Infrared absorption of RbCl:Ag⁺ and RbBr:Ag⁺: A theoretical treatment*

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A general model for $\langle 110 \rangle$ off-center substitutional impurities in alkali-halide crystals is developed. It assumes a defect with a different mass from the ion it replaces and also with formal core-core short-range forces between the defect and its nearest neighbors different from those in the pure crystal. An absorption spectrum was calculated and three parameters, corresponding to the changes of the spring constants between the impurity and its nearest neighbors, were adjusted in order to fit absorption-band positions observed by Nolt and by Kirby, Hughes, and Sievers for RbCl:Ag⁺ at low frequencies. In a following paper this model has been used in conjunction with a very simple one-parameter-model version of lattice anharmonicity to predict a Raman scattering spectrum for RbCl:Ag⁺.

I. INTRODUCTION

The basic theory for the understanding of the vibrational aspects of crystals containing substitutional impurities has been developed by many authors.¹⁻⁵ In these works an important class of impurity treated is the monoatomic or diatomic ion, whose center of mass occupies the position of the host ion it replaces and which has a different mass and/or forces connecting it to its neighbors different from those of the replaced ion. The long-range forces are generally assumed to be unchanged from those of the pure lattice and the force changes are assumed to take place in the short-range terms.

The problem gets more involved if those defects have associated with them an electric or elastic dipole which has preferred alignment directions in the host crystal. In these cases for a cubic host crystal the appropriate point group is no longer the cubic O_h group but is changed to some group of lower symmetry. It has been observed that in cubic ionic crystals the preferred alignment directions for paraelectric and paraelastic defects are $\langle 100 \rangle$,⁶ $\langle 111 \rangle$,^{7.8} or $\langle 110 \rangle$,⁹⁻¹¹ having thus associated with them the point groups with symmetry $C_{4\nu}$, $C_{3\nu}$, and $C_{2\nu}$, respectively.

The purpose of this paper is to extend the models mentioned above to this kind of defect and to compare the properties of the resulting perturbed phonons with experiments. We choose the case of a monoatomic substitutional defect near a cation site in a NaCl structure alkalihalide crystal displaced in the $\langle 100 \rangle$ direction and calculate an absorption coefficient by the method developed by Klein.¹² This method uses perturbed Lifshitz Green's functions and only requires computations in the impurity space, i.e., the space formed by the coordinates of the ions directly affected by the presence of the impurity. In our model we assume the equilibrium position of the defect to be known and the force changes to be restricted to the short-range forces between the defect and its nearest neighbors. The impurity space is thus formed by the 21 Cartesian components of the displacements of the impurity and its six nearest neighbors.

To this model system we apply Lifshitz theory in order to find the perturbed phonon Green's functions, a task made possible by the existence of detailed shell models for the RbCl and RbBr crystals which we treat. We use the Green's functions to calculate an infrared absorption spectrum for our model defect-lattice system and adjust the parameters of the model so as to fit observed infrared absorption spectra, insofar as they are available, and measured values of the electric dipole moment of the off-center Ag^+ ions in RbCl: Ag^+ and RbBr: Ag^+ , the specific systems treated in this study.

Section II A presents the theory of the absorption of infrared radiation by a defect-lattice system. Section II B is devoted to a description of the model used for the off-center defect. Sections II C and II D discuss unperturbed Lifshitz Green's functions and, in practice, the very important symmetry considerations which simplify actual calculations. These are described in Sec. III. Section IV presents the results for RbCl:Ag⁺ and RbBr:Ag⁺ comparing our model for the former system with observations. Conclusions are in Section V.

