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Local-Mode Frequency Due to Light Substitutional Impurities in Alkali-Halide Crystals: Application to the U Center

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The lattice dynamics in harmonic approximation of ionic crystals with very light substitutional impurities is studied in the framework of rigid-ion and shell models. A vibrational model for the lattice defect which takes into account not only the change of mass, but also the changes of the overlap force constant, electronic polarizability and shell charge, is considered and applied for the evaluation of the local-mode frequencies of the U center in NaCl, KCl, and KI crystals. It is shown that changes of electronic polarizability and shell charge give rise to a further local change of force constant for the core motion in the shell model. A simple local change of mass is found to be quite inadequate for accounting for the influence of the U center on the lattice dynamics. Instead, fairly good agreement with the experimental results on the impurity-induced infrared absorption is found if the hydrogen ion in alkali halides is considered as belonging to the halogen family with regard to the overlap potential and electronic polarizability.

1. INTRODUCTION

THE early papers[1,2] dealing with the influence of single defects on the lattice dynamics of ionic crystals are based on the Einstein model or on the Born–von Kármánn model in diatomic simple cubic lattices with nearest neighbor (n.n.) interaction. Satisfactory agreement has been found between the theoretical and experimental data on the local-mode frequency of U centers (H^- substitutional ions) in alkali halides, by considering the impurity as a pure mass defect. However, Zavt[3] noted that this agreement becomes quite unsatisfactory if the lattice dynamics of such ionic crystals is accounted for by the rigid-ion[4,5] model.

In the present paper,[6] this disagreement is interpreted in terms of a more general vibrational model for the U center (see Sec. 2), which takes into account both the change of mass and the change of coupling between the defect and its nearest neighbors. The secular equation of the imperfect crystal is analyzed in the symmetry coordinates relative to the impurity and its nearest neighbors: it is shown that for local modes of very high frequency only the change of force constant at the impurity site may be taken into account. Moreover, not only the rigid ion but also the shell model[7] have been considered for the lattice dynamics.

In the framework of the rigid-ion model (Sec. 2a), the impurity is thought to cause, besides the change of mass, a change in its n.n. overlap force constant; in the shell model (Sec. 2b), the changes of electronic polarizability, shell charge, and n.n. overlap force constant due to the impurity are considered, and the effects caused by the electronic polarizability of the ions on the imperfect lattice dynamics are accounted for. For the sake of simplicity only the negative ions are allowed to become polarized during the lattice vibrations. Actually, the shell model with polarizable negative ions may be used for a few alkali-halide crystals; but it has the advantage that it involves only two more parameters than the rigid-ion model.

The above theoretical frameworks are applied to the U center (Sec. 3); the numerical computations are performed for NaCl, KCl, and KI host crystals at room temperature, and the local-mode frequency is evaluated in both models as a function of the parameters entering the vibrational definition of the center itself. Kellermann's[5] tabulation is used for the Coulomb coupling coefficients and the overlap interaction is considered in the n.n. approximation.

In the same section, the H^- ionic radius in alkali-halide crystals is evaluated on the basis of the Huggins-Mayer[8] form for the overlap potential.

Finally, the theoretical results and the limitations inherent in the present approach are discussed in Sec. 4.

2. LATTICE VIBRATION THEORY IN THE PRESENCE OF A SUBSTITUTIONAL IMPURITY

In the framework of the adiabatic and harmonic approximation, let $\Lambda(\omega^2)$ be the perturbation on the dynamical matrix L of the perfect crystal, representing the change of coupling coefficients and the change of ionic mass due to the substituted impurity ion. The normal modes equation for the vibrational amplitudes ψ in the perturbed lattice reads

$$[L+\Lambda(\omega^2)-\omega^2 I]\psi=0, \tag{1a}$$

and the frequencies ω of the local modes are the roots of

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[1] H. Rosenstock and C. Klick, Phys. Rev. **119**, 1198 (1960).

[2] R. Wallis and A. Maradudin, Progr. Theoret. Phys. (Kyoto) **24**, 1055 (1960).

[3] G. S. Zavt, Fiz. Tverd. Tela **5**, 1086 (1963) [English transl.: Soviet Phys.—Solid State **5**, 793 (1963)].

[4] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954).

[5] E. W. Kellermann, Phil. Trans. Roy. Soc. London **238**, 513 (1940).

[6] After this work was completed, a paper on the same topics appeared [S. S. Jaswal and D. J. Montgomery, Phys. Rev. **135**, A125 (1964)]. There the authors came to the conclusion that it is not sufficient to treat U centers in KCl and NaCl as pure mass defects coupled to the lattice, as suggested earlier by Zavt; their conclusion gives further support to the present more comprehensive vibrational model for the U center.

[7] A. D. B. Woods, W. Cochran, and B. N. Brockhouse, Phys. Rev. **119**, 980 (1960).

[8] F. G. Fumi and M. P. Tosi, Phys. Chem. Solids **25**, 31 (1964).

the secular equation[9,10]

$$\det\{I+(L-\omega^2)^{-1}\Lambda(\omega^2)\}=0. \tag{1b}$$

In the present work, we are interested in the vibrational frequencies due to a very light substitutional impurity. Therefore, the above secular equation is studied in a frequency region far higher than the maximum frequency ω_L of the perfect lattice.

If the impurity has the same charge as the substituted ion, we consider that the perturbation on the force constants involve only the impurity and its six nearest neighbors. Denoting the dimensionless change of force constant at the impurity site by λ and the fractional change of mass due to the impurity (m') with respect to the regular ion (m) by $-\epsilon=(m'-m)/m$, in NaCl crystal structure the nonvanishing elements of $\Lambda(\omega^2)$ in the lattice vectors representation are

$$\frac{e^2}{mv}\lambda\left[\begin{array}{c|cccccc|c}
(0) & (1) & (2) & (3) & (4) & (5) & (6) & \\
\begin{matrix}1&0&0\\0&1&0\\0&0&1\end{matrix} & \begin{matrix}-\frac{1}{2}\chi^{1/2}&0&0\\0&0&0\\0&0&0\end{matrix} & \begin{matrix}-\frac{1}{2}\chi^{1/2}&0&0\\0&0&0\\0&0&0\end{matrix} & \begin{matrix}0&0&0\\0&-\frac{1}{2}\chi^{1/2}&0\\0&0&0\end{matrix} & \begin{matrix}0&0&0\\0&-\frac{1}{2}\chi^{1/2}&0\\0&0&0\end{matrix} & \begin{matrix}0&0&0\\0&0&0\\0&0&-\frac{1}{2}\chi^{1/2}\end{matrix} & \begin{matrix}0&0&0\\0&0&0\\0&0&-\frac{1}{2}{}^{1/2}\chi\end{matrix} & (0) \\
\hline
\begin{matrix}-\frac{1}{2}\chi^{1/2}&0&0\\0&0&0\\0&0&0\end{matrix} & \begin{matrix}\frac{1}{2}\chi&0&0\\0&0&0\\0&0&0\end{matrix} & 0 & 0 & 0 & 0 & 0 & (1) \\
\begin{matrix}-\frac{1}{2}\chi^{1/2}&0&0\\0&0&0\\0&0&0\end{matrix} & 0 & \begin{matrix}\frac{1}{2}\chi&0&0\\0&0&0\\0&0&0\end{matrix} & 0 & 0 & 0 & 0 & (2) \\
\begin{matrix}0&0&0\\0&-\frac{1}{2}\chi^{1/2}&0\\0&0&0\end{matrix} & 0 & 0 & \begin{matrix}0&0&0\\0&\frac{1}{2}\chi&0\\0&0&0\end{matrix} & 0 & 0 & 0 & (3) \\
\begin{matrix}0&0&0\\0&-\frac{1}{2}\chi^{1/2}&0\\0&0&0\end{matrix} & 0 & 0 & 0 & \begin{matrix}0&0&0\\0&\frac{1}{2}\chi&0\\0&0&0\end{matrix} & 0 & 0 & (4) \\
\begin{matrix}0&0&0\\0&0&0\\0&0&-\frac{1}{2}\chi^{1/2}\end{matrix} & 0 & 0 & 0 & 0 & \begin{matrix}0&0&0\\0&0&0\\0&0&\frac{1}{2}\chi\end{matrix} & 0 & (5) \\
\begin{matrix}0&0&0\\0&0&0\\0&0&-\frac{1}{2}\chi^{1/2}\end{matrix} & 0 & 0 & 0 & 0 & 0 & \begin{matrix}0&0&0\\0&0&0\\0&0&\frac{1}{2}\chi\end{matrix} & (6)
\end{array}\right]$$

