FEW PROPERTIES OF IONIC CRYSTALS ON THE SHELL MODEL

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ABSTRACT. The shell model of Dick and Overhauser is discussed and an alternative procedure for evaluating its parameters is suggested. The model then leads to the values for crystal properties which are in better agreement with the experimental values than are the predictions of the original model. The properties considered are the dielectric constants, Reststrahlen frequency and the co-efficient of compressibility. The calculations are specialised for seven alkali halide crystals.

INTRODUCTION

Simple properties of crystals like cohesive energy (Kachhava and Saxena, 1963, 64] compressibility (Kachhava and Saxena, 1964), thermal expansion (Kachhava and Saxena, 1965) and (Saxena and Kachhava, 1966), Gruneisen constant, (Kachhava and Saxena, 1966a, 66b), dielectric constants (Kachhava and and Saxena, 1966c, 67a) elastic constants, (Kachhava and Saxena, 1967b), and Reststrahlen frequency (Kachhava, 1966), etc., can be reasonably explained on the simple Born theory (Born and Huang, 1956) of ionic crystals. Dick and Overhauser (1958) introduced the so- called shell model' to overcome the deficiencies of the Born model in explaining the dielectric, elastic and thermal properties. They particularly considered the dielectric theories and in the process improved upon the theory of Szigeti (1949, 1950). The aim of the present paper is to further discuss the shell model and also to suggest an alternative procedure for evaluating its model parameters. We then compute the low and high frequency dielectric constants, the effective charge, Reststrahlen frequency and compressibility for seven alkali halide crystals. These calculated values are in better agreement with the experimental results than are the values of the earlier calculations (Dick and Overhauser, 1958). For brevity, we shall write D.O. for Dick and Overhauser (1958).

SHELL MODEL

According to the shell model an ion consists of a spherical shell of n outermost polarizable electrons which are harmonically bound to a core constituted by

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the nucleus and the remaining electrons with a restoring force characterized by a spring constant k. Hence the model parameters n_+, k_+; and n_-, k_- referring to the positive and negative ions respectively, present adequate description for the ions. Further, the shell-shell coupling appropriate to the neighbouring ions is represented by the force constant A. For such a model, D.O. employed the interaction potential due to Born and Mayer (1932) to derive generalized expressions for low and high frequency dielectric constants ϵ_0 and ϵ_{cs}, the effective charge, s; the Reststrahlen frequency, ω_0, and the coefficient of compressibility, β. All these physical quantities are expressed in terms of the characteristic parameters, whose evaluation is described in the following section.

MODEL PARAMETERS

Dick and Overhauser (1958) evaluated the model parameters k and n on the basis of the following relations :

$$\alpha_0 = \frac{3}{4\pi N}\left(\frac{\epsilon_0-1}{\epsilon_0+2}\right) = \frac{n^2e^2}{k} \qquad \dots \quad (1)$$

and

$$\epsilon = \epsilon_0+m(\epsilon_0-1)^2[4\pi Nne^2]^{-1}\omega^2. \qquad \dots \quad (2)$$

Here N is the number f ion-pairs per unit volume, e is the electronic charge, ϵ is the dielectric constant corresponding to the frequency ω, and m is the mass of an electron, α_0 is the static pooarizability value. It is implied in this approach through equation 2 that the value of n for an alkali ion or a halogen ion is the same as that for the shell of the corresponding rare gas atom. n is obtained from equation 2 and k from equation 1. It is possible to dispense with this limitation and the alternative procedure is described below following the work of Having a (1960) in part.

Havinga (1960) suggested the following dispersion relation :

$$\left(\frac{e^2}{\alpha}-\frac{4\pi N}{3}e^2\right)n_-^2-\frac{4\pi^2mc^2}{\lambda}n_-+A = 0. \qquad \dots \quad (3)$$

Here α—is the free-ion polarizability of the negative ion, c is the velocity of light and λ_0 the first ultra-violet absorption wavelength. These calculations make use of n_- values as determined by Havinga (1960) using equation 3. We further need a relation for deducing n_+, which is deduced in what follows. We follow the discussion of D.O. to some extent but simply refer to it for the sake of brevity.

We refer to the figure 4 of D.O. showing a polarized crystal with its positive-ion shells displaced relative to the negative-ion shell by a distance, x. The centre of the exchange charge q_1 is at a distance ξ from the centre of negative ion shell;

the centre of the exchange charge q_2 is at a distance η from the middle point of the line joining the centres of the negative-ion shells; while the exchange charges q_3 are at a horizontal distance ρ from the equilibrium positions $0, r_0, 2r_0 \ldots nr_0$. To evaluate ξ, η and ρ, D.O. made two assumptions : (1) before the application of the electric field, the centres of exchange charges are at the points of tangency of the spheres possessing the Zachariasen radii r_+, r_- (Kittel, 1967) and (2) the exchange charge centre moves in such a way that the ratio of its distances to the two ion shell centres is the same before and after the polarization. They finally obtained,

$$\xi = r_- + (x/r_0)r_-, \qquad \ldots \quad (4)$$

$$\eta = r_+ + (x/r_0)r_-, \qquad \ldots \quad (5)$$

and

$$\rho = (x/r_0)r_- \qquad \ldots \quad (6)$$

We further assume that the exchange charge centre moves so that its displacement relative to the centre of either of the shells is proportional to the exchange on the corresponding shell. We then get,