II. THEORY

A. Absorption coefficient

The addition of substitutional impurities to alkali-halide crystals destroys their translational symmetry and drastically alters their infrared activity. If the impurity is off-center the defectlattice system becomes optically anisotropic and

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the absorption coefficient is given by

$$A_{n}(\omega) = -\frac{4\pi\omega}{n_{0}c} \sum_{\alpha\alpha'} \operatorname{Im} \Delta \chi_{\alpha\alpha'} n_{\alpha} n_{\alpha'}, \qquad (1)$$

where ω and c are the frequency and velocity of the incident light. n_0 is the index of refraction of the pure crystal and $\Delta \chi_{\alpha\alpha'}$ is the $\alpha\alpha'$ component of the change in the electric susceptibility tensor of the crystal due to the addition of the impurity. n_{α} is the α component of the unit vector \hat{n} which defines the polarization of the incident light.

For a crystal containing one [110] off-center defect the number of nonzero components $\Delta \chi_{\alpha \alpha'}$ is limited by $C_{2\nu}$ symmetry. The result is the tensor

$$\Delta \chi [110] = \begin{pmatrix} \Delta \chi_{xx} [110] & \Delta \chi_{xy} [110] & 0 \\ \Delta \chi_{xy} [110] & \Delta \chi_{xx} [110] & 0 \\ 0 & 0 & \Delta \chi_{zz} [110] \end{pmatrix}.$$
(2)

If we consider a sample containing a collection of defects, randomly oriented in all 12 possible $\langle 110 \rangle$ directions, the crystal is isotropic with susceptibility given by

$$\Delta \overline{\chi}_{xx} = \Delta \overline{\chi}_{zz} = \frac{1}{3} \left(2 \Delta \chi_{xx} \left[110 \right] + \Delta \chi_{zz} \left[110 \right] \right), \qquad (3)$$

and absorption coefficient

$$A(\omega) = (4\pi\omega/n_0 c)C \operatorname{Im} \frac{1}{3}(2\Delta\chi_{xx}[110] + \Delta\chi_{zz}[110]), \quad (4)$$

where *C* is the concentration of defects. We calculate $\Delta \chi_{\alpha \alpha'}$ by following Klein¹² and obtain

$$\operatorname{Im} \Delta \chi_{\alpha \alpha} [110] = -\frac{(n_{\omega}^{2}+2)^{2}}{9Nv_{0}} \frac{e^{*2}}{[\omega^{2}(\mathrm{TO})-\omega^{2}]^{2}} \times \sum_{\substack{lb\\l'b'}} \frac{\operatorname{sgn}(b) \operatorname{sgn}(b')}{M_{b}M_{b'}} \times \operatorname{Im}[T(lb\alpha, l'b'\alpha')], \qquad (5)$$

where n_{∞} is the high-frequency index of refraction, N and v_0 are the number and volume of unit cells, e^* is the shell-model effective charge, and ω and ω (TO) are the frequencies of the incident light and of the transverse-optical phonons of the pure crystal, respectively. M_b is the mass of ion b and sgnb is a function defined as

 $\operatorname{sgn}(b) = \begin{cases} +1 & \text{for } b \text{ designating a positive ion,} \\ -1 & \text{for } b \text{ designating a negative ion.} \end{cases}$

 $T(lb\alpha, l'b'\alpha')$ are the elements of a matrix T given by

$$T = \Gamma (I + G_0 \Gamma) , \qquad (6)$$

where Γ is the perturbing matrix and G_0 is the matrix for the unperturbed Lifshitz Green's functions. These matrices are defined in Secs. II B and IIC. \sum' indicates that the sum is to be taken

only over coordinates of ions belonging to the impurity space, to be defined presently.

B. Perturbing matrix Γ

We assume the perturbing matrix Γ to be given by the following model. The impurity is assumed to occupy a [110] off-center equilibrium position and to have the same electric charge as the ion it replaces. The long-range Coulomb forces are assumed to be unchanged and the perturbation consists in a mass change from the mass of the host ion which is being substituted ΔM and in a change in the hypothetical short-range spring constants which relate the force on the impurity center of mass to the displacements of its nearest neighbors. We restrict this change by assuming that it takes place only in the longitudinal part of the short-range forces which act between the defect and its nearest neighbors. This model defines the impurity space to be the Cartesian coordinates of the impurity ion and its nearest neighbors, see Fig. 1.

