

## Sidebands of the $U$ -Center-Induced Infrared Absorption Spectra of Alkali-Halide Crystals\*

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A  $U$  center (substitutional  $H^-$  or  $D^-$  ion) in an alkali-halide crystal is known to give rise to triply degenerate localized vibrational modes that are infrared-active. The  $U$ -center-induced infrared lattice absorption spectrum shows a characteristic structure consisting of a central prominent peak flanked on both sides by broad sidebands. The central peak arises from one-phonon absorption processes due to localized-mode phonons, and recently it has been studied extensively. The present paper deals with a theory of the sidebands based on two-phonon absorption processes involving one localized-mode phonon and one band-mode phonon, taking account of phonon coupling mechanisms due to the cubic anharmonicity of the crystal and to the crystal second-order electric dipole moment. Formal expressions are derived for the contributions from these two mechanisms to the sideband absorption coefficient, in terms of the phonon Green's-function matrix for the harmonic perfect-host crystal, the cubic anharmonic force constants, and the second-order electric-dipole-moment coefficients. The phonon spectrum of the perturbed crystal is actually taken into account. A simplified expression for the absorption coefficient is obtained for the case where only that part of the anharmonicity and the electric dipole moment which arises from short-range overlap forces between the impurity and its nearest neighbors is considered. Numerical calculations are carried out for the higher-frequency sideband of a KI crystal containing  $6 \times 10^{17}$   $U$  centers ( $H^-$  or  $D^-$ ) per  $cm^3$ , at  $4.3^\circ K$ , using Hardy's deformation-dipole model for the perfect-host crystal. The  $U$  center is described by a phenomenological "effective mass defect" which takes into account approximately the change in force constants at the impurity site, using the experimental value of the localized-mode frequency. The calculated spectrum is in satisfactory agreement with Timusk's experimental data. It is found that the anharmonicity is the dominant phonon-coupling mechanism. It is about  $10^4$  times stronger than the second-order electric-dipole-moment mechanism near the localized-mode frequency, and about 10 times stronger in the high-frequency limit of the sideband. Some discrepancies in the position of the phonon frequency gap and the relative intensities of the main lines are tentatively attributed to the use of inaccurate phonon data, the effective-mass-defect model for the  $U$  center, and the approximate numerical values for the overlap forces.

### I. INTRODUCTION

WE present in this paper a detailed theory of the sidebands of the  $U$ -center-induced localized-mode infrared lattice absorption spectra in alkali-halide crystals of which a preliminary account has been previously reported.<sup>1</sup>

An isolated hydride or deuteride negative ion substituting for a halogen ion in an alkali-halide crystal ( $U$  center) generally gives rise to localized vibration modes whose frequency is much higher than the maximum vibration frequency of the perfect-host crystal. In a localized mode, the amplitude of vibration is largest at the impurity ion and decreases very rapidly when the distance from the impurity increases. Under an operation of the point-symmetry group of the crystal at the impurity site, the localized vibration modes transform as a polar vector, and therefore are active in the infrared lattice absorption by the crystal. Although the possibility of occurrence of localized modes due to impurities in crystals was discussed by Lifshitz<sup>2</sup> as early as 1943,

they were first observed in 1960 by Schaefer,<sup>3</sup> in the infrared absorption spectra of alkali halide crystals containing  $U$  centers. Schaefer's work was followed by a series of similar experiments carried out with higher-resolution techniques by various authors. In particular, infrared absorption spectra of NaCl, NaBr, KCl, RbCl, KBr, RbBr, and KI containing  $U$  centers have been obtained by Fritz *et al.*<sup>4</sup>; Timusk's experiments<sup>5</sup> were concerned with KBr and KI crystals containing  $H^-$  and  $D^-$  impurities, while Elliott *et al.*<sup>6</sup> have especially studied  $CaF_2$ ,  $SrF_2$ , and  $BaF_2$  crystals containing  $H^-$  and  $D^-$  impurities. The  $U$ -center-induced infrared absorption spectra obtained show a characteristic structure consisting of a central prominent peak flanked on both sides by broad sidebands.

The central peak has been attributed to one-phonon absorption processes involving a localized-mode phonon. Its behavior is at the present time well understood. Reviews of the theory can be found in references.<sup>7,8</sup> Fritz has suggested that the sidebands represent sum-

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<sup>1</sup> Nguyen X. Xinh, *Solid State Commun.* **4**, 9 (1966).

<sup>2</sup> I. M. Lifshitz, *J. Phys. U.S.S.R.* **7**, 215 (1943); **7**, 249 (1943); **8**, 89 (1944).

<sup>3</sup> G. Schaefer, *J. Phys. Chem. Solids* **12**, 233 (1960).

<sup>4</sup> B. Fritz, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 485; B. Fritz, U. Gross, and D. Bäuerle, *Phys. Status Solidi* **11**, 231 (1965).

<sup>5</sup> T. Timusk (private communication to Professor A. A. Maradudin); T. Timusk and M. V. Klein, *Phys. Rev.* **141**, 664 (1966).

<sup>6</sup> R. J. Elliott, W. Hayes, G. D. Jones, H. F. Macdonald, and C. T. Sennett, *Proc. Roy. Soc. (London)* **A289**, 1 (1965).