$$+\epsilon\omega^2\left[\begin{array}{c|cccccc|c}
(0) & (1) & (2) & (3) & (4) & (5) & (6) & \\
\begin{matrix}1&0&0\\0&1&0\\0&0&1\end{matrix} & & & & 0 & & & (0) \\
\hline
 & & & & & & & (1) \\
 & & & & & & & (2) \\
0 & & & & 0 & & & (3), \\
 & & & & & & & (4) \\
 & & & & & & & (5) \\
 & & & & & & & (6)
\end{array}\right] \tag{2a}$$

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[9] I. M. Lifschitz, Suppl. Nuovo Cimento 4, 716 (1956); G. F. Nardelli, *Rendiconti Scuola Intern. di Fisica "E. Fermi," XVIII Corso* (Pergamon Press Ltd., Oxford, 1963).

[10] E. W. Montroll and P. B. Potts, Phys. Rev. **100**, 525 (1955).

where v is the volume of the unit cell and e the modulus of the electron charge; χ denotes the ratio between m and the mass of the other ion in the unit cell. Index 0 labels the impurity site, and indices 1–6 the six nearest neighbors (ions labeled by 1, 3, and 5 lie, respectively, on the positive x, y, and z crystallographic axis). The perturbation on the potential energy matrix considered in this model is consistent with the condition[11] which follows from the invariance of the force on an atom against a rigid-body translational of the crystal.

When expression (2a) is analyzed into the irreducible representation of the full cubic point group, the displacements of the impurity ion are found to be involved only in the Γ_{15} representation, which is contained three times in $\Lambda(\omega^2)$. If by $j=1, 2, 3$ we label the oriented symmetry coordinate corresponding to every one of these representations, in this three dimensional subspace, expression (2a) becomes

$$\Lambda^{(\Gamma_{15})}(\omega^2)=\frac{e^2}{mv}\lambda\begin{bmatrix} 1 & -(\chi/2)^{1/2} & 0 \\ -(\chi/2)^{1/2} & \chi/2 & 0 \\ 0 & 0 & 0 \end{bmatrix} +\epsilon\omega^2\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad (2b)$$

and the local-mode frequencies due to very light substitutional impurities will be the roots of the projection of the secular equation (1b) in the same space.

For defects involving a strong change of mass and moderate change of force constant, the local-mode frequency ω_{loc} is expected to fall well outside the vibrational continuum of the perfect crystal; then, if only expressions which behave like $1/\omega^2$ are retained in the terms involving the change of force constant, the projected secular equation can be written

$$1+[(L-\omega^2)^{-1}]_{11}{}^{(\Gamma_{15})}\epsilon\omega^2-(1/\omega^2)(e^2/mv)\lambda=0, \quad (3a)$$

which, to terms of the order $(e^2/mv)(\omega_L/\omega_{\text{loc}}{}^2)^2$ is equivalent to

$$1+[(L-\omega^2)^{-1}]_{11}{}^{(\Gamma_{15})}((e^2/mv)\lambda+\epsilon\omega^2)=0. \quad (3b)$$

Since Γ_{15} is a three-dimensional representation, the root of (3b) is threefold degenerate.

Let $\mathbf{x}_{l,k}$ be the equilibrium position of the k-type ion in lth unit cell (we take $k=1$ to denote the positive ion), and let the substitutional negative impurity be placed in the cell $l=0$. Since in this paper applications are made to the U center, in what follows the impurity is placed at the negative site; the theory, however, can be developed in a quite analogous way for very light substitutional positive impurities. The (1,1) element of $(L-\omega^2)^{-1}$ in the subspace of the symmetry coordinates defined above turns out to be the (x,x) Cartesian component of the (0,2; 0,2) element of the same matrix in the lattice-vector representation; therefore the secular equation (3b) is found to be exactly equivalent to the third-order determinantal equation

$$\det\{\mathbf{1}+(L-\omega^2)_{02,02}{}^{-1}((e^2/m_2v)\lambda+\epsilon\omega^2)\}=0, \quad (4)$$

when one bears in mind that the cubic point symmetries of the lattice require $(L-\omega^2)_{02,02}{}^{-1}$ to be proportional to the unit tensor, here denoted by $\mathbf{1}$.

The approximation involved in deducing (4) is equivalent to disregarding matrix elements of $\Lambda(\omega^2)$ which do not correspond to the impurity lattice site, i.e., to the assumption

$$\Lambda(\omega^2)=((e^2/m_2v)\lambda+\epsilon\omega^2)\Delta \quad (2c)$$

for the perturbation $\Lambda(\omega^2)$. Here Δ is the $6N\times 6N$ matrix whose elements are those of the unit tensor if the lattice indices both correspond to the impurity site, and zero otherwise.

In what follows, $\Lambda(\omega^2)$ has the expression (2c) even if the frequency-independent part of this expression does not satisfy the condition which follows from the invariance of the force on an atom against a rigid-body translation of the crystal. From the above considerations, it appears that the farther away the local-mode frequency lies, the more the lack of the above translational symmetry can be ignored in the expression (2c) for the perturbation.

The roots of the secular equation (4) or (3b) are easily found once we know the values which are assumed by $(L-\omega^2)_{02,02}{}^{-1}$ as a function of ω^2.

The dimensionless change of force constant λ is a function of the parameters characterizing the physical properties of the impurity (the mass apart); the choice of such parameters will be discussed in the following sections.

a. Rigid-Ion Model

The dynamical matrix L_0 of the perfect rigid-ion lattice is[5,7]

$$\mathbf{L}_0(1,1)=(1/m_1)\mathbf{R}_0+Z^2(1/m_1)\mathbf{C}(1,1), \quad (5a)$$

$$\mathbf{L}_0(2,2)=(1/m_2)\mathbf{R}_0+Z^2(1/m_2)\mathbf{C}(2,2), \quad (5b)$$

$$\mathbf{L}_0(1,2)=\mathbf{L}_0(2,1)^\dagger =(1/m_1m_2)^{1/2}\mathbf{R}+Z^2(1/m_1m_2)^{1/2}\mathbf{C}(1,2), \quad (5c)$$

where $\mathbf{R}_0=\mathbf{R}(1,1)=\mathbf{R}(2,2)$, $\mathbf{R}=\mathbf{R}(1,2)=\mathbf{R}(2,1)$; $\mathbf{C}(1,1)=\mathbf{C}(2,2)$ and $\mathbf{C}(1,2)=\mathbf{C}(2,1)$. $\mathbf{C}(k,k')$ and $\mathbf{R}(k,k')$ are $3N\times 3N$ real matrices (N being the number of unit cells) corresponding, respectively, to the electrostatic and the overlap interactions between k and k'-type ions in the lattice. m_1 and m_2 are the masses of the regular ions and Ze is the charge of the positive ion.

