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Model calculation of the pressure derivative of the high-frequency dielectric constant of alkali-halide crystals

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The mechanism of electronic polarization in insulators is still an unsettled issue. Quite contradictory mechanisms (either strictly intraionic or fully interionic excitations giving rise to polarization) envisaged in the different models appear to determine equally satisfactorily the high-frequency dielectric constants. In the present work we propose to calculate the pressure dependence of the electronic dielectric constant within all the existing models. It is interesting to note that though all of these describe the dielectric constant in a somewhat satisfactory way, their predictions for the pressure dependence of the same are quite different from one to the other and from observation. Next we suggest a modification of the shell-model dielectric theory by including the idea of an effective excited state of the anion in a crystal. The calculations based on a simple version of the new model which appears to favor partly intraionic and partly interionic excitations responsible for the electronic polarization show distinct improvement in agreement with experiment over all the existing models.

I. INTRODUCTION

The mechanism of electronic polarization in insulators is still an ill-understood phenomenon, despite the fact that many attempts have been directed to resolve the problem. All the attempts made so far can be broadly divided into two categories: The models of Clausius-Mossotti,[1] Ruffa,[2] and the shell model of Woods *et al.*[3] use the concept of an individual ionic polarizability associated with each ion which is modified by the environment inside the crystal. The details of the empirical results that serve as the basis of this concept have been earlier discussed by Tessman *et al.*[4] and by Chakrabarti *et al.*[5] based on recent dielectric data.[6] On the contrary, the central concept of the other authors is to disregard totally the existence of the microscopic polarizable units and to treat the entire electronic polarizability as a property of the whole crystal as one unit. The models of Pantelides[7] and Penn[8] make use of this idea. Levine[9] has used the Penn model, originally intended to study the dielectric properties of mostly covalent crystals, to study the insulators.

The central purpose of the present work is to subject the above-mentioned five models to some crucial test by calculating the pressure dependence of the high-frequency dielectric constants of the alkali halides. One of the interesting findings of the present investigation is that all the models which are more or less consistent in the description of the high-frequency dielectric constants lead to quite divergent results for the pressure dependence of the same, not only in magnitude but also, in Pantelides's model, in sign. As a consequence, we have discussed in some detail both the Penn and the Pantelides models. Next, as none of the five models predicts the pressure dependence of the dielectric constant that reproduces observation, we suggest a modification of the shell-model expression for the high-frequency dielectric constant in terms of an effective excited state of the negative ion in the crystal. Finally, we calculate the pressure dependence of the high-frequency dielectric constant in this new model. It is found that the new-model predictions compare quite well with experiment.

In Sec. II we briefly describe the existing models and the method of calculation. In Sec. III we develop the modification of the shell model. In Sec. IV we discuss the results of calculations according to all the models and compare them with experiment.

II. DIFFERENT MODELS AND METHOD OF CALCULATION

A. Clausius-Mossotti model

The classical model envisaged by the Clausius-Mossotti relation[1] pictures an ionic crystal as an assembly of polarizable units held together by electrical forces, and allows one to write the total polarizability of the system as the sum of the individual polarizabilities. Including local-field corrections the expression for the Clausius-Mossotti relation is

$$\epsilon_\infty = [1 + (8\pi/3v)\alpha_e]/[1 - (4\pi/3v)\alpha_e] \ , \qquad (1)$$

where $\alpha_e = \alpha_+ + \alpha_-$, the sum of the (+) and (−) ion polarizabilities, ϵ_∞ is the high-frequency dielectric constant, and v is the volume per unit cell. Assuming the α's to be the property of an ion and constant, the pressure dependence of ϵ_∞ is entirely due to the change of the lattice constant with pressure, i.e.,

$$\epsilon'_\infty = d\epsilon_\infty/dp \ . \qquad (2)$$

B. Ruffa's model

Ruffa[2] has attempted to evaluate all the different factors that alter the value of a free-ion polarizability and has estimated the in-crystal polarizabilities from the relations

