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Model for OH^-, OD^-, and CN^- Impurities in Alkali Halide Matrices

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A model has been developed for calculating the potential barrier-hindering angular motion and possible off-center displacement of the polar impurities in the alkali halide matrices. The general method of the multipole expansion of the intermolecular interaction has been employed. The calculations have been done for the OH^-, OD^-, and CN^- impurities in the KCl, KBr, NaCl, RbCl, and KI matrices. It has been found that the OH^- and OD^- impurities are displaced by about 0.2–0.3 Å from the normal-lattice site in the different alkali halide lattices. For the CN^- case, no appreciable displacement of the impurity c.m. is evidenced. In this case, the effect of the relaxation of the lattice near the impurity is also considered. This has been found to add a small tetragonal term of the type $(4\pi)^{1/2} K'' Y_0^2$ to the octahedral potential. The addition of such a small tetragonal term has recently been demonstrated by Pompi and Narayanamurti to explain successfully the rather unexpected infrared results and also the anomalous specific-heat results of Harrison *et al.* The calculated values of the barrier and the off-center displacement have been used successfully to explain the librational frequency and the tunneling splitting of these impurities in the matrices. The general validity of different approaches has been discussed in the light of the librational frequencies and their isotope effect.

I. INTRODUCTION

Ionic crystals containing a small concentration of dipolar impurities like OH^- and CN^- have attracted considerable experimental[1–9] and theoretical[10–15] attention. The presence of such impurities in the alkali halide crystals has been experimentally seen to cause changes in the dielectric constant, specific heat, and thermal conductivity at low temperatures. The interpretation of these and other phenomena like infrared absorption and paraelectric-resonance studies requires a definite knowledge of the potential in which the impurity ion performs different types of motions. These experiments also present strong evidence for a novel type of lattice distortion, when the mismatch in the size between the impurity and the replaced ion is large. Thus, when the OH^- impurity is substituted for the Cl^- ion in a KCl matrix, experiments suggest that the OH^- impurity shuttles around a number of equivalent off-center positions leading to observable dielectric, thermal, and mechanical effects. In this respect the behavior of the OH^- and CN^- ions is more or less similar to that of a Li^+ ion dispersed in the ionic matrices.[16] A first-principles analysis of the origin of the off-center position of the center of mass (c.m.) and the angle-dependent part of the potential energy (i.e., the barrier-hindering angular motion of the dipolar impurity) is, therefore, of interest.

Attempts[17–19] have been made to calculate the potential barrier and the origin of such off-center displacements for a Li^+ ion in the alkali halide matrices. Such calculations have been done within the framework of a Born-Mayer model with either an arbitrary but steep linear term to avoid collapse[18] or a modification for the polarization and the repulsion effects at short distances.[19]

For the dipolar impurities Lawless[20] used a point-charge–point-dipole model to calculate the rotational barrier for the OH^- impurity in alkali halide matrices. More recently, Chandra *et al.*[21] calculated the barrier height on a more realistic approach. The general method of multipole expansion was used to calculate the rotational barrier parameter K. This method could be applied to any diatomic impurity, provided its quadrupole and hexadecapole moments were known. This calculation gave a good estimate of the barrier height, except in the case of the KBr-OH^- system, where the calculated barrier parameter was about 25% less than

the observed one.

Though the displaced position of the OH^- c.m. is conceivable within the framework of the above calculation,[21] it was not explicitly considered there. It is a well-known theorem of electrostatics that the displacement of a point dipole is equivalent to superimposing a quadrupole moment on the dipole at its original position. The quadrupole moment obtained, therefore, will be the sum of the molecular quadrupole moment and that due to the displacement of the dipole. If the impurity quadrupole moment is known from other methods,[22] the contribution due to the displacement of the dipole can be separated out and the value of the displacement determined. This naturally suggests an equal off-center displacement of the OH^- c.m. in all the host matrices, which is not convincing.

The failure of the above calculation for the case of the KBr-OH^- system and a private correspondence from Lawless,[23] made it clear that for an accurate calculation of the barrier height, the off-center displacement of the impurity c.m. should be explicitly considered.