In the wave vectors representation of wave vector $\mathbf{q}$, the coupling coefficients of the electrostatic interaction

$$\mathbf{C}(\mathbf{q};1,1)=\mathbf{C}(\mathbf{q};2,2)=(e^2/v)\mathbf{C}_1(\mathbf{q}),$$
$$-\mathbf{C}(\mathbf{q};1,2)=(e^2/v)\mathbf{C}_2(\mathbf{q}),$$

have been evaluated by Kellermann,[5] and the coupling coefficients of the overlap interaction in the n.n.

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[11] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, Oxford, 1956), p. 15.

approximation are

$$\begin{aligned}&\mathbf{R}_0(\mathbf{q})=(e^2/v)(A+2B)\mathbf{1}\,,\\&R_{xy}(\mathbf{q})=0\,,\ \text{etc.},\\&R_{xx}(\mathbf{q})=(e^2/v)[A\ \cos r_0q_x+B(\cos r_0q_y+\cos r_0q_z)]\,,\ \text{etc.}\end{aligned}\tag{6}$$

The dimensionless constants A and B are defined as follows:

$$\begin{aligned}\frac{1}{r_0}\left[\frac{d}{dr}\varphi(r)\right]_{r=r_0}&=\left(\frac{e^2}{2v}\right)B\,,\\\left[\frac{d^2}{dr^2}\varphi(r)\right]_{r=r_0}&=\left(\frac{e^2}{2v}\right)A\,,\end{aligned}\tag{7}$$

and are fixed by the static equilibrium condition of the lattice[12] and by one of the elastic constants.

$\varphi(r)$ is the overlap potential between the halogen ion and a neighboring alkali ion at the distance r in the crystal, and r_0 is the equilibrium n.n. distance in the perfect crystal.

Since the substitutional impurity has the same charge as the regular ion, the frequency-independent term of $\Lambda(\omega^2)$ [in the rigid-ion model this term will be indicated by $\Lambda_0\equiv(e^2/m_2v)\lambda_0\Delta$] represents the change of the overlap forces at the negative lattice site $l=0$, $k=2$, i.e., the change $\delta\mathbf{R}_0$ of $\mathbf{R}_0$. It is worthwhile to note that an elastic relaxation around the impurity makes no other contributions to λ_0 through the Coulomb interaction, owing to the cubic symmetry of the relaxation itself. If new constants $\tilde{A}$ and $\tilde{B}$ corresponding to the impurity are defined by (7) at $r=\tilde{r}_0$ (the new n.n. distance from the defect) by merely substituting $\varphi(r)$ for $\tilde{\varphi}(r)$ (the new overlap potential), then λ_0 turns out to be

$$\lambda_0=[\tilde{A}-A+2(\tilde{B}-B)]=\delta(A+2B)\,,\tag{8}$$

when only n.n. interactions are taken into account.

In finding the roots of the secular equation (4), the main difficulty lies in the evaluation of the 3×3 submatrix $(L_0-\omega^2)_{02,02}{}^{-1}$ of $(L_0-\omega^2)^{-1}$.

By writing this submatrix as the Brillouin-zone integral:

$$(L_0-\omega^2)_{02,02}{}^{-1}=\frac{v}{(2\pi)^3}\int_{\text{B.Z.}}d\mathbf{q}\times\left\{\begin{bmatrix}\mathbf{L}_0(\mathbf{q};1{,}1)-\omega^2 & \mathbf{L}_0(\mathbf{q};1{,}2)\\ \mathbf{L}_0(\mathbf{q};2{,}1) & \mathbf{L}_0(\mathbf{q};2{,}2)-\omega^2\end{bmatrix}^{-1}\right\}_{2,2},\tag{9}$$

the inversion of the matrix in the integrand and the Brillouin-zone integration can be easily performed by means of an electronic computer, and $(L_0-\omega^2)_{02,02}{}^{-1}$ can be tabulated for a suitable range of ω^2 values.

b. Shell Model

Cochran's[7] shell model includes central short-range forces between nearest neighbors and Coulomb forces between all the ions, and allows the negative ion to become polarized during the lattice vibrations. According to Cochran, the dynamical matrix L of the perfect lattice, having eliminated the shell motion from the coupled core-shell system of equations, may be written as

$$\begin{aligned}\mathbf{L}(1{,}1)&=(1/m_1)\{[\mathbf{R}_0+Z^2(e^2/v)\mathbf{C}_1]-[\mathbf{R}+Z\mathbf{Y}(e^2/v)\mathbf{C}_2][\mathbf{R}_0+\mathbf{K}+\mathbf{Y}^2(e^2/v)\mathbf{C}_1]^{-1}[\mathbf{R}+Z\mathbf{Y}(e^2/v)\mathbf{C}_2]^\dagger\}\,,\\\mathbf{L}(2{,}2)&=(1/m_2)\{[\mathbf{R}_0+Z^2(e^2/v)\mathbf{C}_1]-[\mathbf{R}_0-Z\mathbf{Y}(e^2/v)\mathbf{C}_1][\mathbf{R}_0+\mathbf{K}+\mathbf{Y}^2(e^2/v)\mathbf{C}_1]^{-1}[\mathbf{R}_0-Z\mathbf{Y}(e^2/v)\mathbf{C}_1]^\dagger\}\,,\\\mathbf{L}(1{,}2)&=\mathbf{L}(2{,}1)^\dagger=(1/m_1m_2)^{1/2}\{[\mathbf{R}-Z^2(e^2/v)\mathbf{C}_2]\\&\qquad-[\mathbf{R}+Z\mathbf{Y}(e^2/v)\mathbf{C}_2][\mathbf{R}_0+\mathbf{K}+\mathbf{Y}^2(e^2/v)\mathbf{C}_1]^{-1}[\mathbf{R}_0-Z\mathbf{Y}(e^2/v)\mathbf{C}_1]^\dagger\}\,.\end{aligned}\tag{10}$$

Here $\mathbf{Y}e=ye\mathbf{I}$ and $\mathbf{K}=(e^2/v)\kappa\mathbf{I}$, where ye, $(y<0)$, is the shell charge of the negative ion and $(e^2/v)\kappa$ is the force constant isotropically coupling the shell to the core of the negative ion. The other symbols have the same meaning as in the previous section: $\mathbf{R}_0$ and $\mathbf{R}$ here represent the matrices of the coupling coefficients for the overlap interaction between the shells of negative and the cores of positive ions; $\mathbf{I}$ is the unit $3N\times3N$ matrix.

The new parameters y and κ appearing in (10) are determined by the dielectric constants ϵ_0 and ϵ_∞.[7] The polarizability of the negative ions in the lattice is related to the above three parameters by

$$\alpha=vy^2/(A+2B+\kappa)\,.$$

Note that the value of α, when deduced from the above crystal constants, actually represents the sum $\alpha_1+\alpha_2$ of the polarizabilities of both ions in the unit cell (see Table II). For consistency, in the scheme of polarizable negative ions, it is understood that y includes a contribution from the positive ion; the relation between y and the true shell charge y_2 of the negative ions turns out to be $y=y_2(\alpha/\alpha_2)^{1/2}$.