$$\alpha_e^+ = \alpha_f^+ E_p^2/(E_p - \alpha e^2/r)^2 \qquad (3)$$

and

$$\alpha_e^- = 16\alpha_f^-(\overline{E}_p)^2/[4\Delta - e^2/r + 3(\overline{E}_p - E)]^2 \ , \qquad (4)$$

where

$$\Delta = 2[e(V_M - V_R)] + E - I + Q_A \ . \qquad (5)$$

(The notation is the same as that of Ruffa.[2]) Since α_e^+ and α_e^- are consistent with the Clausius-Mossotti relation we use them directly in Eq. (1) to get the pressure derivative ϵ'_∞.

C. Penn's model

Starting from the dielectric function and using some suitable assumptions in the framework of the random-phase approximation, Penn[8] has suggested the following formula relating the high-frequency dielectric constant, the plasma frequency, and an average band-gap energy:

$$\epsilon_\infty = 1 + (\hbar\omega_p/E_{\text{av}})^2 Q \ . \qquad (6)$$

Although this expression was originally suggested to describe the dielectric behavior of mostly covalent crystals, VanVechten[9] and Levine[10] have applied it to discuss the dielectric properties of insulators. This formula, it is obvious, is drastically different in both form and content from the previous ones. The concept of individual ionic polarizability is totally absent in this picture. The different quantities occurring on the right-hand side of Eq. (6) are defined as follows:

$$\begin{aligned} &E_{\text{av}}^2 = E_h^2 + C^2 \ , \\ &E_h = (39.74/d^{2.48})\ \text{eV} \ , \\ &C = 14.4b \exp(-k_s r_0)\Delta Z/r_0 \ , \qquad (6\text{a}) \\ &f_i = C^2/(E_h^2 + C^2) \ , \\ &\omega_p = 4\pi N e^2/m \ , \end{aligned}$$

and Q is a constant very close to unity[10] for all crystals. E_h, C, and E_{av} are the homopolar, heteropolar, and average energy gaps, and f_i is the ionicity. d is the nearest-neighbor distance and r_0 equals $\frac{1}{2}d$; $\exp(-k_s r_0)$ is the Thomas-Fermi screening factor; ΔZ equals 6, the number of valence electrons for the crystals under consideration. ω_p is the plasma frequency and N is the number of valence electrons per unit volume.

First of all we check the Penn's formula by calculating the plasma frequencies predicted by the model and comparing them with the observed ones. (See Table I.) It is found that the mean deviation for the 16 alkali halides is about 10%–12% with a maximum of 30%. This is a clear indication of the fact that the effective number of electrons that take part in the plasma oscillation is not equal to the number of the valence electrons. It will be somewhat smaller and will be different in different crystals.

Next, in order to calculate the pressure dependence of ϵ_∞, we recast formula (6) with a slight modification. We consider the crystals to be fully ionic in conformity with other model calculations and also in order to keep the value of the cohesive energy of the crystals unchanged. As we intend to calculate the pressure dependence of ϵ_∞, we extract the implicit lattice constant (d) dependence of the different terms on the right-hand side of Eq. (6). Assuming $\omega_p \propto 1/d^3$, we write Eq. (6) in the following form:

$$\epsilon_\infty = 1 + (A'/r_0^4)\exp(2k_s r_0), \quad k_s = A/\sqrt{r_0} \qquad (7)$$

(where A' and A constants independent of d), which leads to the relation

$$\frac{d\epsilon_\infty}{dp} = (\epsilon_\infty - 1)(k_s - 4/r_0)\frac{dr_0}{dp} \ , \qquad (8)$$

TABLE I. Plasma frequencies in the Penn model.