In the present paper, a general method has been developed for the calculation of the potential barrier-hindering angular motion of the impurity molecule and also the possible off-center position of its c.m.. The method has been applied for calculating these parameters for the OH^-, OD^-, and CN^- impurities in a number of alkali halide matrices. For the OH^- impurity, a value of about 0.2–0.3 Å has been obtained for the off-center displacement of its c.m. in different alkali halide matrices. For the CN^- case, no appreciable displacement of the c.m. is evidenced. In this case, the effect of the relaxation of the lattice near the impurity is also considered. This is found to add a small tetragonal term of the type $(4\pi)^{1/2}K'' Y_0^2$ to the Devonshire octahedral potential. This small tetragonal term has recently been incorporated by Pompi and Narayanamurti[9] to explain with success the rather unexpected infrared optical results and also the anomalous specific-heat results of Harrison *et al.*[24]

II. MODEL

For the rigorous determination of the impurity displacement, one needs to calculate the variation of the system energy as a function of the impurity displacement. This requires an adequate knowledge of the attractive as well as the repulsive potential between the impurity ion and the ions of the host matrix. Calculations of this type have been made for the Li^+ impurity[17–19] for which the form of the potential is well known. Unfortunately, such potentials are not available for the dipolar impurity–host-lattice ion systems.

The calculation of the barrier height and the displaced position of the impurity c.m. is based here on the multipole expansion method of the intermolecular interaction. The idea of a possible off-c.m. displacement of a dipolar impurity was first suggested by Seward and Narayanamurti[2] and later reaffirmed by a number of other workers.[11,12,33] The reason for such a displacement can be stated as follows. The equilibrium configuration of the impurity in the matrix cavity is described by the minimum energy configuration. The interaction energy depends upon the distribution of charges in the dipolar impurity and the atoms of the host lattice. Consequently, the point of the impurity, which rests at the normal-lattice site in the minimum energy configuration will depend upon the distribution of the charges in the impurity. We call this point the center of interaction (CI), because it is this point at which the effective crystalline field interaction acts. Essentially, the CI need not coincide with the c.m. because the latter is governed by the distribution of masses in the impurity. We assume that the angular anisotropy of interactions is also minimum about the CI. To summarize, our assumptions are (i) that the impurity occupies a substitutional site in the undistorted host matrix cage with its CI (and not the c.m.) at the normal-lattice site and (ii) that the angular anisotropy of interaction is minimum about the CI. The concept of such a CI has recently been introduced by a number of workers,[25–27] and the parameter (separation between molecular c.m. and CI) has been demonstrated to be of much importance in understanding a number of molecular problems in the gaseous phase.[25] Such a concept of molecular CI has also led to the understanding of the matrix spectra of HCl- and HBr-type impurities in the rare-gas matrices at low temperatures.[26,27]

So far as the properties of this CI are concerned, the following points may be mentioned. Where there is a symmetric charge distribution in the molecule, the CI can be taken as located at the center of symmetry. For an asymmetric charge distribution, CI is the point about which the angular dependence of the intermolecular interaction is minimum. The relative importance of the various types of these interactions (such as dispersion, induction, exchange, and multipole interactions), which are not necessarily centered at the same point, is determined by the intermolecular distances and the environs of the impurity. The CI of an asymmetric molecule (and hence the point of the impurity, which rests at the normal-lattice site) is, therefore, not only a molecular constant but it also depends upon the environment of the impurity. The position of the CI may also slightly depend upon the experimental conditions, such as temperature, pressure, and state of aggregation,

etc. These latter small effects will not be considered here.

III. BARRIER-HINDERING ANGULAR MOTION AND OFF-CENTER POSITION OF IMPURITY c.m.

The barrier arises due to the angular anisotropy of the interaction between the trapped impurity and the atoms of the host lattice. The dominant interactions are the following: (a) electrostatic interaction between the charges of the host-lattice atoms and the multipole moments of the impurity; (b) induction interaction, i.e., the interaction between the multipole moments of the impurity and the dipole moment induced in the host-lattice atoms due to these multipole moments; (c) induced multipole-induced multipole London dispersion interaction; and (d) exchange interaction, which arises because of the overlap of the two charge distributions.