In the shell model, the substitutional impurity affects not only the overlap forces but also the shell charge ye and the core-shell force-constant $(e^2/v)\kappa$ at the impurity lattice site. Then, the frequency-independent term of $\Lambda(\omega^2)$ splits into two terms, the first having the same meaning as that in Sec. 2a, and the second arising from the change of electronic polarizability of the substituted ion. One finds

$$\Lambda(\omega^2)=\Lambda_0+\Lambda_{\text{pol}}+\epsilon\omega^2\Delta\,.\tag{11}$$

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[12] For the static lattice to be in equilibrium $B=-(2/3)a_MZ^2=-1.165Z^2$, where a_M is the Madelung constant.

Owing to the approximation made in (2c), one needs to know only the 3×3 submatrix $\mathbf{A}_{\text{pol}}(0,2;0,2)$ at the impurity lattice site. The $3N\times 3N$ matrix $\mathbf{A}_{\text{pol}}(2,2)$ can be deduced from the second term in the expression (10) of $\mathbf{L}(2,2)$ by replacing $\mathbf{R}_0$, $\mathbf{Y}$, and $\mathbf{K}$, respectively, with $\mathbf{R}_0+\delta\mathbf{R}_0$, $\mathbf{Y}+\delta\mathbf{Y}$, and $\mathbf{K}+\delta\mathbf{K}$ and then subtracting the unperturbed term. Disregarding any effect due to the change in the state of polarization which arises from the elastic relaxation around the impurity, if we let

$$\begin{aligned}\boldsymbol{\eta}&=(v/e^2)\mathbf{R}_0-Z\mathbf{Y}\mathbf{C}_1=(A+2B)\mathbf{I}-Zy\mathbf{C}_1\,,\\ \boldsymbol{\gamma}&=(v/e^2)(\mathbf{R}_0+\mathbf{K})+\mathbf{Y}^2\mathbf{C}_1=[(A+2B)+\kappa]\mathbf{I}+y^2\mathbf{C}_1\,,\\ \delta\boldsymbol{\eta}&=(v/e^2)\delta\mathbf{R}_0-Z\mathbf{C}_1\delta\mathbf{Y}=\delta(A+2B)\boldsymbol{\Delta}-Z\delta y\mathbf{C}_1\boldsymbol{\Delta}\,,\\ \delta\boldsymbol{\gamma}&=(v/e^2)\delta(\mathbf{R}_0+\mathbf{K})+\delta\mathbf{Y}\mathbf{C}_1\mathbf{Y}+\mathbf{Y}\mathbf{C}_1\delta\mathbf{Y}\\ &=[\delta(A+2B)+\delta\kappa]\boldsymbol{\Delta}+y\,\delta y(\boldsymbol{\Delta}\mathbf{C}_1+\mathbf{C}_1\boldsymbol{\Delta})\,,\end{aligned}\tag{12}$$

we obtain

$$\mathbf{A}_{\text{pol}}(2,2)=-(e^2/m_2v)[(\boldsymbol{\eta}+\delta\boldsymbol{\eta})(\boldsymbol{\gamma}+\delta\boldsymbol{\gamma})^{-1}\times(\boldsymbol{\eta}+\delta\boldsymbol{\eta})^{\dagger}-\boldsymbol{\eta}\boldsymbol{\gamma}^{-1}\boldsymbol{\eta}^{\dagger}].\tag{13}$$

The main difficulty for the evaluation of the above expression lies in the inversion of the $3N\times 3N$ matrix $(\boldsymbol{\gamma}+\delta\boldsymbol{\gamma})$. One may use a series expansion in power of $\delta\boldsymbol{\gamma}$:

$$(\boldsymbol{\gamma}+\delta\boldsymbol{\gamma})^{-1}=\boldsymbol{\gamma}^{-1}-\boldsymbol{\gamma}^{-1}\mathbf{G}_{\delta\gamma}\boldsymbol{\gamma}^{-1}\,,\tag{14a}$$

where

$$\mathbf{G}_{\delta\gamma}=\sum_{n=0}^{\infty}(-1)^n\delta\boldsymbol{\gamma}[\boldsymbol{\gamma}^{-1}\delta\boldsymbol{\gamma}]^n=\sum_{n=0}^{\infty}(-1)^n\mathbf{G}_{\delta\gamma}{}^{(n)}.\tag{14b}$$

Taking into account expression (12) for $\delta\boldsymbol{\gamma}$, the sum of the infinite series (14b) can be carried out working with the wave vectors representation. Defining two dimensionless parameters λ_1 and λ_2 by

$$\begin{aligned}\lambda_1&\equiv\delta(A+2B)+\delta\kappa=v(y+\delta y)^2/(\alpha+\delta\alpha)-vy^2/\alpha\,,\\ \lambda_2&\equiv y\,\delta y\,,\end{aligned}\tag{15}$$

the matrix elements of $\delta\boldsymbol{\gamma}$ are

$$\delta\boldsymbol{\gamma}(\mathbf{q}_1,\mathbf{q}_2)\equiv\mathbf{G}_{\delta\gamma}{}^{(0)}(\mathbf{q}_1,\mathbf{q}_2)=(1/N)\exp[i(\mathbf{q}_2-\mathbf{q}_1)\cdot\mathbf{x}_{02}]\times\{\lambda_1\mathbf{1}+\lambda_2[\mathbf{C}_1(\mathbf{q}_1)+\mathbf{C}_1(\mathbf{q}_2)]\}\tag{16a}$$

and those of $\mathbf{G}_{\delta\gamma}{}^{(n)}(\mathbf{q}_1,\mathbf{q}_2)$ for $n\neq 0$ are

$$\mathbf{G}_{\delta\gamma}{}^{(n)}(\mathbf{q}_1,\mathbf{q}_2)=(1/N)\exp[i(\mathbf{q}_2-\mathbf{q}_1)\cdot\mathbf{x}_{02}]\times\sum_{j=1}^{4}h_j{}^{(n)}(\lambda_1,\lambda_2)\mathbf{b}_j(\mathbf{q}_1,\mathbf{q}_2).\tag{16b}$$

$\mathbf{b}_j(\mathbf{q}_1,\mathbf{q}_2)$, $(j=1, 2, 3, 4)$, are the four 3×3 matrices

$$\begin{aligned}\mathbf{b}_1(\mathbf{q}_1,\mathbf{q}_2)&\equiv\mathbf{1}\,, & \mathbf{b}_2(\mathbf{q}_1,\mathbf{q}_2)&\equiv\mathbf{C}_1(\mathbf{q}_1)\,,\\ \mathbf{b}_3(\mathbf{q}_1,\mathbf{q}_2)&\equiv\mathbf{C}_1(\mathbf{q}_2)\,, & \mathbf{b}_4(\mathbf{q}_1,\mathbf{q}_2)&\equiv\mathbf{C}_1(\mathbf{q}_1)\cdot\mathbf{C}_1(\mathbf{q}_2)\end{aligned}$$

and for any value of the index n, the four coefficients $h_j{}^{(n)}$ depend only on λ_1 and λ_2 and are related by

$$h_j{}^{(n)}(\lambda_1,\lambda_2)=\sum_{i=1}^{4}F_{ji}(\lambda_1,\lambda_2)h_i{}^{(n-2)}(\lambda_1,\lambda_2)\tag{17a}$$

to the four coefficients corresponding to $(n-2)$. F_{ij}, $h_j{}^{(0)}$ and $h_j{}^{(1)}$ may be easily deduced from the explicit expression of the first three terms of the expansion (14b); one finds

$$F=\begin{bmatrix} f_1^2 & f_1f_2 & f_1f_2 & f_2^2\\ f_1f_3 & f_1f_4 & f_2f_3 & f_2f_4\\ f_1f_3 & f_2f_3 & f_1f_4 & f_2f_4\\ f_3^2 & f_3f_4 & f_3f_4 & f_4^2\end{bmatrix};$$

$$h_1{}^{(0)}=\lambda_1\,,\quad h_2{}^{(0)}=h_3{}^{(0)}=\lambda_2\,,\quad\text{and}\quad h_4{}^{(0)}=0;\tag{17b}$$
$$h_1{}^{(1)}=\lambda_1f_1+\lambda_2f_2\,,\quad h_2{}^{(1)}=h_3{}^{(1)}=\lambda_2f_1\,,\quad\text{and}\quad h_4{}^{(1)}=\lambda_2f_3.$$