Crystal	$(\hbar\omega_p)_{\text{th}}$	$(\hbar\omega_p)_{\text{exp}}$[a]
LiF	22.73	25.3
LiCl	16.18	15.8
LiBr	10.97	15.7
LiI	13.15	13.7–14.7
NaF	17.97	•••
NaCl	13.67	15.0–15.5
NaBr	12.84	13.4–14.3
NaI	11.48	12.3–13.3
KF	14.38	•••
KCl	11.45	13.9
KBr	10.84	13.2–13.5
KI	9.92	11.8
RbF	13.49	13.0
RbCl	10.84	12.9–13.9
RbBr	10.47	12.3
RbI	9.56	11.1

[a] See Ref. 12.

where the only unknown constant, k_s, is taken from Levine. The results of the calculation according to Eq. (8) are given in Table II.

D. Pantelides's model

Pantelides has recently asserted that it is only the interionic excitations that provide the mechanism which actually determines the value of ϵ_∞ in insulators. Quantum mechanically we can write for the high-frequency dielectric constant,

$$\epsilon_\infty = 1 + 4\pi\chi = 1 + \frac{8\pi e^2\hbar^4}{vm^2} \sum_{j'j} \frac{\langle j'|\bar{V}_z|j\rangle^2}{\epsilon_{ij}^3} , \tag{9}$$

where $|j\rangle$ are the occupied one-electron states and $|j'\rangle$ are the excited states in the crystal. Here Pantelides assumes that the excitation energies obey a simple power-law dependence on d, and hence we can write

$$\epsilon_\infty = 1 + Ad^S . \tag{10}$$

Pantelides, of course, advances some semiqualitative arguments in favor of Eq. (10) to point out that the constant A depends only on the cation in a crystal, and with a set of four values of A for Li, Na, K, and Rb he determines the 16 high-frequency dielectric constants of the alkali halides by taking $S = 3$. The empirical relation (10) is really striking. It is, however, to be noted that the expression (9) has been derived neglecting the effect of exchange and overlap of neighboring ions and also the local-field effect. In order to calculate the pressure dependence of ϵ_∞ within this model we write, using Eq. (10),

$$\frac{d\epsilon_\infty}{dp} = SAd^{S-1}\frac{dd}{dp} . \tag{11}$$

This expression clearly shows that the pressure dependence of ϵ_∞ for all crystals should turn out to be negative, while all the experimental values are positive, as can be seen from the results given in Table II.

The reason for this is not difficult to see. In the Pantelides relation (10) the assumption that A is independent of d leads to this absurdity. The approximate d dependence of A can be found out if we compare Eq. (10) with Eq. (1). Both equations are empirically valid. Hence upon comparison we find

$$A = \frac{2\Pi(\alpha_+ + \alpha_-)}{d^3[d^3 - \frac{2}{3}\Pi(\alpha_+ + \alpha_-)]} \tag{12}$$

$$\simeq \left(\frac{2\Pi}{d^6}\alpha_- + \frac{4\Pi^2}{3}\frac{\alpha_-^2}{d^9}\right) + \left(\frac{2\Pi}{d^6}\alpha_+ + \frac{4\Pi^2}{3}\frac{\alpha_+^2}{d^9}\right) + \frac{8\Pi^2}{3}\frac{\alpha_+\alpha_-}{d^9} . \tag{12a}$$

It is further noted that the value of A calculated from Eq. (12) compares quite well with that deduced from Eq. (10). Hence there is no contradiction between the two relations. It is also noted that the first term of Eq. (12a) is a constant in a sequence where the cation is fixed and the anion changes from F^- to I^-. In the Na halides for example, the quantities calculated from Eq. (12a) for NaF, NaCl, NaBr, and NaI are 0.037, 0.038, 0.039, and 0.038 and the constancy changes drastically if we alter the cation. This is what nearly prompts one to argue that it is the anion states of a crystal which are strongly controlled by the cation, which is further strengthened by the fact that no such effect is observed with the third term of Eq. (12a). Although the Pantelides relation pre-

TABLE II. Pressure dependence of ϵ_∞ in different models ($\times 10^{-12}$).[a]