The perturbing matrix is given by

$$\Gamma(\omega^2) = \Delta \phi - \omega^2 \Delta M. \tag{7}$$

 $\Delta \phi$ is a 21×21 matrix for the change in the potential energy of the crystal due to the introduction of the impurity in the pure crystal. Its elements can be calculated by considering the change in the potential energy which the crystal undergoes when the ions are displaced arbitrarily. For example, the change $\Delta \phi_{01}$ in potential energy between ions 0 and 1 is given in terms of the displacements $\bar{u}(0)$ and $\bar{u}(1)$ by





$$\Delta \phi_{01} = \frac{1}{2} \Delta k_1 \{ (r_0 - d/\sqrt{2}) [u(1x) - u(0x)] + (-d/\sqrt{2}) [u(1y) - u(0y)] \}^2 / [(r_0 - d/\sqrt{2})^2 + (d/\sqrt{2})^2] \}$$

to second order in $|\Delta \tilde{I}_{01}| = |\tilde{u}(1) - \tilde{u}(0)|$. r_0 , d, and Δk_1 are specified in Fig. 1. Since we are only interested in elements of $\Delta \phi$ which belong to the impurity space, we write

$$\Delta \phi = \sum_{a} \Delta \phi_{0a}, \quad a = 1, 2, 3, \overline{1}, \overline{2}, \overline{3}, \qquad (9)$$

where $\Delta \phi_{0a}$ is the change in potential energy due to a general displacement of ion 0 (the defect) and ions *a*, which are nearest neighbors of the impurity.

 ΔM is the 21 × 21 matrix corresponding to the mass change introduced in the impurity space by the defect. It gives rise to diagonal elements in the perturbing matrix of which only three, involving coordinates of the impurity are different from zero. All other terms are zero, since the remaining masses of the ions in the impurity space are unchanged. The result for $\Gamma(\omega^2)$ in Cartesian components is given in Table I where we have used the following abbreviations:

$$\begin{split} A &= \frac{d}{(d^2 + r_0^2)^{1/2}} , \quad B = \frac{r_0}{(d^2 + r_0^2)^{1/2}} , \\ C &= \frac{r_0 - d/\sqrt{2}}{(d^2 + r_0^2 + \sqrt{2}r_0 d)^{1/2}} , \quad D = \frac{d/\sqrt{2}}{(d^2 + r_0^2 - \sqrt{2}dr_0)^{1/2}} , \\ E &= \frac{r_0 + d/\sqrt{2}}{(d^2 + r_0^2 + \sqrt{2}dr_0)^{1/2}} , \quad F = \frac{d/\sqrt{2}}{(d^2 + r_0^2 - \sqrt{2}r_0 d)^{1/2}} , \\ \alpha &= \Delta k_1 + \Delta k_2 + \Delta k_3 A^2 - \omega_f^2 \Delta M , \\ \beta &= 2\Delta k_3 B^2 - \omega_f^2 \Delta M , \\ \gamma &= -2\Delta k_1 CD + 2\Delta k_2 EF + \Delta k_3 A^2 \end{split}$$

where *d* is the static off-center displacement of the impurity, r_0 is the pure-crystal nearest-neighbor distance, and ΔM is the difference of mass between the impurity and the host ion it substitutes.

C. Unperturbed Green's function G_0 The elements of the unperturbed Green'sfunctions matrix are given by³

$$G_{0}(lb\alpha, l'b'\alpha' | \omega^{2}) = \frac{1}{N(M_{b}M_{b'})^{1/2}} \times \sum_{\vec{k},j} \frac{e_{\alpha}(b | \vec{k} j) e_{\alpha'}(b | \vec{k} j)}{\omega^{2}(\vec{k} j) - \omega^{2}} \times e^{-i\vec{k} \cdot [\vec{k}(lb) - \vec{k}(l'b')]}, \quad (10)$$

where ω^2 is an independent variable and all other quantities can be determined from a shell model for the perfect crystal. *N* is the number of unit cells in the crystal, M_b is the mass of ion *b*, and \vec{k} is the wave vector for the pure crystal vibrating at frequency $\omega(\vec{k}j)$, where *j* is the branch index. The phonon polarization vectors $e_{\alpha}(b|\vec{k}j)$ are chosen so as to form a complete orthonormal set.³ The elements of matrix G_0 must reflect the symmetry of the pure lattice, which is O_h , and their nonzero distinct elements are given in Table II, where *a* stands for $G_0(0x, 0x)$, *b* for $G_0(\overline{3x}, \overline{3x}), \ldots$, etc., in a notation defined in Table II.