Since the angular-dependent part of the exchange interaction is not precisely known, it is not considered here. The radial-dependent part will not give any contribution to the barrier if the center of the exchange forces is taken to be the same as the CI. The explicit expressions for the other interactions are well known.[28] These can be rearranged and written in terms of spherical harmonics, summed over all the neighboring and far neighboring atoms to give the barrier parameter as[29]

$$K=\sum_{\substack{i=\text{different}\\ \text{shells}}}\rho_i\left(\frac{9}{2}\,\frac{\alpha_H\Theta_s^2}{R_i^8}-\frac{7}{2}\,\frac{C_H\Phi_s}{R_i^5}+\frac{7}{12}\,\frac{\alpha_H C_s\Phi_s}{R_i^8}\right) \tag{1}$$

or

$$K=A\Theta^2+B\Phi_s\,, \tag{2}$$

where

$$A=\sum_i\rho_i\,\frac{9}{2}\,\frac{\alpha_H}{R_i^8} \tag{3}$$

and

$$B=\sum_i\rho_i\left(-\frac{7}{2}\,\frac{C_H}{R_i^5}+\frac{7}{12}\,\frac{\alpha_H C_s}{R_i^8}\right)\,. \tag{4}$$

TABLE I. Constants of the shell summation used for the calculation of the barrier parameter.

	Number of atoms in the shell	ρ_i	R_i
First shell	6	+1.0	R
Second shell	12	−0.5	$\sqrt{2}\,R$
Third shell	8	−0.888 89	$\sqrt{3}\,R$
Fourth shell	6	+1.0	$2\,R$
Fifth shell	24	+0.8	$(\sqrt{5})\,R$
Sixth shell	24	−1.0	$(\sqrt{6})\,R$
Seventh shell	12	−0.5	$(\sqrt{8})\,R$
Eighth shell	30	−0.925 93	$3\,R$

The subscripts s and H denote, respectively, the host lattice and the solute or the impurity ion. The symbols C, μ, Θ, Ω, and Φ stand for the charge, dipole, quadrupole, octupole, and hexadecapole moments, respectively. The values of the shell summation constants ρ_i and R_i for the first few neighboring shells have been listed in Table I.

The molecular moments Θ_s and Φ_s are those expressed about the CI (the point which rests at the normal-lattice site). These can be expressed in terms of the impurity multipole moments expressed with respect to the c.m. and the (c.m.−CI) separation a, as follows:

$$\Phi_{s(\mathrm{CI})}=\Phi_{s(\mathrm{c.m.})}-4a\Omega_{s(\mathrm{c.m.})}+6a^2\Theta_{s(\mathrm{c.m.})}-4a^2\mu_{s(\mathrm{c.m.})}+a^4C_s$$

and

$$\Theta_{s(\mathrm{CI})}=\Theta_{s(\mathrm{c.m.})}-2a\mu_{s(\mathrm{c.m.})}+a^2C_s\,. \tag{5}$$

Substitution of these in (2) gives

$$K=(A\Theta_s^2+B\Phi_s)-4a(A\mu_s\Theta_s+B\Omega_s)+2a^2(2A\mu_s+A\Theta_sC_s+3B\Theta_s)-4a^3(A\mu_sC_s+B\mu_s)+a^4(AC_s^2+Bc_s). \tag{6}$$

The barrier parameter K is also a measure of the strength of the angular anisotropy of interactions. Hence, according to the definition of the CI, dK/da should vanish and d^2K/da^2 should be positive. This gives

$$a^3(AC_s^2+BC_s)-3a^2(A\mu_sC_s+B\mu_s)+a(2A\mu_s^2+A\Theta_sC_s+3B\Theta_s)-(A\mu_s\Theta_s+B\Omega_s)=0. \tag{7}$$

The constants A and B depend only upon the matrix parameters. Equations (6) and (7) in this way give the value of the barrier parameter and the off-center displacement of the impurity c.m., respectively, in terms of the multipole moments of the impurity and the constants of the matrix.