Here

$$\begin{aligned}f_1&\equiv(\lambda_1J_0+\lambda_2J_1)\,,\\ f_2&\equiv(\lambda_1J_0+\lambda_2J_2)\,,\\ f_3&\equiv\lambda_2J_0\,,\quad\text{and}\\ f_4&\equiv\lambda_2J_1\,,\end{aligned}\tag{18}$$

where J_0, J_1, and J_2 are the following Brillouin-zone integrals:

$$\begin{aligned}J_0\mathbf{1}&\equiv(v/(2\pi)^3)\int_{\text{B.Z.}}d\mathbf{q}\boldsymbol{\gamma}^{-1}(\mathbf{q})\,,\\ J_1\mathbf{1}&\equiv(v/(2\pi)^3)\int_{\text{B.Z.}}d\mathbf{q}\mathbf{C}_1(\mathbf{q})\cdot\boldsymbol{\gamma}^{-1}(\mathbf{q})\\ &=y^{-2}[1-(A+2B+\kappa)J_0]\mathbf{1}\,,\\ J_2\mathbf{1}&\equiv(v/(2\pi)^3)\int_{\text{B.Z.}}d\mathbf{q}\mathbf{C}_1{}^{\dagger}(\mathbf{q})\cdot\boldsymbol{\gamma}^{-1}(\mathbf{q})\cdot\mathbf{C}_1(\mathbf{q})\\ &=y^{-2}(A+2B+\kappa)J_1\mathbf{1}.\end{aligned}\tag{19}$$

In (19) we have borne in mind that the cubic point symmetries of the lattice force the above integrals to be proportional to the unit tensor.

Inserting the solution of the recurrent equation (17a) in the right-hand member of (16b), the sum of the infinite series (14b) can be then performed and the result is

$$\mathbf{G}_{\delta\gamma}(\mathbf{q}_1,\mathbf{q}_2)=(1/N)\exp[i(\mathbf{q}_2-\mathbf{q}_1)\cdot\mathbf{x}_{02}]\times\sum_{i,j=1}^{4}(h_i{}^{(0)}-h_i{}^{(1)})[I-F]_{ij}{}^{-1}\mathbf{b}_j(\mathbf{q}_1,\mathbf{q}_2).\tag{20}$$

In the right-hand member of the above expression, I is the 4×4 unit matrix.

Use of (20) and (14a) in (13) gives finally the wanted expression for the polarization term in (11); in the lattice-vectors representation, the (0,2;0,2) element of

Λ_{pol} turns out to be

$$\mathbf{\Lambda}_{\mathrm{pol}}(0,2;0,2)=(e^2/m_2v)\left\{\lambda_0{}^2J_0-2\lambda_0p_1+\begin{bmatrix}h_1{}^{(0)}-h_1{}^{(1)}\\ h_2{}^{(0)}-h_2{}^{(1)}\\ h_3{}^{(0)}-h_3{}^{(1)}\\ h_4{}^{(0)}-h_4{}^{(1)}\end{bmatrix}^{\dagger}[I-F]^{-1}\begin{bmatrix}p_1{}^2\\ p_1p_2\\ p_2p_1\\ p_2{}^2\end{bmatrix}\right\}\mathbf{1}$$
$$=(e^2/m_2v)\lambda_{\mathrm{pol}}\mathbf{1}\,, \tag{21}$$

where p_1 and p_2 have the following expressions:

$$p_1=(A+2B+\lambda_0)J_0-ZyJ_1\,,$$
$$p_2=(A+2B+\lambda_0)J_1-ZyJ_2\,. \tag{22}$$

The main result of this section is contained in expression (21). This expression allows us to account for all the effects arising from the change of shell charge and electronic polarizability due to the substituted ion in terms of the further change λ_{pol} of force constant, which is still a function of λ_0.

Expression (21) can be evaluated by means of an electronic computer; Figs. 5, 6, and 7 show the behavior of λ_{pol} as a function of the impurity shell charge and polarizability. It may be interesting to note that a decrease of electronic polarizability and shell charge of the substituted ion can give rise to a weakening or to a small stiffening in the force constant for the core motion; in the case $\lambda_0\equiv\delta(A+2B)=0$, i.e., when the overlap force constant remains unchanged, the greatest effect is a weakening.

3. APPLICATION TO THE *U* CENTER

The previous theoretical results were applied to the *U* center in NaCl, KCl, and KI crystals at room temperature. These crystals were chosen in view of the following considerations:

(i) The electronic polarizability of the positive ions is considerably smaller than the polarizability of the negative and substituted H^- ions (see Table I). Then the shell model with polarizable negative ions can be safely applied.

(ii) The *U*-center infrared absorption occurs at frequencies so far from the fundamental infrared absorption, that only the perturbation at the impurity lattice site may be considered in the secular equation, as explained in Sec. 2.

(iii) Experimental data are available for such crystals.[13]

The constants used in the calculations are reported in Table I and the most characteristic quantities involved in the rigid-ion and shell models are reported in Table II; $\mathbf{C}_1(\mathbf{q})$ and $\mathbf{C}_2(\mathbf{q})$ were taken from Kellermann's tabulation.

In order to check the reliability of the models for accounting for the lattice dynamics, the normal mode frequencies for the above three crystals without imperfections were evaluated at Kellermann's points in

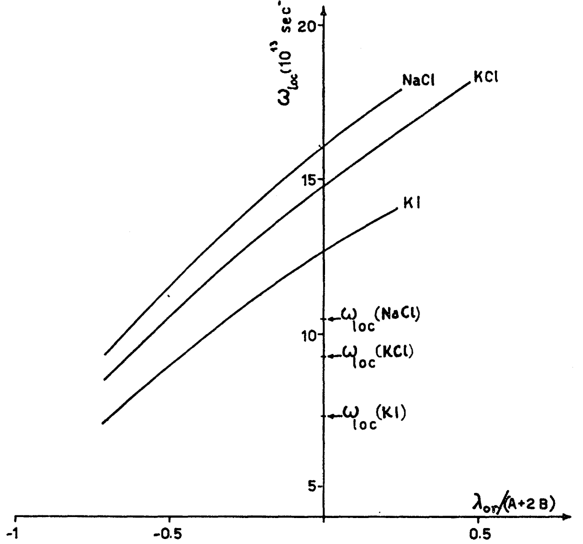

FIG. 1. Rigid-ion model. Theoretical *U* center local mode frequency as a function of λ_{0r}, the local change of the overlap force constants. The upper curve corresponds to a *U* center in NaCl, the lower to one in KI.