D. Symmetry considerations

The introduction of an off-center defect in a pure crystal, besides destroying the translational symmetry, also reduces the point group from cubic (general alkali-halide crystal) to some other group of lower order. For a [110] offcenter defect the symmetry point group is C_{2n} . The basis functions of a reducible representation of the C_{2n} group spanned by the impurity space are given by the Cartesian components of the amplitudes of the displacements of impurity space ions from their equilibrium positions. These amplitudes we represent by a 21-dimensional column vector $\chi(f)$, whose components can be expressed in terms of Cartesian or symmetry coordinates. The symmetry coordinates are formed by the basis functions of the irreducible representations of the $C_{2\nu}$ group. They are obtained by standard projection methods and yield seven symmetry coordinates of the type A_1 , three

TABLE I. Perturbing matrix in Cartesian coordinate form. Listed are nonzero elements $\Gamma(ai, bj) = \Gamma(bj, ai) = \Gamma(bi, aj)$, where $a, b = 0, 1, \overline{1}, 2, \overline{2}, 3, \overline{3}; i, j = x, y, z$.

$\Gamma(\overline{3}x, \overline{3}x) = -\Gamma(\overline{3}x, 0x) = \Gamma(\overline{3}x, \overline{3}y) = -\Gamma(\overline{3}x, 0y) = -\Gamma(0x, 3x) = -\Gamma(0x, 3y) = \Gamma(3x, 3x) = \Gamma(3x, 3y) = -\Gamma(0x, 3y) = -\Gamma$
$\Gamma(\overline{3}y,\overline{3}y) = -\Gamma(\overline{3}y,0y) = \Gamma(0y,3y) = \Gamma(3y,3y) = \frac{1}{2}\Delta k_3 A^2$
$\begin{split} &\Gamma(\overline{3}x,\overline{3}z) = -\Gamma(\overline{3}x,0z) = \Gamma(0x,3z) = -\Gamma(3x,3z) = \\ &\Gamma(\overline{3}y,\overline{3}z) = -\Gamma(\overline{3}y,0z) = \Gamma(0y,3z) = -\Gamma(3y,3z) = \Delta k_3 A B / \sqrt{2} \end{split}$
$\Gamma(\overline{2}x,\overline{2}x)=-\Gamma(\overline{2}x,0x)=\Gamma(\overline{1}y,\overline{1}y)=-\Gamma(\overline{1}y,0y)=\Deltak_2F^2$
$\Gamma(\overline{2}x,\overline{2}y) = -\Gamma(\overline{2}x,0y) = \Gamma(\overline{1}x,\overline{1}y) = -\Gamma(\overline{1}x,0y) = \Delta k_2 EF$
$\Gamma(\overline{1}x,\overline{1}x) = -\Gamma(\overline{1}x,0x) = \Gamma(\overline{2}x,\overline{2}y) = -\Gamma(\overline{2}x,0y) = \Delta k_2 E^2$
$\Gamma(1x,1x) = -\Gamma(0x,1x) = \Gamma(2y,2y) = -\Gamma(0y,2y) = \Delta k_1 C^2$
$\Gamma(2x,2x) = -\Gamma(0x,2x) = \Gamma(1y,1y) = -\Gamma(0y,1y) = \Delta k_1 D^2$
$\Gamma(0x,1y) = \Gamma(0x,2y) = -\Gamma(1x,1y) = -\Gamma(2x,2y) = \Delta k_1 C D$
$\Gamma(\overline{3}z,\overline{3}z) = -\Gamma(\overline{3}z,0z) = -\Gamma(0z,3z) = \Gamma(3z,3z) = \Delta k_1 B^2$
$\Gamma(0x, 0x) = \Gamma(0y, 0y) = \boldsymbol{\alpha}$
$\Gamma(0z,0z)=\beta$
$\Gamma(0x,0y) = \gamma$

