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Shift of the Band Center of OH^- and OD^- Impurities in Alkali Halide Matrices

G. K. Pandey and D. K. Shukla
Physics Department, Allahabad University, Allahabad, India

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The shift of the band center of the OH^- and OD^- impurities in different alkali halide matrices can be well understood in terms of Buckingham's theory if one considers that the lattice gets locally distorted near the impurity. The amount of lattice distortion needed to explain the shifts of the band centers agrees well with that obtained on the basis of different specific models.

INTRODUCTION

Recent experiments[1–4] on the matrix properties of hydroxyl-ion-doped alkali halide crystals have presented several interesting features. The tunneling splitting, the paraelectric resonance, and the isotope effect of the librational frequencies have now been well understood in terms of different theoretical models.[5,6] The origin of the near-infrared absorption at about 10–50 cm^{-1} from the band center (the so-called non-Devonshire lines) has also been recently discussed qualitatively[7] as well as quantitatively.[8]

In the present paper, we wish to treat the shift of the band center of the infrared absorption, which corresponds to the stretching motion of the impurity. The prominent observation is that of a blue shift in these systems, whereas in other similar systems, normally red shifts have been observed.[9]

THEORY

Buckingham[10] has given a general theory for the shift of the band center of an impurity trapped in a solid-state matrix. The shift is given by

$$(\Delta\omega)_{0\text{-}1}=\frac{B_e}{hc\omega_e}\left(U''-\frac{3A}{\omega_e}U'\right) . \qquad (1)$$

Here B_e is the rotational constant, ω_e is the harmonic part of the stretching frequency, and A is the anharmonicity constant. U is the interaction between the impurity ion and the atoms of the host lattice and is given by

$$U=-\frac{6e^2}{R}-\frac{6\alpha_H\,\mu_s^2}{R^6}-\frac{6\alpha_H\,\Theta_s^2}{R^8}+6b\exp\left(\frac{r_+ + r_- - R}{\rho}\right) . \qquad (2)$$

Here the first term is the charge-charge interaction term and does not contribute to the shift of the band center. The second and third terms are the dipole-induced-dipole and quadrupole-induced-quadrupole interaction terms, respectively. These terms give a red shift to the band center,

$$(\Delta\omega)_{\substack{\mu-\alpha\mu\\ +\Theta-\alpha\Theta}}=\frac{-6B_e}{hc\omega_e}\cdot 2r_e^2\,\alpha_H\left[\left(\frac{d\mu_s}{dr}\right)^2\frac{1}{R^6}+\left(\frac{d\Theta_s}{dr}\right)^2\frac{1}{R^8}\right] . \qquad (3)$$

The fourth term is the repulsive interaction term for which we have taken a Born-Mayer-Huggins generalized form.[11] The advantages of this form of the repulsive parameter have been discussed in detail elsewhere.[11] This gives a blue shift to the band center, which may be expressed as

$$(\Delta\omega)_{\text{rep}}=\{A+[(x^2+2x)/\rho^2]B-(x/\rho)C\}e^x , \qquad (4)$$

where

$$x=(r_+ + r_- - R)/\rho \qquad (5)$$

and

$$A=\frac{6B_e}{h\omega_e c}\left(\frac{\partial^2 b}{\partial\xi^2}-\frac{3A}{\omega_e}\frac{\partial b}{\partial\xi}\right) ,$$

$$B=\frac{6B_e}{h\omega_e c}\left[b\left(\frac{\partial\rho}{\partial\xi}\right)^2\right] , \qquad (6)$$

$$C=\frac{6B_e}{h\omega_e c}\left[2\frac{\partial b}{\partial\xi}\frac{\partial\rho}{\partial\xi}+b\left(\frac{\partial^2 b}{\partial\xi^2}-\frac{3A}{\omega_e}\frac{\partial\rho}{\partial\xi}\right)\right] .$$

Here b and ρ are the constants of the Born-Mayer-Huggins generalized potential, r is the internuclear distance of the O-H bond, and r_e is its equilibrium value. $\xi=(r-r_e)/r_e$. It can be seen that the parameter x depends upon the nature of the matrix as well as that of the impurity. On the other hand, the parameters A, B, and C only depend on the properties of the impurity. In fact, these latter quantities depend upon the change of the potential parameters with the vibrational quantum number of the impurity.