Crystal	Clausius-Mossotti	Ruffa	Shell model	Penn	Pantelides	Present	Expt
KCl	7.11	6.05	6.18	1.75	−5.46	5.32	5.25[b]
KBr	11.24	9.45	8.14	2.22	−7.39	7.19	7.52[b]
KI	18.82	15.34	13.33	3.06	−11.53	12.20	12.13[b]
NaCl	6.79	5.14	4.30	1.65	−4.63	3.49	3.56[b]
NaBr	10.85	8.12	7.48	2.39	−6.59	6.51	5.08[c]
RbCl	8.90	7.97	8.50	1.84	−6.12	7.48	6.37[d]
RbBr	12.40	10.82	10.8	2.37	−8.35	10.00	9.20[d]
RbI	19.48	16.38	15.77	3.10	−12.72	14.18	13.0[e]

[a] The overlap potential and other parameters for different crystals are taken from Refs. 15–17.

[b] See Ref. 13.

[c] For NaBr the value was estimated by Fontella *et al.*[13] assuming the fractional change to be the same in going from NaCl to NaBr as from KCl to KBr.

[d] See Ref. 14.

[e] For RbI the value was estimated by Achar *et al.*[14] from the pressure coefficients of other alkali halides by assuming the additivity rule for the electron polarizabilities and their pressure dependences.

dicts the wrong sign for the pressure dependence of ϵ_∞, we do not think that the empirical relation is fortuitous. It deserves careful consideration on the background of a more fundamental calculation.

E. Shell model

The shell-model dielectric theory is quite well known and has been discussed by several authors.[3] In the shell model each ion (i) is divided into two parts: one consisting of the nucleus and the core charges $z_i + y_i$, where z_i is the total ionic charge, and the other an electronic shell of charge $-y_i$ held to the core by a spring constant, k_i. We consider the case where only the negative ion is assumed to be polarizable, while the positive ion is rigid (simple shell model). In this description it can be shown that the electronic polarizability per unit cell of the crystal is given by[3]

$$\alpha = y^2e^2/(k+R_0) \ , \tag{13}$$

where, $R_0 = 2\phi'' + 4\phi'/d$ and ϕ is the short-range overlap potential given by $\phi = b\exp(-d/\rho)$. It is well known that Eq. (13) is consistent with the Clausius-Mossotti relation. Hence it can be directly substituted in Eq. (1) to give the pressure dependence of ϵ_∞. In the shell model, y and k are assumed to be independent of d. The calculated values of the pressure dependence are given in Table II.

III. SHELL MODEL WITH AN EFFECTIVE EXCITED STATE OF THE ANION IN A CRYSTAL

That the free-ion polarizability value will change when the ion is transferred to a crystal is well known both from empirical evidences and theoretical considerations. The works of Ruffa,[2] Chakravarti *et al.*,[5] and Ledovskaya[11] clearly point out that there are three effects which can be distinctly discerned: (a) the overlap effect due to the surrounding ions, (b) the effect of the electric field produced by the ions in the crystal, and (c) the effect due to generation of new excited states of the negative ion when the outermost electron of the ion becomes associated with a positive ion center. The last mentioned effect is essentially important because such excited states do not exist for a free ion and a qualitatively different mechanism is involved in the generation process of these states which are interionic in character.

In the shell model the free-ion polarizability is given by

$$\alpha_f = y^2e^2/K \ . \tag{14}$$

Now, when this ion is transferred to the lattice the shell model considers only the effect of overlap due to surrounding ions through a change of K resulting in the relation given earlier [Eq. (13)]:

$$\alpha_{\mathrm{SM,\,crystal}} = y^2e^2/K' , \quad \text{where } K' = K + R_0 \ . \tag{15}$$

It is to be noted that the shell model completely ignores the other two effects mentioned above. Ruffa tried to consider the last two effects, but as we have already noted, Ruffa's method suffers from various arbitrary assumptions and his treatment of the overlap effect is also inadequate. We want to incorporate the essence of the last two effects within the formulation of the shell model.