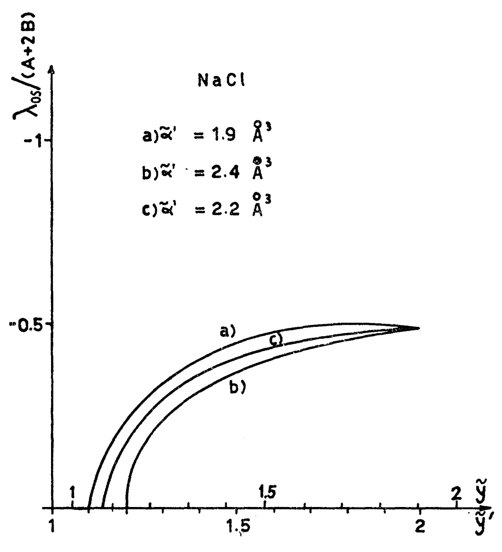

FIG. 2. Shell model. The local change of overlap force constant λ_{0s} versus $\tilde{y}'$ (the shell charge of the imperfect unit cell), or $\tilde{y}$ (the true shell charge of the impurity) for three values of $\tilde{\alpha}'$ (the electronic polarizability of the imperfect unit cell): NaCl.

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[13] G. Schaefer, Phys. Chem. Solids **12**, 233 (1960). See also A. Mitsuishi and H. Yoshinaga, J. Phys. Soc. Japan **18**, 321 (1963); Progr. Theoret. Phys. (Kyoto) **23**, 241 (1963).

TABLE I. Values of constants used in calculations (room temperature).

	$r_0\times10^8$ (cm)	$c_{11}\times10^{-12}$ (dyne cm^{-2})	ϵ_∞	ϵ_0	$m_1\times10^{23}$ (g)	$m_2\times10^{23}$ (g)	α_1 (Å^3)	α_2 (Å^3)
NaCl	2.820[a]	0.494[b]	2.25[c]	5.62[c]	3.8156	5.8845	0.28[c]	2.92[c]
KCl	3.147[a]	0.407[b]	2.13[c]	4.68[c]	6.4891	5.8845	1.13[c]	2.92[c]
KI	3.533[a]	0.274[b]	2.69[c]	4.94[c]	6.4891	21.0624	1.13[c]	6.41[c]

[a] D. Cubicciotti, J. Chem. Phys. 31, 1646 (1959).
[b] G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, p. 368.
[c] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), p. 85.

TABLE II. Values of the most characteristic quantities involved in rigid-ion and shell models.

	$(e^2/v)\times10^{-4}$ (dyne cm^{-1})	y	$(A+2B)$	κ	$\alpha/v=y^2/(A+2B+\kappa)$	α (Å^3)	J_0 [see expression (19)]
NaCl	0.513695	−2.15	8.21	57.79	0.070	3.15	1.61×10^{-2}
KCl	0.369626	−2.73	9.72	104.15	0.065	4.07	0.93×10^{-2}
KI	0.261229	−2.60	10.20	68.68	0.086	7.59	1.39×10^{-2}

the Brillouin zone[14] and good agreement with the experimental data about the fundamental infrared absorption was found, as it appears from Table III. However, the shell model with polarizable negative ions, and even less the rigid-ion model, do not so well account for the effective shape of the dispersion curves of the vibrational frequencies.[15] Nevertheless, in a frequency region well away from the maximum of the vibrational continuum, the elements of $(L-\omega^2)^{-1}$ which are involved in the secular equation (4) are quite insensitive to the detailed structure of the dispersion curves, so the models here adopted are though to allow in principle a good evaluation of the U center local-mode frequency. The roots of Eq. (4) can be then directly compared with the experimental frequencies.

The expression (9) for the rigid-ion model and the analogous expression for the shell model were evaluated by means of a Remington USCC90 electronic computer by choosing suitable sets of ω values; then the roots of the secular equation (4) were determined in both models, once having fixed the parameters[16] λ_{0r} [see (8)] or λ_{0s}, λ_1 and λ_2 [see (15)] characterizing the defect, by looking for the values ω for which expression (4) vanishes.

TABLE III. Experimental results for the fundamental infrared dispersion frequency and theoretical transverse optical frequencies at $\mathbf{q}=0$.

	$\omega_{\text{T.O.}}$ (10^{13} sec^{-1})		
	Experimental	Rigid-ion model	Shell model
NaCl	3.09[a]	2.99	2.98
KCl	2.67[a]	2.57	2.56
KI	1.85[a]	1.78	1.78

[a] M. Born and K. Huang, Ref. a, Table I. S. S. Mitra, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1962), Vol. 13, p. 55.

The theoretical values of the local-mode frequencies obtained in the framework of the rigid-ion model for U centers in NaCl, KCl, and KI are reported in Fig. 1 as a function of the dimensionless change λ_{0r} of force constant; the experimental values[13] of $\omega_{l_{00}}$ are also indicated.

Owing to the large number of parameters characterizing the defect in the shell model, it is difficult to report similar plots in this case. The curves in Figs. 2, 3, and 4 show, as a function of the shell charge $\tilde{y}'e$ and for three different values of the electronic polarizability $\tilde{\alpha}'$ of the imperfect unit cell, the change of force constant λ_{0s} that must be assumed in order to fit the experimental local-mode frequencies to the theoretical ones. $\tilde{y}'e$ and $\tilde{\alpha}'$ represent the shell charge and electronic polarizability of the imperfect unit cell (see Sec. 2a), i.e., the sum of

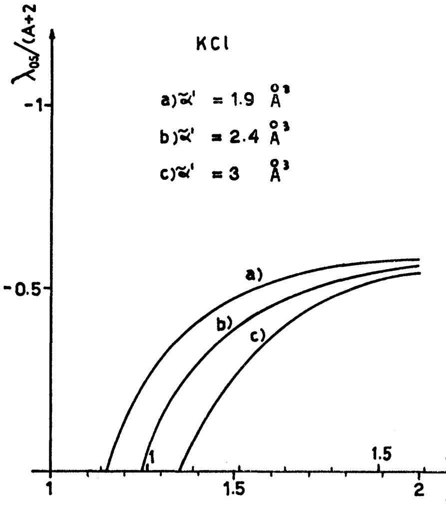

FIG. 3. Same caption as Fig. 2 for KCl.

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[14] The rigid-ion normal-mode frequencies were found the same as those evaluated by A. Karo, J. Chem. Phys. 31, 1489 (1959); 33, 7 (1960).

[15] A. D. B. Woods, B. N. Brockhouse, R. A. Cowley, and W. Cochran, Phys. Rev. 131, 1025 (1963); 131, 1030 (1963).

[16] Here and in the following a subscript r or s will be added to λ_0 in order to emphasize that λ_{0s} in the shell model does not take, generally, the same values as does λ_{0r} in the rigid-ion model.

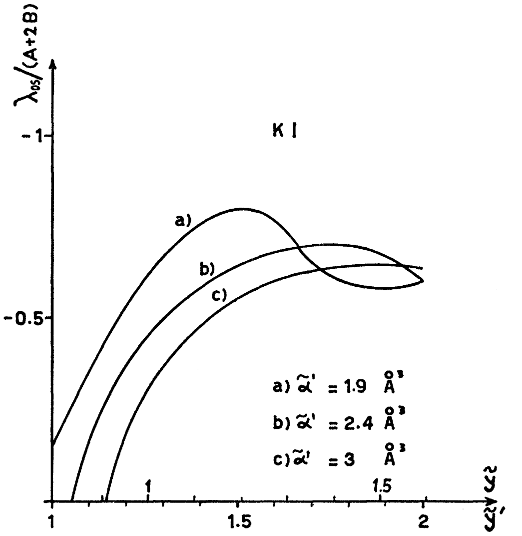

FIG. 4. Same caption as Fig. 2 for KI.