IV. EFFECT OF LATTICE RELAXATION NEAR IMPURITY

In cases where the size of the impurity is either greater than or of the same magnitude as that of the substituted ion of the host lattice, a relaxation of the nearest-neighbor atoms may result. An important type of the lattice relaxation has recently been proposed.[9,30] In this it is assumed that the nearest-neighbor atoms lying along the axis of the dipolar impurity are pushed away, and those perpendicular to the axis of the dipole are pulled towards the impurity ion. Figure 1 shows this type of lattice relaxation together with the induced elec-

tronic dipole moments in the nearest-neighbor atoms. The displacements (ξ and η) and the corresponding induced dipole moments (λ and μ) are taken to be radial with respect to the impurity CI. When this is considered, the Devonshire octahedral potential is modified to the form

$$V(\theta,\phi) = 5K(\sin^4\theta \sin^2\phi \cos^2\phi + \sin^2\theta \cos^2\theta) + K' \cos^4\theta + (\tfrac{5}{4})^{1/2} K'' (3\cos^2\theta - 1) . \quad (8)$$

Here θ and ϕ are the polar angles describing the orientation of the dipole in a lattice fixed-coordinate system. The constants K, K', and K'' are given by

$$K = (8\xi + 36\xi^2)\left(\frac{9}{2}\frac{\alpha_H \Theta_s^2}{R^8} + \frac{7}{12}\frac{C_s \Phi_s \alpha_H}{R^8}\right) + (5\xi + 15\xi^2)\left(-\frac{7}{2}\frac{C_H \Phi_s}{R^5}\right) - \xi(1 + 6\xi + 21\xi^2)\left(-\frac{25}{2}\frac{C_H \Phi_s}{R^5}\right) + \text{that given in Eq. (2)}, \quad (9)$$

$$K' = [20(\xi+\eta) + 90(\xi^2 - \eta^2)]\left(\frac{9}{2}\frac{\alpha_H \Theta_s^2}{R^8} + \frac{7}{12}\frac{\alpha_H C_s \Phi_s}{R^8}\right) + [25(\xi+\eta) + 75(\xi^2 - \eta^2)]\left(-\frac{7}{2}\frac{C_H \Phi_s}{R^5}\right) + [(\xi+\eta) + 6(\xi^2 - \eta^2) + 21(\xi^3 + \eta^3)]\left(-\frac{125}{4}\frac{\alpha_H \Phi_s}{R^5}\right) , \quad (10)$$

$$K'' = \frac{2}{3\sqrt{5}}\left[(\xi+\eta)\left(-\frac{27}{2}\frac{C_H \Theta_s}{R^3} + \frac{18\alpha_H \mu_s^2}{R^6} + \frac{27\alpha_H C_s \Theta_s}{R^6} + \frac{36\alpha_H \Theta_s^2}{R^8}\right) + (\xi^2 - \eta^2)\left(-\frac{54 C_H \Theta_s}{R^3} + \frac{675}{2}\frac{C_s \Phi_s}{R^5} + \frac{63\alpha_H \mu_s^2}{R^6} + \frac{189}{2}\frac{\alpha_H C_s \Theta_s}{R^6} - \frac{172\alpha_H \Theta_s^2}{R^8}\right)\right] . \quad (11)$$

V. RESULTS AND DISCUSSIONS

A. OH^- and OD^- Systems

Tables II and III summarize the various constants used in the calculations. Table IV gives the values of the barrier parameter K and the displaced position of the impurity center of mass a, which have been calculated on the basis of the present model. We should now show that these values are in accord with some experimentally observed results. The experimental observations, which can be directly correlated to these parameters, are the librational level and the tunneling frequency of the impurities in the matrices.