In order to achieve this, we consider the effects in turn. Expression (15) is strictly valid for a crystal where the net electric field at the ion site is zero, e.g., a rare-gas crystal. In the case of ionic crystals, there is an electric field both at the cation and at the anion sites. Ruffa,[2] and more recently Chakrabarti *et al.*,[5] have shown that the effect of the electric field on the polarizability is to change the effective excited state by a factor according to the following expression. The details are given in their works. We now simply switch on the electric field at the ionic sites, which alters expression (15) as follows:

$$\alpha = \frac{\alpha_{\mathrm{SM,\,crystal}}}{(1 \mp b\alpha_M e^2/E_p d)^2} \tag{16}$$

(the negative and positive signs refer to the cation and anion polarizabilities), where α_M is the Madelung constant, d is the nearest-neighbor separation, E_p is the mean excitation energy, and b is a constant. The value of b predicted from theory turns out to be same for both positive and negative ions and is equal to 1. Now, we shall advance conclusive experimental evidence to show that the theoretical prediction is quite justified for positive ions, but is found to be drastically different for the negative ion.

Since the main effect of the electric field is to alter the effective excitation energy of the free ion, Eq. (16) may be interpreted by assuming the effective excitation energy in the crystal to be (see Chakrabarty *et al.*[5])

$$E = E_p \mp 1\alpha_M e^2/d \ . \tag{17}$$

To check this relation we assume E_p to be nearly equal to the ionization energy for free cations and to the electron affinity for free anions, while E will be nearly equal to the threshold energy for the corresponding states in the crystal. In this case

$$b \equiv \frac{E_{\mathrm{th}} - E_p}{\alpha_M e^2/d} \simeq 1 \tag{18}$$

for both cations and anions. [The extreme right-hand-side value follows from Eq. (17), while the middle one is evaluated from experimental quantities and is listed in Table III; E_{th} is the threshold energy for the outermost electron of anion in the crystal.]

In Table III we calculate the ratio b for both ions in the case of crystals for which all the relevant data are available. Experimental results clearly indicate that for the positive ions the average value for the eight crystals is 1.4, which is quite close to the theoretically predicted one. For the negative ions, however, the value of b is found to be two to three times less than the theoretical prediction. This fact may be understood in the following way. The electric field at the lattice point where the ion is placed is not produced by the point charges but by the neighboring ions. The negative field produced by the anions at cation centers alters the polarizability of the cations in accordance with the above theoretical considerations. However, the situation is entirely different for anions. The presence of a positive ion in the vicinity of a negative ion in addition to producing the electric field generates a set of additional excited states that contribute to the polarizability of the negative ion. Hence, we maintain that this deviation in the value of b for negative ions is due to the fact that the outermost valence p electrons on anions polarize through the generation of new excited states formed from the cation orbitals, while there is no such effect for the cations. These interionic excitations may be thought to simulate an effective excited state for the anion in a crystal, which in turn modulates the electric field at the anion site through the factor b that ultimately alters its polarizability. It is well known that the effect is very difficult to estimate theoretically; on the other hand, the parameter b contains all the necessary information about the effective excited state. Consequently, if we use the experimental value of b, we may assume that the essential part of the third effect will be properly included. Next, we shall conclude by subjecting the new model to the crucial test of predicting the pressure dependence of ϵ_∞ that will finally establish the validity of our assumption. The final expression for the polarizability of the anion in crystal in the new model is given by

$$\alpha^-_{\text{crystal}} = \frac{y^2e^2}{(1+b\alpha_M e^2/E_p d)^2}\,\frac{1}{(k+R_0)} \quad . \tag{19}$$

Using this expression in Eq. (1) we calculate the pressure dependence of ϵ_∞, and the results are given in Table IV. Some qualitative justification of Eqs. (16) and (19) is discussed in the Appendix. Since we have not used the Tessman-Kahn-Shockley (TKS) polarizability value, it is also instructive to compute the value of $\delta\alpha/\alpha$ in the present model. The values for the anions are given in Table IV, which shows, as expected, a variation of $\delta\alpha/\alpha$ for the same ion in different crystals.