$\tilde y e$ or respectively $\tilde\alpha$ (the shell charge and electronic polarizability of the impurity) and the corresponding contribution coming from the neighboring positive ions.

Curves (c) in Figs. 2, 3, and 4 correspond to the value of $\tilde\alpha$ due to Calder, Cochran *et al.*,[17] plus the alkali-ion polarizability. In the same figures the shell charge of the impurity is reported on the $\tilde y$ axis.

In order to give an idea of the role that the polarizability of the ions plays in the lattice dynamics of *U* center-doped alkali-halide crystals, Figs. 5, 6, and 7 show λ_{pol} as a function of the impurity shell charge and polarizability.

In Table IV the values of ω_{loc} deduced in both models from (4) are reported, when only the change of mass is taken into account in the perturbation, i.e., when *U* centers are considered as pure mass defects; for comparison, the experimental values of the induced infrared absorption are also reported. The fourth and fifth columns of the same table give the values of λ_{0r} and λ, which represent the result of the best fit between ω_{loc} as measured and as calculated in both models. The last column shows the values of λ_{0s} at $\tilde y = -1.1$ on the curves (c) in Figs. 2, 3, and 4.

It should be possible to deduce the correct values of λ_{0r} or $\lambda = \lambda_{0s} + \lambda_{\text{pol}}$ from the knowledge of the crystal properties of the impurity. Unfortunately the properties of the substitutional H^- in alkali halides are not well enough known, so a large uncertainty exists in attributing the values of λ_{0r} or λ_{0s}, $\tilde\alpha$ and $\tilde y$ adequate for the *U* center. When we have some information about $\tilde\alpha$ and $\tilde y$, the present results can be used, in turn, to give an insight into the H^--alkali-ion overlap potential, and in particular to estimate the crystal radius of H^- ions substitutional in alkali-halide crystals.

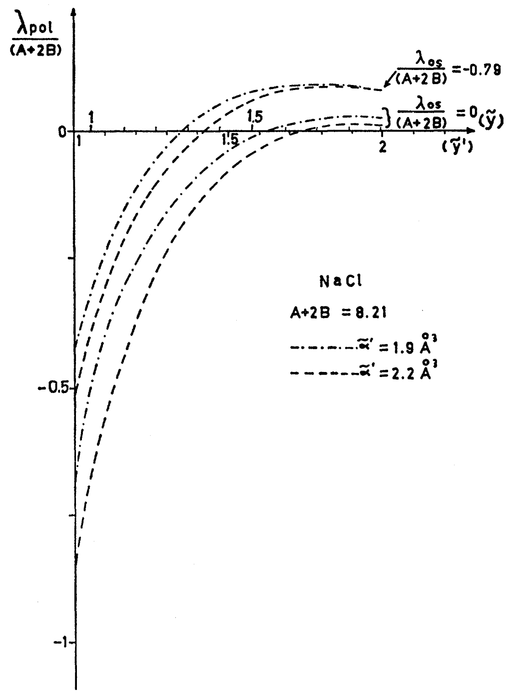

FIG. 5. Shell model. The values of λ_{pol} (the change of local force constant arising from the changes of electronic polarizability and shell charge) versus the impurity shell charge $\tilde y'$ or $\tilde y$, for two values of $\tilde\alpha'$ (the electronic polarizability of the imperfect unit cell) and for two values of λ_{0s}: NaCl.

Experimental and theoretical information[18] about the electronic structure of *U* centers suggests that we assume $\tilde y = y_{H^-} \cong -1$, i.e., assume that not much more than a single electron contributes to the H^- shell charge. Moreover, the H^- electronic polarizability was estimated by Calder *et al.*[17] in lithium hydride crystals, where the bonding is generally regarded as preponderantly ionic: they found $\alpha_{H^-} = 1.9$ Å³, so this value can be assumed for $\tilde\alpha$.

However, no information exists, so far as we know, about the H^--alkali ion overlap potential in crystals. Nevertheless, there is a general feeling that in alkali-halide crystals the H^--alkali bonds display a remarkable ionic character, so the Huggins-Mayer[8] form

$$\tilde\varphi(r) = \tilde b \tilde c_{-+} \exp[(r_{H^-} + r_+)/\rho] \exp(-r/\rho) \qquad (23)$$

seems appropriate to describe this overlap potential.

In this case, assuming Pauling's value 0.625 for $\tilde c_{-+}$ and the Fumi and Tosi[8] values for r_+, the uncertainty concerns the values of $\tilde b$ and r_{H^-}, ρ being fixed as 0.3394 Å. Lacking careful knowledge of $\tilde b$, the more reliable value can be thought to be close to 0.4×10^{-12} erg/molecule for the $H^- - Na^+$, and to 0.34×10^{-12}

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[17] R. S. Calder, W. Cochran, D. Griffiths, and R. D. Lowde, Phys. Chem. Solids **23**, 621 (1962).

[18] B. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10.

TABLE IV. The local-mode frequencies ω_{loc} of the U centers, thought of as a pure mass defect, compared with the experimental ones. The 5th, 6th, and 7th columns show the change of force constants from the best fit between ω_{loc} as measured and as calculated in the rigid-ion and in the shell model, with $y_{H^-}=1.07$ and $\alpha_{H^-}=1.9$ Å^3.

	$\epsilon=\dfrac{m_2-m_H}{m_2}$	$\omega_{loc}(10^{13}$ sec$^{-1})$ Experimental	$\omega_{loc}(10^{13}$ sec$^{-1})$ Theoretical pure mass defect in rigid-ion model	$\omega_{loc}(10^{13}$ sec$^{-1})$ Theoretical pure mass defect in shell model	$\lambda_{0r}/(A+2B)$ Best-fit rigid-ion model	$\lambda/(A+2B)$ Best-fit shell model	$\lambda_{0s}/(A+2B)$ Best-fit shell model $y_{H^-}=1.07$ $\alpha_{H^-}=1.9$ Å^3
NaCl	0.9718	10.46[a]	16.1	14.5	−0.62	−0.43	≈0
KCl	0.9718	9.28[a]	14.8	13.8	−0.63	−0.52	≈0
KI	0.9921	7.31[a]	12.7	11.8	−0.68	−0.52	−0.44

[a] G. Schaefer, see Ref. 13.

erg/molecule for the $H^- - K^+$ bonds, as is suggested from the sequence of b values[8] relative to sodium and potassium halides, respectively. r_{H^-} is regarded as a free parameter. With this choice of $\tilde{b}$, by (6), (7), and (23), r_{H^-} is related to λ_{0r} in the rigid-ion or to λ_{0s} in the shell model, once we know the elastic relaxation of the n.n. around the defect. r_{H^-} is then deduced from the values of λ_{0r} or λ_{0s} in Table IV. The lack of knowledge about the elastic relaxation can be overcome by empirical methods, as explained in a previous paper.[19] r_{H^-} turns out to be 1.3 or 1.7 Å when evaluated by the rigid-ion or the shell model, respectively.