The librational frequency can be calculated by different approximate formulas. In the first case, when the potential barrier-hindering angular motion is small for the angular motion to be just librational, the Devonshire model[13] is a good approximation. It has been very well realized that the Devonshire model[13] is unable to explain adequately the librational levels and their isotope effect for the case of the OH^- alkali halide systems. This is clear from the fourth column of Table IV, where the values of the librational frequencies as obtained from the Devonshire model have been summarized. This same conclusion is also drawn

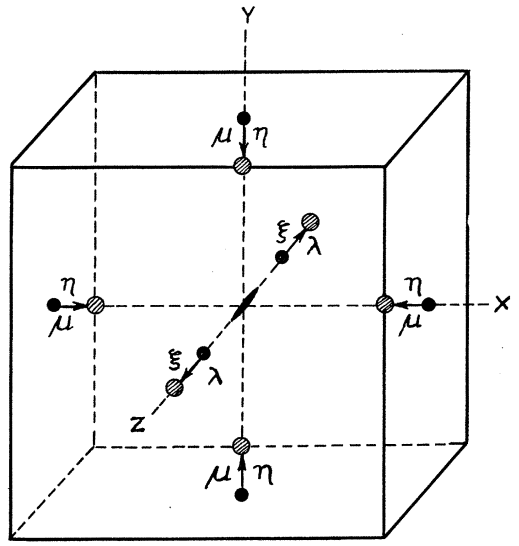

FIG. 1. Displacements ξ and η and corresponding displacement dipole moments λ and μ. All displacements and induced dipoles are radial with respect to the impurity CI (i.e., the point of the impurity which rests at the normal-lattice site of the matrix). The impurity is shown to align along the $\langle 001 \rangle$ orientation. ●, normal position of the lattice points; ●, relaxed position.

TABLE II. Lattice parameters used in the calculations.

	KCl	KBr	NaCl	RbCl	KI
R (Å) [a]	3.12	3.25	2.80	3.26	3.53
α^+ (Å^3) [b]	3.29	3.29	1.57	4.56	3.29
α^- (Å^3) [b]	4.98	6.44	4.98	4.98	8.68

[a]N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon, London, 1940).
[b]S. Roberts, Phys. Rev. 81, 865 (1951).

TABLE III. Impurity constants used in the calculations.

	OH^-	OD^-	CN^-
B (cm^{-1}) [a]	18.9	10.0	1.25
μ_s (Debye) [b]	4.59	4.59	0.3
Θ_s (Debye Å) [b]	9.15	9.15	0.78
Ω_s (Debye Å^2) [b]	2.556	2.556	...
Φ_s (Debye Å^3) [b]	0.25	0.25	−0.06
Bond length (Å) [c]	0.974	0.974	1.444

[a]C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955).
[b]For the OH^- impurity, the multipole moments are about the impurity CI in the KCl matrix, i.e., about a point which is 0.2801 Å away from the c. m. towards the oxygen atom. For the CN^- impurity these are about the c. m.
[c]Obtained from the known value of the rotational constant.

from the last column of Table I in Ref. 31, where quite different values of the barrier parameter are obtained for the OH^- and OD^- impurities. In fact, these systems do not fall in the low-barrier limit. For the case of larger barriers also, Devonshire has solved the appropriate Schrödinger equation, which gives the librational frequency as

$$\nu_{11b} = (20KB)^{1/2} - 4.5B \ . \qquad (12)$$

The fifth column of Table IV gives the values of ν_{11b} as obtained from Eq. (12). It can be seen that although this calculation presents an improvement in the right direction, it does not account satisfactorily for the observed librational frequencies.

The reason can be stated as follows. Devonshire's calculation for the large barriers treats the motion of the impurity in two angular coordinates, i.e., it considers the three-dimensional librational motion of the impurity molecule. For the large value of the barrier parameter K, it may be difficult for

TABLE IV. Calculated values of the barrier parameter and off-center position of c.m. for the OH^- impurity. From this barrier parameter the librational frequencies have been calculated for the normal as well as deuterated samples and compared with the experimental data.

