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Molecular Model for U Centers in NaCl and KCl†

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In the harmonic approximation, the molecular model has been used to study the vibrations of U centers in NaCl and KCl where we have considered an impurity ion and its nearest neighbors moving while the rest of the crystal is at rest. For interactions we have used the rigid-ion model with short-range forces limited to nearest neighbors only. The 21×21 matrix obtained in this way has been diagonalized to get the eigenfrequencies and eigenvectors. If the U center is treated as an isotopic impurity, the resulting vibration frequencies are almost the same as those obtained from the Green's-function method using the rigid-ion model. Thus within the framework of the rigid-ion approximation, the molecular model is a good representation of the system. The maximum amplitude of the neighboring ions corresponding to the local-mode frequency is very small compared to that of the impurity. This lends further support to the molecular model. Using the experimental infrared absorption frequency due to U centers in NaCl and KCl, we have estimated the weakening of overlap forces between the impurity and its nearest neighbors.

INTRODUCTION

FOLLOWING the observation of local modes due to U centers in alkali halides by Schaefer,[1] a number of attempts have been made to predict their frequencies theoretically. Earlier calculations[2,3] based on some simple models gave reasonable agreement between theory and experiment when the U center was treated as a substitutional isotopic impurity. However, later calculations,[4,5] treating the U center as an isotopic impurity, and using the Green's-function method, showed disagreement of about 50% with experiment. In Ref. 5 an attempt has been made, on the basis of the rigid-ion model (RI) and the shell model, to estimate the change in force constants associated with the impurity.

In this note we wish to consider a molecular model (MM) for the study of U centers in NaCl and KCl in the harmonic approximation. In this model, we consider the impurity ion and its six nearest neighbors taking part in the motion while the rest of the crystal is at rest. We consider both H^- and D^- as substitutional impurities. The interaction potential is based on the RI model with central overlap forces limited to nearest neighbors only. The 21×21 matrix obtained in this way is diagonalized to get the eigenfrequencies and eigenvectors. The eigenvectors are used to compute the relative amplitude of the impurity and its nearest neighbors. The eigenfrequencies obtained by considering the U centers as isotopic impurities are compared with results of more sophisticated calculations[4] based on the Green's-function method. Experimental local-mode frequencies due to U centers in NaCl and KCl[1,6] are used to estimate the change in overlap forces around the impurity ion.

THEORY

Considering the impurity ion and its nearest neighbors in NaCl structure, the usual equations of motion can be written as

$$M_l \ddot{U}_\alpha(l) = -\sum_{\alpha' l'} \Phi_{\alpha\alpha'}(ll') U_{\alpha'}(l'), \qquad (1)$$

where M_l is the mass of the lth particle; $U_\alpha(l)$ is the αth component of the displacement from equilibrium of the lth particle ($\alpha = x, y, z$; l runs from 0 to 6), and where

$$\Phi_{\alpha\alpha'}(ll') = [\partial^2\Phi/\partial U_\alpha(l)\partial U_{\alpha'}(l')]_0,$$

with Φ being the potential energy of the whole crystal.

With solutions of the form $e^{i\omega t}$ and substituting $(M_l)^{1/2}U_\alpha(l) = W_\alpha(l)$ we get

$$\omega^2 W_\alpha(l) = \sum_{\alpha' l'} [\Phi_{\alpha\alpha'}(ll')/(M_l M_{l'})^{1/2}] W_{\alpha'}(l'). \qquad (2)$$

For the RI model the potential energy is the sum of Coulomb and repulsive parts, i.e.,

$$\Phi = \sum [e(1)e(2)/|r_{12}| + V(|r_{12}|)], \qquad (3)$$

where the summation extends over all the possible pairs of ions in the crystal, each pair being counted once only. Splitting $\Phi_{\alpha\alpha'}(ll')$ into Coulomb and repulsive parts, respectively, we get

$$D_{\alpha\alpha'}{}^c(ll') \equiv (M_l M_{l'})^{-1/2} \Phi_{\alpha\alpha'}{}^c(ll')$$
$$= (M_l M_{l'})^{-1/2} \left[\partial^2 \left\{ \sum \frac{e(1)e(2)}{|r_{12}|} \right\} \Big/ \partial U_\alpha(l) \partial U_{\alpha'}(l') \right]_0, \qquad (4)$$

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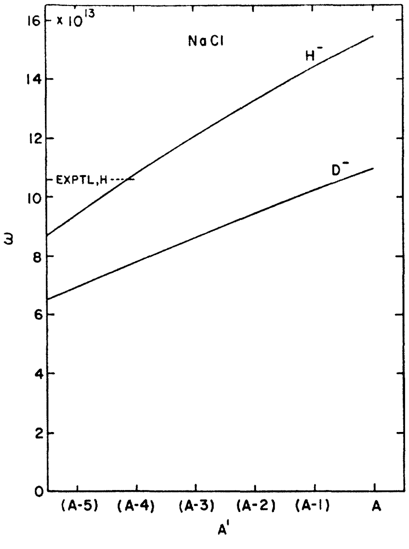

FIG. 1. Local-mode frequency ω versus A' for H$^-$ and D$^-$ in NaCl.

and

$$D_{\alpha\alpha'}{}^{R}(ll')\equiv(M_lM_{l'})^{-1/2}\Phi_{\alpha\alpha'}{}^{R}(ll')=(M_lM_{l'})^{-1/2}\times[\partial^2\{\sum V(|r_{12}|)\}/\partial U_\alpha(l)\partial U_{\alpha'}(l')]_0. \quad (5)$$

We consider the two cases: (i) $l=l'$ and (ii) $l\neq l'$ separately.