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(8)

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2	g	С	h	е	h	b	g	0	0	-i	0	i	0	0	0	0	0	0	0	0	0
3	с	g	h	е	h	g	b	0	0	0	0	0	0	0	0	0	-i	0	i	0	0
3	0	0	0	0	0	0	0	b	h	g	е	g	h	с	0	i	0	0	0	-i	0
2	0	0	i	0	-i	0	0	h	b	h	f	h	d	h	i	0	0	0	0	0	-i
1	0	i	0	0	0	-i	0	g	h	b	e	c	h	g	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	e	f	e	a	е	f	e	0	0	0	0	0	0	0
1	0	-i	0	0	0	i	0	g	h	с	е	b	h	g	0	Ó	0	0	0	0	0
2	0	0	-i	0	i	0	0	ĥ	d	h	f	h	b	h	-i	0	0	0	0	0	i
3	0	0	0	0	0	0	0	с	h	g	, e	g	h	Ь	0	-i	0	0	0	i	0
3	0	0	i	0	-i	° 0 ·	0	0	i	0	0	0	-i	0	Ь	h	h	f	h	h	d
$\overline{2}$	0	0	0	0	0	0	0	i	0	0	0	0	0	-i	h	b	g	c	g	c	h
ī	i	0	0	0	0	0	-i	0	0	0	0	0	0	0	h	g	b	е	C C	g	h
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	f	e	е	a	e	e	f
1	-i	0	0	0	0	0	i	0	0	0	0	0	0	0	h	g	с	e	b	g	h
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TABLE II. Symmetry reduced form of the unperturbed Lifshitz Green's functions in the impurity space.

of type A_2 , five of type B_1 , and six of type B_2 . We summarize them in Table III.

The use of symmetry coordinates, besides simplifying our calculations, allows one to distinguish the contribution to the absorption coefficient from normal modes belonging to different symmetries A_1 , B_1 , and B_2 . A_2 is infrared inactive.

III. COMPUTATIONAL PROCEDURES

The real and imaginary parts of the unperturbed Lifshitz Green's functions are given by⁴

$$\operatorname{Im} G_{0}(lb\,\alpha,\,l'b'\,\alpha'\,|\,\omega^{2}) = \frac{\pi}{N(M_{b}M_{b'})^{1/2}} \times \sum_{\vec{k},j} e_{\alpha}(b\,|\vec{k}j)e_{\alpha'}(b'\,|\vec{k}j) \times \cos\{\vec{k}\cdot[\vec{R}(lb)-\vec{R}(l'b')]\} \times \delta(\omega^{2}(\vec{k}j)-\omega^{2})$$
(11)

and

 $\operatorname{Re}G_{0}(lb\alpha, l'b'\alpha'|\omega^{2})$

$$= \frac{1}{\pi} \operatorname{P} \int_0^{\omega_{\max}^2} \frac{\operatorname{Im} G_0(lb\,\alpha, l'b'\,\alpha'\,|\omega^2)}{\omega'^2 - \omega^2} \,d\,\omega'^2\,,\qquad(12)$$

where P stands for principal value.