System	Calculated barrier height (cm^{-1})	Displacement of impurity c.m. (Å)	Calculated librational frequency A[a] (cm^{-1})	B[b] (cm^{-1})	C[c] (cm^{-1})	D[d] (cm^{-1})	Observed librational frequency (cm^{-1})
KCl-OH^-	584.04	0.2801	254.24	263.35	297.43	326.2	297.5[e] 293[f]
KCl-OD^-	584.04	0.3310	213.55	211.25	231.98	276.6	231.5[e]
KBr-OH^-	470.01	0.2122	236.26	263.39	309.14	354.9	309.7[e] 309[f]
KBr-OD^-	470.01	0.2631	200.46	206.57	232.42	294.7	233[e] 235[f]
NaCl-OH^-	741.20	0.2037	333.40	347.98	395.45	486.2	390.0[e] 385[f]
NaCl-OD^-	741.20	0.2546	266.36	269.30	295.89	396.5	...
RbCl-OH^-	634.55	0.3379	244.98	248.00	274.71	263.9	270.5[e]
RbCl-OD^-	634.55	0.3888	201.14	203.05	220.25	251.7	...
KI-OH^-	370.92	0.2050	195.00	231.76	278.96	311.4	279[e]
KI-OD^-	370.92	0.2559	172.48	182.43	208.89	260.6	213[f]

[a]Obtained from Devonshire model for low barriers.
[b]Obtained from Devonshire model for large barriers. In this $\nu_{11b} = (20KB)^{1/2} - 4.5B$.
[c]Corresponding to torsional oscillation model in one plane. For this $\nu_{11b} = (20KB)^{1/2}$.
[d]Obtained from the point-mass model of Dreyfus (Ref. 32).
[e]M. V. Klein, B. Wedding, and M. A. Levine, Phys. Rev. 180, 902 (1969).
[f]D. Harrison and F. Lüty, Far Infrared Librational Excitations of OH^- and OD^- Dipoles in Alkali Halides, International Symposium on Color Centers in Alkali Halides, Rome, 1968 (unpublished).

TABLE V. Calculated and observed values of the tunneling splittings for the OH^- and OD^- impurities.

System	a (Å)	Calculated tunneling splitting[a] (cm^{-1})	Observed tunneling splitting (cm^{-1})
KCl-OH^-	0.2801	0.18	0.21[b]; 0.18[c]
KCl-OD^-	0.3310	0.04	
KBr-OH^-	0.2122	4.71	
KBr-OD^-	0.2631	1.19	
NaCl-OH^-	0.2037	2.74	1.60[d]; 2.8[e]
NaCl-OD^-	0.2546	0.49	
RbCl-OH^-	0.3379	0.01	
RbCl-OD^-	0.3888	0.00	
KI-OH^-	0.2050	9.02	
KI-OD^-	0.2509	2.84	

[a]Obtained from our calculated value of barrier parameter K and off-center displacement parameter a. The results are from the tunneling model of Gomez *et al.* (Ref. 11).

[b]Reference 3.

[c]Reference 33.

[d]R. E. Aldrich, W. J. Burke, and K. A. McCarthy, Solid State Commun. 5, 899 (1967).

[e]B. Wedding and M. V. Klein, Phys. Rev. 177, 1274 (1969).

the molecule to perform angular motion in three dimensions. There are planes having smaller potential energy, and it is quite likely that the molecule makes angular motion in this plane of lowest potential energy. For example, for the ⟨100⟩ equilibrium orientation of a dipolar impurity in an octahedral potential, it can be shown that the potential energy for the molecular angular displacement is least when this displacement is in the xy or xz plane. For such a case of torsional oscillation in one plane the librational frequency is given by

$$\nu_{11b} = (20KB)^{1/2} . \tag{13}$$

The sixth column of Table IV presents the calculated values of the librational frequencies as obtained from Eq. (13). It can be seen from the table itself that this calculation explains adequately the librational frequencies as well as their variation on isotopic substitution. This result is also supported by similar conclusions of Klein *et al.*[31]

