarizabilities of individual alkali and halide ions are derived for ions in environments with sixfold and with eightfold co-ordination. These satisfy the quantum mechanical expectation that such polarizabilities depend on the square of the corresponding ionic radius and on the number of electrons known to occupy the outermost subshell. The new analysis of the dielectric data of alkali halides is now consistent with the treatment of the corresponding data from oxides.

1. Introduction

As has been demonstrated by several authors (see, for example, [1]), the lattice dynamical shell model is remarkably successful for fitting the phonon dispersion curves of alkali halide crystals. The model has also been shown by Sangster *et al* [2] to give an understanding of dielectric behaviour and to lead to a simple equation for the sum of the anion and cation polarizabilities in those compounds, *viz.*,

$$(\alpha_A + \alpha_H) = \alpha_\infty + F_0^{-1}(Z - Z')^2 \quad (1)$$

where

$$\alpha_\infty = \frac{3V}{4\pi} \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \quad (2)$$

$$F_0 = \frac{\mu\omega_0^2}{e^2} \frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2}. \quad (3)$$

Here ε_0 and ε_∞ are the static and high-frequency dielectric constants, ω_0 the transverse optical frequency, μ the reduced mass, Z the ionic charge and Z' the Sziget charge (as defined by Sangster *et al*).

As emphasized previously [2], the right-hand sides of these equations are determined solely by experimental data so that the derived polarizability sums ($\alpha_A + \alpha_H$) should be acceptable provided that the shell model equations adequately describe the dielectric behaviour of an alkali halide. In support of this argument, it is worth noting that reliable experimental results are available [3] and that from these data a consistent set of polarizabilities for individual alkali and halide ions have been derived for which equation (1) is satisfied for all 20 alkali halide crystals with an rms error of around 1% [2].

This last step, however, does depend on the assumption that the derived polarizability values are for *free ions* and also on fitting the polarizability of free Li^+ to Pauling's calculated value. As explained by Grimes and Grimes [4], there are now reasons to believe that the left-hand side of equation (1) is a sum of *in crystal* ion polarizabilities.

In this paper we compare results from alkali halide crystals [2] with *in crystal* ion polarizabilities for oxides [4]. The latter were obtained from the polarizabilities for individual ions, α , after they had been derived using the quantum mechanical result

$$\alpha = \frac{8}{9}a_0(2l + 1)[a_0\langle r^2 \rangle]^2 \quad (4)$$

where the factor $[a_0\langle r^2 \rangle]^2$ is a form of mean square radius of the outermost electron subshell (r is its radius in dimensionless atomic units and a_0 the radius of the first Bohr orbit in hydrogen) which can be related to the square of a traditional measure of ionic size [4] and l is the orbital angular momentum quantum number of the electron subshell concerned. Significantly, this calculation has been shown to give results for total *in crystal* polarizability, ($\alpha_M + \alpha_O$), for oxides with rock-salt structure, which are in good agreement with results obtained using equation (1) [4]. The logical conclusion would seem to be that the theory for oxides should also apply to alkali halides. As we show in what follows, this check reveals a discrepancy which indicates that an important contribution has been neglected in the shell model.

2. Analysis

As explained in section 1, the derivation of individual alkali and halide polarizabilities from equation (1) involves making assumptions. To avoid possible error with the shell model therefore, it is safest to work with polarizability sums ($\alpha_A + \alpha_H$). These depend only on the validity of equation (1). Alternatively, individual *in crystal* ion polarizabilities are derivable from equation (4) using known modified crystal radii.

Table 1. Ion polarizabilities for oxides [5] and radii for the corresponding ions.

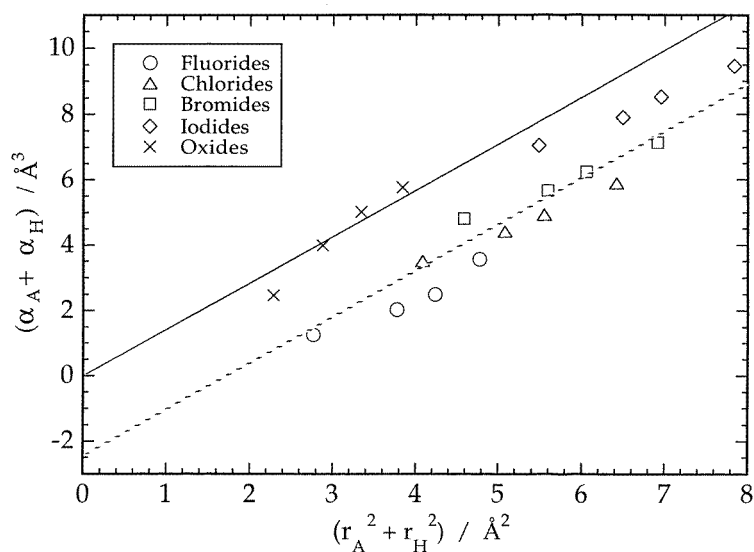
	r_M (Å)	r_O (Å)	$(r_M^2 + r_O^2)$ (Å ²)	$(\alpha_M + \alpha_O)$ (Å ³)	r_m/r_O
MgO	0.92	1.20	2.286	2.466	0.76
CaO	1.20	1.20	2.880	3.986	1.00
SrO	1.38	1.20	3.344	5.021	1.15
BaO	1.55	1.20	3.843	5.768	1.29

Consider the alkali halides formed exclusively from p^6 ions. Using equation (4) it is easily seen that, for such compounds,

$$(\alpha_A + \alpha_H) = k(r_A^2 + r_H^2). \quad (5)$$

Table 2. Ion polarizabilities for alkali halides [2] and radii for the corresponding ions.