RESULTS AND DISCUSSIONS

Table I gives the values of the various parameters used in the present calculations. Table II gives the calculated shifts of the band center and compares it with the experimentally observed results. The total shift has been expressed as the sum of a red and a blue contribution, as described above. It can be seen from the table that the blue shift, corresponding to the repulsive interaction, dominated over the red shift. This is in qualitative agreement with the experimental results. For the quantitative discussion, it may be mentioned that the shifts are to be calculated under the handicap of no

TABLE I. Constants used in the calculations.

System	R[a] (Å)	α_H[b] (Å^3)	r_+[c] (Å)	r_-[c] (Å)	ρ[c] (Å)	r_e[d] (Å)	$\frac{d\mu_S}{dr_e}$[e] (Debye/Å)
KCl-OH^-	3.139	3.29	1.463	1.179	0.338	0.974	$0.143e$
KBr-OH^-	3.293	3.29	1.463	1.179	0.338	0.974	$0.143e$
KI-OH^-	3.526	3.29	1.463	1.179	0.338	0.974	$0.143e$
RbCl-OH^-	3.270	4.56	1.587	1.179	0.328	0.974	$0.143e$
NaBr-OH^-	2.981	1.57	1.170	1.179	0.330	0.974	$0.143e$
NaCl-OH^-	2.814	1.57	1.170	1.179	0.330	0.974	$0.143e$
NaF-OH^-	2.310	1.57	1.170	1.179	0.330	0.974	$0.143e$
LiF-OH^-	2.010	1.00	0.816	1.179	0.299	0.974	$0.143e$

[a] N. F Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon, London, 1940).

[b] S. Roberts, Phys. Rev. 81, 865 (1951).

[c] See Ref. 11.

[d] See Ref. 6.

[e] See Ref. 1.

precise information about the parameters A, B, and C. Their values, therefore, are to be determined from the observed values of the shifts themselves. We use the shift data of LiF, NaF, and NaCl matrices to obtain the potential parameters A, B, and C of Eq. (6).[12] These are obtained as $A = 167.304$, $B = -8.1669\times 10^{-16}$, and $C = -5.2359\times 10^{-8}$ units. The fifth column of Table II presents the shifts obtained for these and a number of other matrices with the above-mentioned values of the parameters A, B, and C. It can be seen that such a calculation does not explain the observed shifts in a consistent manner. The following reasons can be attributed to this discrepancy:

(i) The polarizability values of the cations and anions become increasingly uncertain for small interionic separations.[13] Since the parameters A, B, and C have been obtained from the observed shifts in NaF, LiF, and NaCl matrices, it is quite likely that the uncertain values of polarizability in these cases might adversely affect the values of the coefficients A, B, and C, thereby giving an incorrect shift in other systems.

(ii) Localized lattice vibrations of the surrounding lattice points can also affect the position of the band center. This effect has been found to be important in understanding the shift of the librational and tunneling levels of these impurity systems.[14, 15]

(iii) When an impurity is added to the crystal, the nearest-neighboring atoms move to new equilibrium positions, depending upon the host matrix and the nature of the impurity. Such displacements have recently been found to be of much importance in understanding the thermal conductivity[16] as well as anomalous quadrupolar broadening of the NMR line[17] in the NaCl-F^- system. The OH^- ion can be regarded in a first approximation as a distorted F^- ion, because both of these ions are isoelectronic. It is quite likely, that these same displacements of the nearest-neighbor atoms are responsible for the difference in the calculated and observed shift of

TABLE II. Calculated and observed values of the shift of the band center, when lattice distortion is not considered and when it is considered.