More recently Dreyfus[32] has compared the hindered-rotor model and the tunneling model for the energy levels in the lowest mainfold. In doing so he has concluded that the two models provide sufficiently identical results (tunneling splitting), when ν_{11b} is expressed by a formula like Eq. (12) and when the dipolar impurity is considered as a point mass concentrated at its c.m. This point mass is combined with a virtual infinite mass located at the normal-lattice site. The moment of inertia of the dipole is taken as if it were a point mass situated at a certain finite distance from the normal-lattice site. We have presented a slightly different picture. In our model we have identified a CI about which the angular anisotropy of the interaction is minimum. This point has been located at the normal-lattice site and it has been emphasized that the angular motion of the impurity in the matrix occurs about the CI and not about the c.m. Under such a condition the moment of inertia of the impurity governing the angular motion will be given by

$$I_{CI} = I_{c.m.} + ma^2 , \tag{14}$$

and hence the effective value of the rotation constant B now becomes

$$B_{CI} = B_{c.m.} \Big/ \left(1 + \frac{ma^2}{I_{c.m.}}\right) = \frac{h}{8\pi^2 I_{c.m.} c} \Big/ \left(1 + \frac{ma^2}{I_{c.m.}}\right) . \tag{15}$$

This should be compared with the effective value of B in the Dreyfus work:

$$B_{eff}(\text{Dreyfus}) = \frac{h}{8\pi^2 c(2ma^2)} . \tag{16}$$

The next to last column of Table IV gives the values of the librational frequencies, which are obtained using our calculated values of a and k and the Dreyfus model.[32] It can be seen that the Dreyfus model consistently predicts larger values of the librational frequencies. This is probably due to the neglect of the diatomic nature of the impurity, which plays an important part in the librational motion. The effective moment of inertia of the impurity is thus underestimated, which leads to the larger values of the librational frequencies.

For the calculation of the tunneling splitting there are two different models available: One is the Devonshire model[13] and the other is the tunneling model.[11,33] It has been demonstrated by Dreyfus[32] that over a certain range of the barrier parameter, the two models provide identical results. Table V gives

TABLE VI. Calculated and observed values of the barrier parameter K for the CN^- impurity.

		Barrier parameter K		
System	Librational frequency (cm^{-1})	Obtained from the observed librational frequency (cm^{-1})	Obtained from Eq. (6) of the present formulation (cm^{-1})	Obtained from Eq. (9) considering lattice relaxation as well (cm^{-1})
KCl-CN^-	12 ± 1[a]	22.2 ± 2.5	22.7	22.7
KBr-CN^-	12 ± 1[a]	22.2 ± 2.5	18.0	18.0
KI-CN^-	11 ± 1[a]	18.0 ± 2.5	11.3	18.0
RbCl-CN^-	19 ± 1[a]	35.1 ± 2.5	19.1	35.1

[a]Reference 2.

the values of the tunneling-splitting parameter obtained by using our calculated values of the barrier parameter K and the displacement parameter a. It can be seen that the limited experimental data are well reproduced by our calculated values of K and a. For cases where tunneling frequency data are not available, our calculated values stand as theoretical ones to be verified by later experiments. The good agreement of the observed librational and tunneling frequencies to the values obtained from the calculated values of the barrier parameter K and the c.m. displacement parameter a proves the adequacy of the latter calculated values and also that of the model.

The general behavior of the variation of the displacement parameter with the host matrix and the equilibrium orientation of the impurity can also be compared with the information obtained from other sources. From the sign of the barrier parameter K as positive, a $\langle 100 \rangle$ equilibrium orientation is predicted. This is in agreement with the conclusions of Kuhn and Lüty[4] and many others.[20,34,35] The value of the parameter a increases in the sequence NaCl, KCl, RbCl, i.e., it increases with the covalent radius of the nearest-neighbor atom when the displaced ion is the same. The value of a for the KBr matrix is smaller than that for the KCl matrix, although the cavity size is larger for KBr. This behavior is consistent with the similar results on the KCl-Li^+ and KBr-Li^+ systems.[19] Our calculated value of the displacement parameter for the KCl-OH^- system (0.2801 Å) agrees well with that obtained by Bron and Dreyfus[33] (0.28 Å).