(i) $(l=l')$,

$$D_{\alpha\alpha'}{}^{c}(ll)=M_l^{-1}\left[\partial^2\left\{\sum\frac{e(1)e(2)}{|r_{12}|}\right\}\Big/\partial U_\alpha(l)\partial U_{\alpha'}(l)\right]_0.$$

Here the summation involves the interaction of the ion under consideration with the rest of the crystal. This term is zero due to the symmetry of the crystal.

(ii) $(l\neq l')$,

$$\begin{aligned}D_{\alpha\alpha'}{}^{c}(ll') &= (M_lM_{l'})^{-1/2}\left[\partial^2\left\{\frac{e(l)e(l')}{|r(ll')|}\right\}\Big/\partial U_\alpha(l)\partial U_{\alpha'}(l')\right]\\ &= -\frac{3e(l)e(l')}{r^{05}(ll')}r_\alpha{}^0(ll')r_{\alpha'}{}^0(ll')+e(l)e(l')\delta_{\alpha\alpha'}/r^{03}(ll'), \quad (6)\end{aligned}$$

where $\mathbf{r}^0(ll')$ is the equilibrium separation vector joining l and l'.

TABLE I. Local-mode frequencies (in 10^{13} rad/sec) from the molecular model (MM) and rigid-ion (RI) model and from the experiment.

Impurity ion	Impurity mass	MM ω	NaCl RI ω	Expt. ω	MM ω	KCl RI ω	Expt. ω
H$^-$	1.009	15.44	15.9	10.52	14.16	14.2	9.36
D^-	2.015	10.97	11.2	⋯	10.05	10.1	6.73
Ratio		1.41	1.42		1.41	1.41	1.39

TABLE II. Born-Mayer parameters for the impurity and the perfect crystals.

	ρ (10^{-8} cm)		λ_{+-} (10^{-9} ergs)	
	H$^-$ or D$^-$	Cl$^-$	H$^-$ or D$^-$	Cl$^-$
Na$^+$	0.581	0.328	0.062	1.47
K$^+$	0.590	0.324	0.082	3.69

(i) $(l=l')$,

$$D^{R}{}_{\alpha\alpha'}(ll)=M_l^{-1}[\partial^2\{\sum V(|r_{12}|)\}/\partial U_\alpha(l)\partial U_{\alpha'}(l)]_0. \quad (7)$$

The summation extends over the nearest neighbors only. Using Kellermann's notation,[7] we define A and B for nearest-neighbor interaction in the perfect crystal by

$$2V'\equiv2[dV/dr]_0=\{e^2/(2r_0{}^3)\}r_0B, \quad (8a)$$

and

$$2V''\equiv2[d^2V/dr^2]_0=\{e^2/(2r_0{}^3)\}A, \quad (8b)$$

where r_0 is the nearest-neighbor separation. If we use V_I for the overlap energy of the impurity with each of its nearest neighbors, we define in the same way

$$2V_I{}'\equiv2[dV_I/dr]_0=\{e^2/(2r_0{}^3)\}r_0B', \quad (9a)$$

and

$$2V_I{}''\equiv2[d^2V_I/dr^2]_0=\{e^2/(2r_0{}^3)\}A', \quad (9b)$$

we assume no relaxation around the impurity. In this case,

$$B'=B=-1.165.$$

If we label the impurity by $l=0$ and its nearest neighbors by $l=1$ to 6, their coordinates are $0(0,0,0)$, $1(r_0,0,0)$, $2(-r_0,0,0)$, $3(0,r_0,0)$, $4(0,-r_0,0)$, $5(0,0,r_0)$, and $6(0,0,-r_0)$. Using the notation mentioned above, the nonvanishing terms in Eq. 7 can be written as

$$D_{\alpha\alpha}{}^{R}(ll)=M_l^{-1}\sum[V''(\text{or }V_I{}'')r_{\alpha12}{}^{02}/r_0{}^2+V'(\text{or }V_I{}')(1/|r_0|-r_{\alpha12}{}^{02}/r_0{}^3)]. \quad (10)$$