		Calculated shift[a]			Calculated shift[b]		
System	Observed shift of the band center (cm^{-1})	Red shift [Eq. (3)] (cm^{-1})	Blue shift [Eq. (4)] (cm^{-1})	Total shift (cm^{-1})	Red shift [Eq. (3)] (cm^{-1})	Blue shift [Eq. (4)] (cm^{-1})	Total shift (cm^{-1})
KCl-OH^-	76.5 ± 0.5[c]	−0.5	56.5	56.0	−0.6	77.6	77.0
KBr-OH^-	53.0 ± 0.5[c]	−0.4	30.2	29.8	−0.5	53.5	53.0
KI-OH^-	38.5 ± 1.0[c]	−0.2	6.7	6.5	−0.3	38.8	38.5
RbCl-OH^-	68.0 ± 0.5[c]	−0.5	52.9	52.4	−0.6	67.6	67.0
NaBr-OH^-	61.5 ± 1.0[c]	−0.3	30.9	30.6	−0.4	61.9	61.5
NaCl-OH^-	90.0 ± 0.5[c]	−0.5	90.5[d]	90.0	−0.6	90.6	90.0
NaF-OH^-	163.5[e]	−1.5	165.0[d]	163.5	−1.5	165.0	163.5
LiF-OH^-	166.5[f]	−2.0	168.5[d]	166.5	−2.0	168.5	166.5
KCl-OD^-	55.7 ± 0.5[c]	−0.4	41.1	40.8	−0.4	56.5	56.1
KBr-OD^-	39.2 ± 0.5[c]	−0.3	22.0	21.7	−0.4	38.9	38.5
NaCl-OD^-	60.2[g]	−0.4	65.9	65.5	−0.4	65.9	65.5
IiF-OD^-	118.2[h]	−1.4	122.7	121.2	−1.4	122.6	121.2

[a] When lattice distortion is not considered.

[b] When lattice distortion is considered.

[c] Reference 1.

[d] Used in back calculating the unknown constants A, B, and C of Eq. 6.

[e] M. L. Meistrich, J. Phys. Chem. Solids 29, 1119 (1968).

[f] T. G. Stoebe, J. Phys. Chem. Solids 28, 1375 (1967).

[g] Reference 3.

[h] K. Guckelsberger, K. Neumaier, and H. R. Zelsmann, Phys. Letters 31A, 397 (1970).

TABLE III. The lattice-distortion parameter required to explain the observed shift of the band center, as compared with their calculated values on the basis of Brauer's theoretical model, the Hardy's model, or obtained from other experimental studies.

	Percentage lattice-distortion parameter			
System	Required to explain the observed shift of the band center	Calculated from Brauer's model[a]	Hardy's method as modified by Klein[b]	Other experimental values
KCl-OH$^-$	−3.0	−3.0	−4.0	−2.7[c]
KBr-OH$^-$	−4.2	−5.0	−4.2	...
KI-OH$^-$	−8.2	−7.1	−3.6	...
RbCl-OH$^-$	−2.0	−2.3	−3.3	...
NaBr-OH$^-$	−5.6	−6.1	−6.2	...
NaCl-OH$^-$	−4.2	−5.2	−6.5	−4.2[d]
NaF-OH$^-$	0.0	0.0	0.0	0.0
LiF-OH$^-$	0.0	0.0	0.0	0.0

[a] See Ref. 18.

[b] J. R. Hardy, J. Phys. Chem. Solids 15, 39 (1960); Ref. 16.

[c] Obtained from the stress-dichroism experiment of H. Hartel and F. Luty (Ref. 19).

[d] Obtained from the quadrupolar-broadening study of NaCl-F$^-$ system by Y. Fukai (Ref. 17).

the band center.

For item (i), it can be said that the polarizability value affects only the red contribution of the shift. As can be seen from Table II, this is just 1% of the total shift and hence any error in the polarizability value will not affect the results much.

For item (ii), it has been observed[15] that this effect is more important for the tunneling level than for the librational level. It has been very well realized that the larger the frequency of the motional state of the impurity the smaller is the effect of the localized vibrations on it. The shift of the band center is, therefore, not expected to be much affected by this.

It is item (iii), therefore, which is held to be the chief cause of the present disagreement between the calculated and observed shifts. To evaluate this effect, one should first calculate theoretically the isotropic displacement of the nearest-neighbor atoms of the impurity, and then work out its effect on the position of the band center. However, we do it in the reverse way. Table III gives the values of the displacements needed to fit the calculated shifts to the experimental values. These are then compared to their calculated values obtained from the Brauer's theoretical method[18] and also from the other types of experiments.[17,19] It can be seen that the amount of lattice-distortion parameter needed to explain the present results agree well with those calculated on the basis of different theoretical models. The isotope effect of the shift of the band center is also suitably explained by the same value of the lattice-distortion parameter as for the hydrogenated samples and by the same value of the repulsive interaction parameters. This provides additional evidence as to the correctness of our conclusions.

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