Now, in order to look into Eq. (19), let us expand it and observe the different leading terms:

$$\alpha^-_{\text{crystal}} = y^2e^2/k - y^2e^2R_0/k^2 - y^2e^2 2b\alpha_M e^2/kE_p d \; . \tag{20}$$

Equation (20) clearly shows that there are three different terms; the first one may be identified as the free-ion polarizability, the second is the contribution to the polarizability due to overlap, and the third represents the joint effect of the electric field and the effective excited state. The expression clearly shows that neither of the two extreme pictures is true; that is, that the polarizability in a crystal is completely due to intraionic excitations nor that it may be attributed only to interonic excitations. Rather, the present analysis favors an intermediate picture. The first term is solely due to intraionic excitation. The last two terms are predominantly determined by interionic excitations.

Though our calculations have been confined to a negative-ion polarizable shell model, it is of some interest to see the behavior of a positive ion when transferred to a lattice. Following the previous analysis, we write down the corresponding expres-

TABLE III. Estimated values of the parameter b for ions in different crystals, from Eq. (17).[a]

Crystal	Cation	Anion
KCl	1.2	0.5177
KBr	1.4	0.544
KI	1.6	0.395
NaCl	1.2	0.529
NaBr	1.3	0.580
RbCl	1.5	0.602
RbBr	1.6	0.412
RbI	1.8	0.567

[a] The threshold energies are taken from Ref. 12, the ionization energy and the electron-affinity and mean-excitation-energy estimates are from Ref. 2.

TABLE IV. $\delta\alpha/\alpha$ value for the anion in the present calculation.

Crystal	$\delta\alpha/\alpha$	Crystal	$\delta\alpha/\alpha$	Ion	$(\delta\alpha/\alpha)_{\text{TKS}}$[a]
KCl	0.28	NaBr	0.32	Cl^-	0.23
KBr	0.29	RbCl	0.27	Br^-	0.14
KI	0.24	RbBr	0.22	I^-	0.10
NaCl	0.23	RbI	0.27		

[a] Evaluated from the Pauling free-ion and Tessman-Kahn-Shockley polarizabilities which are taken from Ref. 21. This is included for comparison with the present values.

sion for the cation:

$$\alpha^{+}_{\text{crystal}} = \frac{y_+^2 e^2}{k_+} - \frac{y_-^2 e^2}{k_+^2} R_0 + \frac{2b_+ \alpha_M e^2}{E_{p+} d} \, \frac{y_+^2 e^2}{k_+} . \qquad (21)$$

The different terms in this equation may be interpreted in a similar way. It has been long known from empirical evidence[4] and theory[11] that the positive-ion polarizability increases when the ion is in a lattice, while the negative-ion polarizability decreases under similar conditions. It is satisfying to note that both Eqs. (21) and (20) conform to these desired requirements, and it is brought about jointly by the electric field and the effective excited state that the polarizability increase in the case of a positive ion is more than the decrease for the negative ion owing to the fact that $b/E_p < b_+/E_p^+$.

Equations (19)–(21) have also a natural interpretation when viewed on the background of the shell-model theory. The overlap interaction causes a change in the spring constant by replacing k by $k + R_0$, while the electric field and the effective excited state induce a change in the shell charge by replacing y by

$$y/[1 + (b/E_p)(\alpha_M e^2/d)] .$$

In the simple shell model y is treated as a constant, while in the new model it is a variable depending upon the nearest-neighbor distance. However, it should be stressed that the present variable-charge shell model is essentially different in form and physical content from that introduced by Feldkamp.[18]