$$\xi = r_- + \frac{n_-}{n_+ + n_-} x, \qquad \ldots \quad (7)$$

$$\eta = r_+ + \frac{n_-}{n_+ + n_-} x, \qquad \ldots \quad (8)$$

and

$$\rho = \frac{n_-}{n_+ + n_-} x. \qquad \ldots \quad (9)$$

A comparison of relations given by equations 7 to 9 with the corresponding ones of equations 4 to 6 leads to the following unique relationship :

$$\frac{r_-}{r_0} = \frac{n_-}{n_+ + n_-}. \qquad \ldots \quad (10)$$

Now as $r_+ + r_- = r_0$, we get immediately

$$n_+ = \frac{r_+}{r_-} n_-, \qquad \ldots \quad (11)$$

It is thus possible to obtain n_+ from equation 11 after n_- is determined, as described above k_- and k_+ are then computed from equation 1. The model parameters thus obtained along with other relevant fundamental quantities are collected in table 1.

RESULTS

In order to test the scheme of determining the model parameters suggested above we first calculate the s values from equation 31 of D.O. and these are recorded in the last column of table 1. Also listed are the calculated values of D.O. together with experimental values. It will be seen that the theory of D.O. with the set of new model parameters leads to s values which are in better agreement with the experimental values than are the original values of D.O.

We next employ equation I.1 of D.O. to evaluate ϵ using both the sets of model parameters. Both the calculated sets along with the experimental values are recorded in table 2. The results reveal the superiority of new over the old parameters. The same indeed holds for ϵ_0 also as computed from Eqs. (I.2) and (V.29) of D.O. The experimental data used in these computations are from the compilations of Martin (1965).

In table 3 we report the two sets of computed ω_0 and β values on the equations given by D.O. as well as the experimental results. Here also we find that in most of the cases the revised parameters lead to better agreement with the experiment. The compressibility of NaF is not well reproduced, but for this crystal all the others are reproduced within an average absolute deviation of 10.8 per cent.

Table 1

The parameters of the shell model

Crystal	n_-	n_+	k_- (10^7 dyne cm^{-1})	k_+ (10^7 dyne cm^{-1})	$\lambda \times 10^7$	$\frac{\mu}{e} \times 10^6$	$\frac{\nu}{e^2} \times 10^5$	Exptl.	Eq.(V.31) of D.O.	
									D.O.	Present
LiCl	4.3	1.61	0.116	2.06	9.35	3.64	1.59	0.78	0.82	0.83
LiBr.	3.8	1.32	0.070	1.42	14.98	5.37	2.07	0.74	0.91	0.79
LiI	4.0	1.24	0.052	1.22	20.03	7.75	3.14	0.72	0.90	0.76
NaF	0.9	0.66	0.018	0.056	74.08	4.09	0.403	0.83	0.93	0.81
NaCl	2.8	1.52	0.049	0.298	23.80	5.28	1.56	0.77	0.91	0.78
NaBr	2.6	1.30	0.033	0.218	33.66	7.42	2.04	0.74	0.89	0.73
NaI	2.9	1.30	0.027	0.218	41.22	10.2	3.09	0.74	0.89	0.71

Table 2

Experimental and calculated values of ϵ_∞ and ϵ_0

	ϵ_∞			ϵ_0				
		Theo., eq.(V.33) of D.O.			Theo., Eq.(v.32) of D.O.		Eq.(V.29)of D.O.	
Crystal	Exptl.	D.O.	Present	Exptl.	D.O.	Present	D.O.	Present
LiCl	2.75	3.48	3.32	11.95	857	22.45	15.5	13.08
LiBr	3.16	3.76	3.52	13.25	170	12.01	17.7	14.11
LiI	3.80	4.82	4.40	16.85	—	27.98	24.1	18.28
NaF	1.72	1.77	—	5.10	8.51	8.57	5.90	4.89
NaCl	2.31	2.67	2.38	5.91	15.2	7.79	7.29	5.98
NaBr	2.63	2.89	2.60	6.38	14.1	6.69	7.97	6.22
NaI	3.03	3.66	3.04	7.26	14.3	8.10	9.09	6.89

Table 3

Experimental and calculated values of ω_0 and β

	(10^{13} per sec)			(10^{12} cm^2 per dyne)		
		Eq.(V.27)of D.O.			Eq.(V.30) of D.O.	
Crystal	Exptl.	D.O.	Present	Exptl.	D.O.	Present
LiCl	3.84	0.43	1.77	3.36	3.69	3.55
LiBr	3.26	1.00	3.85	4.20	5.00	4.72
LiI	2.71	—	2.36	5.82	4.36	6.53
NaF	4.63	5.86	3.44	2.15	1.98	0-93
NaCl	3.09	2.10	2.59	4.17	4.72	3.97
NaBr	2.54	1.65	2.32	5.02	5.21	4.56
NaI	2.20	1.37	1.92	6.64	6.77	5.92

Thus, results of these calculations for s, ϵ_{cs}, ϵ_0, ω_0 and β and their comparison with experimental data lead to the better appreciation of the shell model, which for quite sometime seemed to describe only the qualitative features of ionic crystals.

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