The unperturbed eigenfrequencies $\omega(\vec{k}j)$ and the unperturbed polarization vectors $\vec{e}(b | \vec{k}j)$ we obtain from a shell-model calculation. We use model number 3 of Raunio and Rolandson for RbCl,¹³ and

RbBr,¹⁴ and evaluate $\omega(\vec{k}j)$'s and $\vec{e}(b|\vec{k}j)$'s for k vectors at 1686 points in the Kellerman $\frac{1}{48}$ section of the Brillouin zone.¹⁵ This is equivalent to a total of about 64000 points in the full Brillouin zone. Since this number is limited we choose squared frequency intervals $\Delta \omega^2$ so as to have enough unperturbed frequencies in each interval as to insure that ImG_0 varies smoothly from interval to interval. The squared frequency ω^2 is defined as the middle point of each $\Delta \omega^2$ interval. In the numerical calculations, we divided the squared frequencies in intervals $\Delta \omega^2 = \frac{1}{100} \omega^2$, and had therefore $\sim 10^2$ distinct squared frequencies in each interval. The resulting elements of G_0 vary quite smoothly with ω^2 , being almost linear for frequencies up to about 60 cm^{-1} for both RbCl and RbBr. On the other hand this mesh of $\frac{1}{100} \omega^2$ did not provide enough resolution in order to produce the sought-for low-lying absorption bands. This problem we bypassed by performing a linear interpolation on the imaginary part of the Green's functions, since they are smoother than the real parts. The real parts are then found as Hilbert transforms of the imaginary parts as shown in Eq. (12). At low frequencies this is a good procedure due to the almost linear behavior of ImG_0 . At higher frequencies, the more complicated behavior of ImG_0 may give rise to the suspicion that the interpolation is not advisable. But, since we have divided the spectrum in equal squared frequency intervals, the corresponding frequency intervals become smaller at higher frequencies,

thus still ensuring accurate values for the interpolation.

IV. RESULTS FOR THE ABSORPTION COEFFICIENT

A. Rubidium chloride doped with silver-RbCl:Ag⁺

The absorption coefficient given by Eqs. (4) and (5) contains four adjustable parameters introduced through the perturbing matrix Γ into matrix T as we have seen in Secs. I-III. These parameters are the changes in the spring constants Δk_1 , Δk_2 , Δk_3 and the displacement d of the defect from the on-center position. The absorption spectrum for RbCl:Ag⁺ has been measured, and this allows us to adjust the theoretical absorption curves to the experimental results in this case.

In Fig. 2 we reproduce the experimental curve obtained by Nolt¹⁶ and Kirby, Hughes, and Sievers.¹⁷ They used a sample containing 164 ppm of silver, and obtained three absorption bands at 21.3, 26.5, and 36.5 cm⁻¹. Through electric field dichroism they were able to establish that the absorption occurring at 36.5 cm⁻¹ corresponds to a vibration of the defect in a configuration equivalent to our $\chi(B_15)$ described in Table III. The symmetry of the other two peaks they were not able to identify without ambiguity. These results are consistent with the results of stress induced dichroism experiments by Nolt.¹⁶

To adjust our parameters we proceed in the following way. We use the observed¹⁸ value for the electric dipole moment of Ag⁺ in RbCl of $p = 0.78 \ e$ Å to deduce an off-center displacement of d = 0.33 Å for the silver ion. This assumes that the local field is given by the Lorentz local field $E_{loc} = [3/(2+\epsilon)] E$ and that the charge on the Ag⁺ ion is equal to one electron charge. By adjusting the changes in the spring constants we observed that any increase or decrease of the effective spring constant (increase or decrease of



FIG. 2. Absorption spectrum of RbCl:Ag⁺ according to Nolt, Kirby, Hughes, and Sievers.