B. CN^- System

The calculated of the barrier in this case requires a two-parameter fit to the four available experimental data. As can be seen from Table VI, this could not be attained. The impurity quadrupole and hexadecapole moments required to fit the KCl and KBr data give sufficiently lower values of the barrier parameter for the KI and RbCl matrices. The excellent three-parameter fit to the ten experimental data for the OH^- case does establish the general validity of the model, but its failure in the case of the CN^--doped systems invokes some difficulty. There can be two possible methods for attributing to this discrepancy. First, it may be possible that the CN^- impurity occupies slightly off-center displaced position[8] in the KI and RbCl matrices. This possibility arises due to the larger cavity dimensions in these two matrices. To examine this a three-parameter fit (as was done for the case of the OH^- impurity) was tried, which ended in failure. This indicates that possibly the CN^- impurity does not sit off center in the ionic matrices. Such a conclusion has also been drawn by a number of other workers.[34,35] The other possibility is the relaxation of the lattice near the impurity. This has recently been evidenced from the electric-field-induced dichroism experiments on the RbCl-CN^- system.[9] The fourth column of Table VI gives the value of the barrier parameter when lattice relaxation is also considered. The lattice-relaxation parameter required to fit the results are $\xi = 0.056$ for the KI and $\xi = 0.076$ for the RbCl matrix. This in itself may be trivial because, in fact, it becomes a four-parameter fit to the four experimental data. The value of the tetragonal distortion parameter K'' obtained from these values of ξ, etc., is 5.0 cm^{-1} for the KI and 3.6 cm^{-1} for the RbCl matrix. The ratio K''/K for the RbCl case becomes 0.1, in agreement with the predicted value of Pompi and Narayanamurti.[9]

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Simple Shell-Model Calculation of Lattice Dynamics and Thermal Expansion of Alkali Halides*

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A six-parameter shell model which takes into account anion polarizability, noncentral nearest-neighbor interactions, central second-neighbor interactions, and the effective charge of the core and shell of the anion has been utilized for the determination of the lattice dynamics of LiF, NaCl, KCl, and RbI. The model parameters are determined from experimental data on the long-wavelength optical-mode phonon frequencies, the three elastic constants, and the high- and low-frequency dielectric constants. By the incorporation of the pressure derivatives of these quantities into the lattice-dynamical model, the individual-mode Grüneisen parameters and the temperature dependence of the thermal-expansion coefficient are calculated. Reasonable agreement is found between the calculated values and the available experimental data on these quantities.

I. INTRODUCTION

The first complete lattice-dynamical treatment of alkali halides was done by Kellermann[1] in 1940 for NaCl using a rigid-ion model with full formal ionic charge. Since then a large number of treatments have appeared on diatomic cubic crystals using more complicated models, viz., the shell model,[2-4] deformation-dipole model,[5] breathing-shell model,[6] and others.[7] Many of these models employ a large number of parameters obtained from a fit of extensive phonon-dispersion data measured by neutron-scattering techniques. The use of a large number of fitting parameters sometimes yields physically unrealistic values for some of the model parameters, thus reducing the lattice-dynamical treatment to a mere curve-fitting procedure. Such models are thus unsuitable for crystals for which extensive data on phonon dispersion do not exist. Furthermore, these models are not easily adaptable to the calculation of other thermodynamical properties, such as the thermal expansion, without invoking additional model parameters. For example, in some calculations of the coefficient of thermal expansion, additional anharmonic parameters had to be invoked,[8] which in turn were evaluated by fitting the thermal-expansion data, thus rendering the so-called agreement between calculated and experimental values relatively insignificant.

In the present work, a simple shell model is used in which all the model parameters are obtained without recourse to phonon-dispersion data. The model takes into account short-range first- and second-neighbor interactions and assumes the anion to