4. DISCUSSION

The vibrational model we employed for the U center takes into account the change of coupling between the

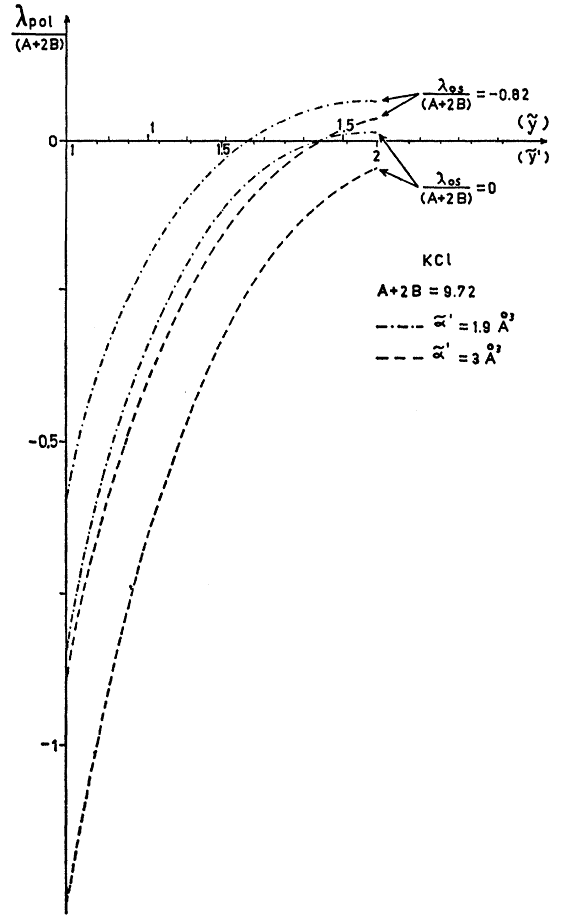

FIG. 6. Same caption as Fig. 5 for KCl.

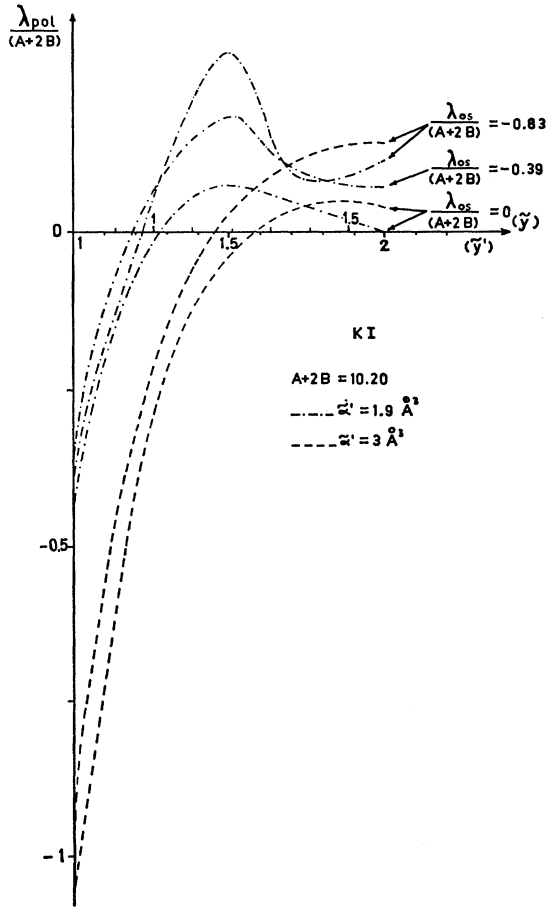

FIG. 7. Same caption as Fig. 5 for KI.

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[19] R. Fieschi, G. F. Nardelli, and N. Terzi, Phys. Letters 12, 290 (1964).

impurity and its nearest neighbors only to terms of the order $(e^2/mv)/\omega_{\mathrm{loc}}^2$ and neglects the polarization effects which arise from elastic relaxation around the defect. In our opinion, however, it is not worth carrying out a more sophisticated approximation, since the evaluation of (9) may be already affected by some lack of precision, owing to Kellermann's coarse net of points in the Brillouin zone. In spite of this, according to us this model accounts for the value of the *U* center local-mode frequency, owing to the high relative position of the *U* frequency with respect to the maximum of the vibrational continuum. It accounts for the isotopic effect within the inverse-square-root law of the masses also, but it does not allow a detailed analysis of the deviations from this law. The effects here disregarded could play some role in the *U* center-induced resonant scattering or in determining the structure of an eventual smooth local mode a little above the vibrational continuum.

Our results yield the following information about the influence of *U* centers on the lattice dynamics of alkali halides.

First of all, it appears from Table IV that the *U* center cannot be described as a pure mass defect when the lattice dynamics is considered in a less simplified scheme then previous ones.[1,2] The change of mass alone gives rise to local modes at frequencies much higher than the real ones; about 50 to 70% or 40 to 60% higher, in rigid-ion or shell model, respectively. In the framework of the rigid-ion model, this fact was pointed out by Zavt,[3] who suggested that this discrepancy could be removed if one assumes that the high positive root of Eq. (1b) represents the frequency of a single local vibration arising only from the longitudinal optic modes of the perfect crystal and that the frequency observed in the impurity absorption spectrum corresponds to two local vibrations arising from the transverse optic modes. In Zavt's explanation, it is implicitly assumed that the perturbation arising from the local change of mass does not mix transverse and longitudinal modes of the perfect lattice. According to the present theoretical results, however, a defect which affects only its lattice site gives rise to a relevant coupling between the transverse and longitudinal modes (only at zero wave vector does the coupling vanish) so that the local mode frequency turns out to be threefold degenerate, owing to the cubic symmetries of the lattice.

The above discrepancy is here explained in terms of a change of force constants. In the shell model, this change can arise not only from the modifications on the overlap potential, as it occurs in the rigid-ion model, but, in a relevant way, it arises from the change of electronic polarizability and shell charge due to the substituted ion (see Figs. 5, 6, and 7) also. Some uncertainty, however, concerns the choice of values for λ_{0r} or λ_{0s}, $\tilde{\alpha}$, and $\tilde{y}$ in order to account for the dynamics of the impurity in the lattice. $\tilde{\alpha}=1.9$ Å^3 [17] for the electronic polarizability and $\tilde{y}e\cong -e$ for the shell charge of H^- in alkali-halide crystals seem to be quite reliable values, while the generalized Huggins-Mayer[20] potential with an appropriate value for ρ might be a better approximation for the overlap potential[21] than the Huggins-Mayer, here employed.

The next remark concerns the ionic crystal radius of H^- in alkali halides: the value 1.7 Å, found on the basis of the shell model, agrees with Puling's prediction[22] which sets the radius of this ion between those of Br^- and I^-; on the contrary the value $r_{H^-}\cong 1.3$ Å found in the rigid-ion model[23] seems to agree with Goldschmidt's prediction.[22] The inconsistency between these two values of the H^- crystal radius could be ascribed to the poorness of the rigid-ion model.

As a final remark, it is worthwhile to note that the frequencies of the local modes deviate from the inverse-square-root law of the mass of the impurity (only at the asymptotic limit $\omega_{\mathrm{loc}}\rightarrow\infty$ and for pure mass defect does this law occur) owing to the peculiar structure of the secular equation (1b). The anharmonicity effect might further affect the mass dependence.

ACKNOWLEDGMENTS

We are grateful to Dr. A. Liverani of the Computing Group of Milano University for his help in the numerical calculations.

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[20] M. P. Tosi and F. G. Fumi, Phys. Chem. Solids **25**, 45 (1964).

[21] M. P. Tosi (private communication).

[22] *Landolt-Börnstein Tables,* edited by K. H. Hellwege (Springer-Verlag, Berlin, 1955), Vol. I, part 4.

[23] Due to a trivial printing error in a previous paper, the value of 1.0 Å appeared for the H^- crystal radius estimated in rigid-ion model.