	B_2	$\begin{split} \chi(B_2 t) &= (1/\sqrt{2}) \left[\chi(1x) - \chi(2y) \right] \\ \chi(B_2 2) &= (1/\sqrt{2}) \left[\chi(\overline{1}x) - \chi(\overline{2}y) \right] \\ \chi(B_2 3) &= (1/\sqrt{2}) \left[\chi(2x) - \chi(1y) \right] \\ \chi(B_2 4) &= (1/\sqrt{2}) \left[\chi(2x) - \chi(\overline{1}y) \right] \\ \chi(B_2 5) &= \frac{1}{2} \left[\chi(3x) + \chi(\overline{3}x) - \chi(\overline{3}y) \right] \\ \chi(B_2 6) &= (1/\sqrt{2}) \left[\chi(0z) - \chi(0y) \right] \end{split}$
impurity space.	B1	$\begin{split} \chi(B_11) &= \frac{1}{2} [\chi(3x) - \chi(\overline{3}x) \\ &+ \chi(3y) - \chi(\overline{3}y)] \\ \chi(B_12) &= (1/\sqrt{2}) [\chi(1z) + \chi(2z)] \\ \chi(B_13) &= (1/\sqrt{2}) [\chi(1z) + \chi(2z)] \\ \chi(B_14) &= (1/\sqrt{2}) [\chi(3z) + \chi(\overline{3}z)] \\ \chi(B_15) &= \chi(0z) \end{split}$
TABLE III. Symmetry coordinates in the	A_2	$\begin{array}{l} \chi(A_21) = \frac{1}{2} \left[\chi(3x) - \chi(\overline{3}x) \right] \\ -\chi(3y) + \chi(\overline{3}y) \right] \\ \chi(A_2^{22}) = (1/\sqrt{2}) \left[\chi(1z) - \chi(2z) \right] \\ \chi(A_2^{23}) = (1/\sqrt{2}) \left[\chi(\overline{1}z) - (\overline{2}z) \right] \end{array}$
	A_1	$\begin{split} \chi(A_1 1) &= (1/\sqrt{2})[\chi(1x) + \chi(2y)] \\ \chi(A_1 2) &= (1/\sqrt{2})[\chi(\overline{1}x) + \chi(\overline{2}y)] \\ \chi(A_1 3) &= (1/\sqrt{2})[\chi(2x) + \chi(1y)] \\ \chi(A_1 4) &= (1/\sqrt{2})[\chi(2x) + \chi(\overline{1}y)] \\ \chi(A_1 5) &= \frac{1}{2}[\chi(3x) + \chi(\overline{3}x) \\ + \chi(3y) + \chi(\overline{3}y)] \\ \chi(A_1 6) &= (1/\sqrt{2})[\chi(3x) - \chi(\overline{3}x)] \\ \chi(A_1 7) &= (1/\sqrt{2})[\chi(0x) + \chi(0y)] \end{split}$
	Representation	Symmetry coordinates

the Δk 's) was followed by a shift of the peaks to higher or lower frequencies as expected. By analyzing the position of the springs in Fig. 1 and the normal modes given in Table III it is easy to recognize that the peak sensitive to changes in Δk_3 belongs to symmetry B_1 which from experiments is known¹⁷ to be at 36.5 cm^{-1} . We noted further that the A_1 peaks are sensitive to Δk_1 and Δk_2 changes while the B_2 peaks are most sensitive to Δk_1 changes. The results we show in Fig. 3. By choosing, on the basis of Fig. 3, $\Delta k_1 = -12700$ dyn/cm, $\Delta k_2 = -10\,200$ dyn/cm, and $\Delta k_3 = -9500$ dyn/cm, we get the theoretical spectra of Fig. 4(a). The theoretical absorption band peaks occur at 21.0, 27.2, and 36.5 cm^{-1} . This is the closest adjustment possible for the mesh we used for the frequencies.

We were not able to choose Δk parameters so as to get theoretical relative peak heights to be the same as the experimental ones. We investigated the sensitivity of these results to the specific defect model used by performing a calculation in which we include also the contribution to the perturbing matrix from transverse spring constant changes. Even with changes of the order of 100% in the unperturbed transverse spring constants given by the shell model, the alteration in calculated infrared absorption was insignificant. The position of the peaks remained unchanged and the heights changed by less than 1%.

Figure 4(b) is the absorption spectra calculated separately for each symmetry, i.e., the contribution to the absorption by the modes belonging separately to the A_1 , B_1 , and B_2 symmetries. This allows us to identify the symmetry of the



FIG. 3. Position changes of A_1 , B_1 , and B_2 absorption peaks for different nearest-neighbor spring-constant changes in RbCl:Ag⁺

mode associated with each absorption band: the peaks at 21.3, 27.1, and 36.5 cm⁻¹ are of pure B_2 , A_1 , and B_1 symmetry character, respectively. The absorption at 98 cm⁻¹ is due to contributions of all infrared active modes, principally B_2 . The strong peak at 118 cm⁻¹ is due to the restrahl frequency. At 140 cm⁻¹ is another absorption band, again due to contributions of A_1 , B_1 , and mainly B_2 .