After summation

$$\begin{aligned}D_{\alpha\alpha}{}^{R}(00)&=M_0{}^{-1}\{e^2/(2V_a)\}(2A'+4B),\\ D_{xx}{}^{R}(11)&=D_{xx}{}^{R}(22)=D_{yy}{}^{R}(33)=D_{yy}{}^{R}(44)\\ &=D_{zz}{}^{R}(55)=D_{zz}{}^{R}(66)\\ &=(A+A'+4B)M_1{}^{-1}\{e^2/(2V_a)\}, \quad (11)\end{aligned}$$

and all other

$$D_{\alpha\alpha}{}^{R}(ll)=(2A+4B)M^{-1}{}_l\{e^2/(2V_a)\},$$

where $V_a\equiv2r_0{}^3=$volume of unit cell.
(ii) $(l\neq l')$,

$$D_{\alpha\alpha'}{}^{R}(ll')=+(M_lM_{l'})^{-1/2}\times[\partial^2V(|r(ll')|)/\partial U_\alpha(l)\partial U_{\alpha'}(l')]_0.$$

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The nonvanishing terms from this expression are given by

$$D_{\alpha\alpha}{}^{R}(0l)=-(M_0M_l)^{-1/2}\times[(A'-B)r_\alpha{}^{02}(0l)/r_0{}^2+B]e^2/(2V_a). \quad (12)$$

Adding the Coulomb and repulsive parts, we get a 21×21 real and symmetric matrix. Diagonalization of this matrix yields the eigenvalues and an orthonormal set of eigenvectors. The eigenvectors corresponding to a mode ω_i satisfy the equation

$$\omega_i{}^2W_\alpha(l)=\sum_{\alpha'l'}D_{\alpha\alpha'}(ll')W_{\alpha'}(l'), \quad (13)$$

and the amplitude of an ion in this mode is

$$U_\alpha(l)=W_\alpha(l)/(M_l)^{1/2}. \quad (14)$$

RESULTS AND DISCUSSION

The crystal data required in these calculations are r_0 and the compressibility which are given in Ref. 8. The value of A obtained from r_0 and the compressibility is 9.988 for NaCl and 11.304 for KCl.

With H^- and D^- as impurities in NaCl and KCl the eigenvalues and eigenvectors for a given A' were obtained by diagonalizing the 21×21 matrix. The largest eigenvalue is triply degenerate and corresponds to the local-mode frequency. The rest of the eigenfrequencies lie below the maximum frequency of the host crystal, and the amplitude of the impurity ion in these modes is either zero or negligible compared to that of its nearest neighbors. The local-mode frequency was computed as a function of A' and the results are shown in Figs. 1 and 2. In the isotopic approximation for U centers, present results are compared with those of the RI model using the Green's-function method[4] in Table I. The two results are in agreement.

In order to estimate the change in overlap forces we use the experimental values[1,6] of the local-mode frequencies due to U centers in NaCl and KCl to get the appropriate values of A' from Figs. 1 and 2. The value of A' for NaCl is 5.64. Its value for KCl is 6.2, which is almost the same both for KCl(H) and KCl(D), as it should be. The estimate of overlap forces between the impurity and its nearest neighbors is obtained by using the Eqs. (9a) and (9b) to fit the Born-Mayer potential $V_I=\lambda_{+-}\exp(-r/\rho)$ to these values of A'. The results are compared with those of the perfect crystal[9] in Table II.

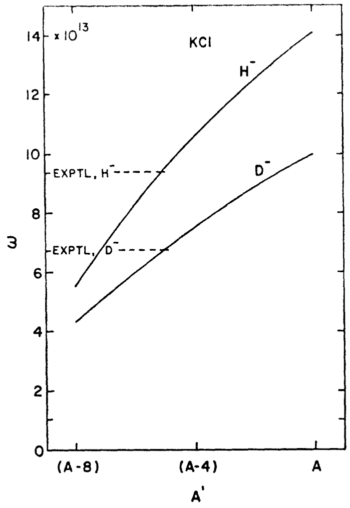

FIG. 2. Local-mode frequency ω versus A' for H^- and D^- in KCl.

TABLE III. Ratio of the maximum amplitude of the nearest neighbor to that of the impurity corresponding to the local-mode frequency.

	H^-	D^-
NaCl	0.019	0.045
KCl	0.011	0.022

Using Eq. (14) we have computed the amplitude of the nearest neighbors relative to that of the impurity. The results corresponding to the experimental local-mode frequencies are listed in Table III.

We see that the present results for the local-mode frequencies are in agreement with the Green's-function calculation in the isotopic approximation. Thus the molecular model is very good so far as U centers are concerned. The very small relative amplitude of the nearest neighbors further supports this model.

Since we have used the RI model, any detailed calculations of overlap forces would not mean much. Still, a considerable softening of the overlap forces is indicated by large decrease in the second derivative of the overlap interactions. Thus we get a rough estimate of the overlap interaction of the impurity with the positive ion of the host crystal in terms of simple Born-Mayer parameters.

It is clear from the present calculations that in order to study the localized modes due to impurities which are quite light as compared to host atoms, one doesn't need sophisticated techniques like the Green's-function method. As we have seen, the molecular model is equally good. But what is really important is the model of the impurity itself and its surroundings. Any realistic calculations should take into account, if possible, relaxation around the impurity, anharmonicity, dipole-dipole interactions, change in polarizability, and change in overlap forces, and hence the change in short-range deformations.

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