	r_A (Å)	r_H (Å)	$(r_A^2 + r_H^2)$ (Å ²)	$(\alpha_A + \alpha_H)$ (Å ³)	r_A/r_H
NaF	1.22	1.13	2.765	1.254	1.08
KF	1.58	1.13	3.773	2.037	1.40
RbF	1.72	1.13	4.235	2.497	1.52
CsF	1.87	1.13	4.774	3.566	1.66
NaCl	1.22	1.61	4.080	3.518	0.76
KCl	1.58	1.61	5.089	4.414	0.98
RbCl	1.72	1.61	5.551	4.936	1.07
CsCl	1.94	1.63	6.421	5.900	1.19
NaBr	1.22	1.76	4.586	4.817	0.69
KBr	1.58	1.76	5.594	5.671	0.90
RbBr	1.72	1.76	6.056	6.255	0.98
CsBr	1.94	1.775	6.915	7.144	1.09
NaI	1.22	2.00	5.488	7.062	0.61
KI	1.58	2.00	6.496	7.909	0.79
RbI	1.72	2.00	6.958	8.530	0.86
CsI	1.94	2.02	7.844	9.449	0.96

**Figure 1.** Polarizability sum as a function of the sum of the squares of the modified crystal radii for the ions concerned.

Thus a graph of $(\alpha_A + \alpha_H)$ calculated using equation (1), versus $(r_A^2 + r_H^2)$, is predicted to be a straight line of slope $k = 8a_0/3 = 1.411 \text{ \AA}$. Figure 1 shows that this prediction is reasonably well satisfied by oxides of the alkaline earths (see table 1), but with the alkali halides (table 2) the fit is much less good. Treated as a whole the alkali halides exhibit a trend of about the right slope (shown dotted in figure 1) but are low by about 2.2 \AA^3 , a discrepancy which is too large to be accounted for by experimental error.

3. Discussion

The most striking feature of figure 1 is the revelation that among the alkali halides there is a general trend, fluorides showing the worst fit followed by chlorides, bromides and iodides in that order. Inspection of table 2 shows that there is a rough correlation with the corresponding radius ratios, fluorides with the largest radius ratios manifesting the greatest deviations. This suggests that the discrepancies arise from the neglect of second-nearest-neighbour interactions in the shell model, for these interactions are more important with very high- and very low-radius-ratio alkali halides, corresponding to extensive cation–cation or anion–anion wave-function overlap respectively. It is known, for example, that incorporation of second-nearest-neighbour interactions substantially improves the fitting of phonon dispersion curves [6]. These additional interactions are also found to be important for the theory of cohesion in alkali halides [7].

If this interpretation is correct the incorporation of second-nearest-neighbour interactions into the shell model would be anticipated to move the fluoride data points in figure 1 towards the line corresponding to equation (5). With iodides, on the other hand, where second-nearest-neighbour interactions are much less important, smaller movements in the same direction would be expected.

In the case of the alkaline earth oxides it should be noted that the divalency of the ions involved would make the nearest-neighbour term more important than the contribution from second-nearest neighbours. Thus the neglect of the latter is not so significant for the calculation of *in crystal* polarizabilities for these compounds.

Table 3. Modified crystal radii and *in crystal* polarizabilities calculated from equation (4)—comparison with [8].

Ion (<i>n</i>) ^a	Mod. cryst. radius (Å)	Pol. (Å ³) (4)	Pol. (Å ³) [8]
Li ⁺ sp(6)	0.96	0.43	0.0290
Na ⁺ (6)	1.22	2.10	0.2495
K ⁺ 2sp(6)	1.58	3.52	1.0571
Rb ⁺ (6)	1.72	4.17	1.5600
Cs ⁺ (6)	1.87	4.93	2.5880
3sp(8)	1.94	5.30	
F ⁻ sp(6)	1.13	1.80	0.9743
Cl ⁻ (6)	1.61	3.66	3.2350
3sp(8)	1.63	3.73	
Br ⁻ (6)	1.76	4.37	4.5330
3sp(8)	1.775	4.46	
I ⁻ 2sp(6)	2.00	5.64	6.7629
3sp(8)	2.02	5.75	

^a (*n*), co-ordination number of environment.

4. Some implications

It is clear from sections 1 and 2 that the use of equation (1) can lead to underestimated values for *in crystal* polarizabilities for the ions in alkali halide structures. The method which depends on known ionic radii seems to be more reliable. Therefore, assuming either sixfold or eightfold co-ordination, new *in crystal* polarizabilities are calculated here using

equation (4) and modified crystal radii for each of the individual ions from the alkali halide series.

The total *in crystal* polarizability ($\alpha_A + \alpha_H$) for each alkali halide with rocksalt structure (each ion in an environment with sixfold co-ordination) can now be calculated from table 3. Alkali halides forming CsCl structures (each ion in an environment with eightfold co-ordination) are predicted to possess an *in crystal* polarizability which is different from that for a sixfold co-ordinated structure. With both structures, in accordance with equation (5), the new values are larger than those estimated in [8].

Although these results differ from the results from previous analyses [2, 8], they are consistent with an individual ion polarizability being dependent on the square of its ionic radius [4]. Such polarizabilities are also consistent with the number of electrons known to occupy an outermost subshell [9]. Most importantly, perhaps, the dielectric data from alkali halides and from oxides, for the first time ([5], see the top of p 600), are seen to be analysable on the same basis.

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