B. Rubidium bromide doped with silver-RbBr:Ag⁺

There have been no infrared absorption experiments done on the RbBr:Ag⁺ system and we are not able to adjust our model to experimental data. We produce a graph similar to Fig. 3 which gives us the behavior of the peaks under different values of the spring constants. The value we used for the displacement of the impurity from the off-center position is again obtained from the electro-caloric measurements of Kapphan and Lüty¹⁸ who obtained for the uncorrected dipole moment 0.95 *e*Å. We correct this value in the same manner we did for RbCl:Ag⁺ and obtain for the displacement d = 0.41Å, where we used the value 5 for the dielectric constant of pure RbBr.¹⁷

The resulting diagram in Fig. 5 shows that for RbBr:Ag⁺ we also have three low-frequency absorption bands. They behave under changes of the spring constants in a manner quite similar to that of the low-frequency peaks of RbCl:Ag⁺. This indicates that the mass of the nearest-neighbors anion is not important in determining infrared absorption frequencies. This would be the



FIG. 4. Theoretical absorption spectra for RbCl:Ag⁺. (a) Total absorption spectrum. (b) Contributions to the absorption from normal modes of different symmetries.



FIG. 5. Position changes of A_1 , B_1 , and B_2 absorption

peaks for different nearest-neighbor spring-constant changes in RbBr:Ag⁺.

case if the modes corresponding to low-frequency peaks involved only very small nearest-neighbor amplitudes compared with the amplitude of the motion of the impurity. This argument strongly suggests that the normal modes which induce the absorptions of RbCl:Ag⁺ at 21.3, 26.5, and 36.5 cm⁻¹ are almost purely of the types $\chi(B_26)$, $\chi(A_17)$, and $\chi(B_15)$ described in Table III since these are the symmetry coordinates which involve defect motion.

It is interesting to note that a totally harmonic theory such as we have used here produces absorption peaks of nonzero width. Since the theory is a harmonic one this width is not, properly speaking, to be ascribed to a lifetime broadening. It is better thought of as a band of infrared-active mode frequencies produced by a harmonic perturbation.

V. CONCLUSIONS

The main purpose of this paper has been to develop a model which might be able to describe basic features of the lattice dynamics of systems containing (110) off-center substitutional impurities. We have developed a model for a [110] offcenter substitutional impurity which assumes the impurity to have a mass different from that of the ion for which it substitutes and also that there is a change in the formal short-range core-core forces which couple the impurity to its nearest neighbors. We use the off-center position of the impurity obtained from electro-caloric experiments of Kapphan and Lüty. We are left with three adjustable parameters: the changes in the spring constants which connect the impurity to its nearest neighbors. For RbCl:Ag⁺ we adjust them so as to fit the position of three observed low-frequency absorption bands. The theory does not correctly give the observed relative peak heights. The perturbed phonons found in this way will, hopefully, be useful in the understanding of phenomena in which the lattice vibrations play a significant role such as, for example, reorientation processes of off-center Ag⁺ in RbCl. On comparing the variation of absorption peak positions due to changes of the spring constants (Figs. 3 and 5) for RbCl:Ag⁺ and $RbBr:Ag^+$ we were able to conclude that the low-frequency absorption bands are probably mainly due to the movement of the impurity. We predict low-lying infrared absorption bands for RbBr:Ag⁺. If they are observed Fig. 5 would help one to find force constant changes and hence perturbed phonons for this system.

In our results we take advantage of the flexibility offered by theoretical calculations to separate the contributions to the absorption coefficient of normal modes belonging to different symmetries. This enables us to identify, without ambiguity, the symmetry of low-frequency absorption bands for RbCl:Ag⁺.

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