IV. RESULTS AND DISCUSSION

One of the major aims of the present investigation is to demonstrate empirically that the various dielectric models that otherwise give a more or less correct description of the dielectric behavior of ionic solids lead to quite divergent results when predicting the pressure dependence of the high-frequency dielectric constant. Table II clearly shows this. This is because the difference in the fine points of the physical content between the models becomes important and magnified in this calculation. The results also indicate a general trend, that the predicted values of ϵ_∞' gradually become closer to experiment going from the Clausius-Mossotti, the Ruffa, to the shell model, all being greater than observation, while the value due to Penn is definitely less than observation in all cases. The results of the Pantelides model, however, have the incorrect sign. The present calculations show distinct improvement over all the existing models. Still, in all cases the agreement is not equally satisfactory. For the three rubidium salts the disagreement is slightly larger. This may partly be attributed to the neglect of the positive-ion polarizability which is rather large in these cases. Similarly, the experimental uncertainty in these cases is also large. For the NaBr crystal the estimated experimental value is uncertain also since it is an extrapolated one. We have not been able to present any calculation for the crystals containing F^- ions although satisfactory measurements of ϵ_∞' are available for some of them. This is because experimental threshold energies are not available for the F^- ion.

Next we discuss some of the implications of the new model introduced in this work. It is theoretically satisfying to note that the present model in a way incorporates the effects of the electric field and of the effective excited state of the negative ion in the shell-model framework, which is totally neglected in the conventional shell model. We have already noted in Sec. III that this is equivalent to making the shell charge a function of the interionic separation. As a consequence this will affect in turn the phonon frequencies of the solid. In a forthcoming communication we shall investigate the lattice dynamics and photoelasticity of crystals within this new model.

Finally we would like to point out that, although we have not been able to resolve the fundamental problem of the polarization mechanism in insulators mentioned in the Introduction, the present phenomenological model advances a rough idea about the two types of excitation to which the electronic polarization in a crystal is due.

APPENDIX

In writing the final expression for the effective mean excitation energy in Eq. (16) for an anion in the crystal, we consider separately two distinct effects, namely, that of the electric field and of the additional excited states and then we superimpose them. In Ref. 5 it has been shown that for anions the effect of the electric field of the surrounding ions cannot be treated by a perturbation method with the free ions as the starting point. On the other hand, if we think that the negative ions are placed in a hypothetical lattice of very large lattice constant, perturbation theory will be again applicable and the effect of the electric field may be thought of as producing a change in the effective excitation energy given by

$$\overline{E} = E_p (1 + 1\alpha e^2/E_p d) .$$

In this expression we have totally neglected the effect of the new states of the anion associated with the positive-ion centers. The assumption of large lattice separation justifies the neglect of the overlap between these states and the ground-state wave functions of the anion. At the next stage the ions are brought closer to a distance of the order of the real lattice separation and consequently, due to appreciable overlap, the new states become significant and their effect is superposed on the mean excitation energy given above. To achieve this let us consider the observation of Pantelides and Harrison[19,20] who have noted that, for a variety of substances including alkali halides, the various matrix elements connecting states located at two different nearest-neighbor ions obey an inverse d dependence. We assign the entire d dependence to the corresponding mean excitation energy which itself is inversely related to d. So we assume the mean excitation energy due to the new states to have a form $-\text{const}/d$, the negative sign indicating the fact that these states will increase the polarizability by decreasing the total mean excitation energy. It may, of course, so happen that the more general form of the expression should be $-\text{const}/d^n$, where n is a suitable number. However, for simplicity and to avoid the introduction of an additional parameter, we keep the value of n equal to unity. Finally, the two effects combined together give an effective mean excitation energy

$$\bar{E} = E_p(1 + b\alpha e^2/E_p d) ,$$

where

$$b = 1 - aE_p/\alpha e^2 .$$

It is presumed that the major part of the effect of the new states is included in the second term in b, but it may be possible that the first term might be affected as well which anyhow does not matter since we parametrize the entire b (its method of evaluation from experiment is discussed in the text).

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