<sup>7</sup> R. J. Elliott, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965).

<sup>8</sup> A. A. Maradudin, *Rept. Progr. Phys.* **28**, 331 (1965).

mation and difference bands involving a localized-mode phonon and a continuum (or band-mode) phonon coupled by the anharmonicity of the crystal potential. Klemens<sup>9</sup> has suggested that the second-order electric-dipole moment can also play a role as a coupling mechanism in these two-phonon processes. A brief discussion of both these coupling mechanisms has been given by Sennett.<sup>10</sup> A theory of the sidebands due to  $H^-$  impurities in  $\text{CaF}_2$  has been worked out by Elliott *et al.*<sup>6</sup> In this theory, the  $H^-$  impurity is considered as vibrating in a tetrahedral anharmonic rigid potential well, the continuum part of the phonon spectrum is taken as that of the perfect-host crystal, and the anharmonic coefficients are taken as adjustable parameters to get the best fit between measured and calculated spectra. The theoretical results turned out to be satisfactory and showed that the model used was good, at least for the case considered. However, the approximation of the continuum part of the phonon spectrum of the perturbed crystal by that of the unperturbed crystal prevents the resonant modes, if they exist, from showing up in the sidebands. This is not the case in Timusk and Klein's theory of the sidebands of the infrared  $U$  center in  $\text{KBr}$ .<sup>5</sup> In the latter theory, the perturbation of the continuum phonon spectrum of the crystal due to the presence of the impurity is actually taken into account. The lattice dynamical model of the  $U$  center is characterized by a mass defect associated with a change in force constant at the lattice site it occupies. This change in force constant is calculated from the measured localized-mode frequency. The theoretical treatment considers the  $H^-$  ion vibrating along the  $x$  axis as anharmonically coupled to a configuration coordinate  $X$  made up of the symmetrical displacements in the  $x$  direction of its two nearest-neighbor positive ions at (100) and (100). The theory does not contain any adjustable parameters. The results of Timusk and Klein's calculation of the high-frequency sideband of the  $U$  center in  $\text{KBr}$ , using a shell model for the host crystal, are in very good agreement with their experimental data except for the presence, in their calculated spectra, of a localized-mode peak, occurring in the gap, which has not been observed.

The theory we present in this paper is based on two-phonon processes involving one localized-mode phonon and one continuum-mode phonon. As in Timusk and Klein's theory, the phonon spectrum of the perturbed crystal is taken into account. Also, we use the same lattice dynamical model for the  $U$  center, namely a mass defect associated with a force-constant change at the impurity site whose value is to be derived from the experimental value of the localized-mode frequency. However, our treatment differs substantially from that of Timusk and Klein, as well as that of Elliott *et al.* In particular, contributions from both the anharmonicity

and the second-order electric-dipole-moment coupling mechanisms to the absorption coefficient will be calculated. General formulas will be derived in Sec. II for these contributions in terms of the third-order coefficients of the crystal potential (cubic anharmonicity) and the second-order coefficients of the crystal electric-dipole moment in the respective expansions of these operators in Taylor's series in powers of the atomic displacements. These formulas will be applied, in Sec. III, to the calculation of the structure of the infrared high-frequency sideband due to  $U$  centers in  $\text{KI}$ , using a deformation dipole model for the host crystal and only taking account of those parts of the anharmonicity and second-order electric dipole moment which arise from the distortion of the electronic-charge distribution due to short-range forces. The calculated spectrum is in satisfactory agreement with Timusk's experimental data. It will be shown that the anharmonicity is by far the dominant coupling mechanism in  $\text{KI}$ . Some discrepancies in the position of the phonon frequency gap and the relative intensities of the main lines will be tentatively attributed to the use of inaccurate phonon data, the effective-mass-defect model for the  $U$  center and the approximate numerical values for the overlap forces.

## II. THEORY

We assume that the light waves have an essentially infinite wavelength. For a centrosymmetric cubic or isotropic crystal, the real part of the crystal conductivity tensor then has the expression<sup>11</sup>

$$\sigma_{\mu\nu}(\omega) = \frac{1}{2}\omega \frac{1}{\hbar V n(\omega)} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle M_\nu(t) M_\mu(0) \rangle, \quad (1)$$

where  $n(\omega)$  is the Bose thermal distribution function  $n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}$ ,  $\omega$  is the frequency of the infrared radiation,  $V$  is the volume of the crystal, and  $\mathbf{M}(t)$  is the crystal dipole moment operator in the Heisenberg representation:

$$\mathbf{M}(t) = e^{iH/\hbar} \mathbf{M}(0) e^{-iH/\hbar}, \quad (2)$$

$H$  being the vibrational Hamiltonian of the perturbed (i.e., the impurity-doped) crystal. The angular brackets in Eq. (1) denote a thermodynamic average over the canonical ensemble described by the same Hamiltonian  $H$ , whose expression in terms of the atomic displacements  $\{\mathbf{u}(k)\}$  and their time derivatives  $\{\dot{\mathbf{u}}(k)\}$  can be written as

$$\begin{aligned} H = & \frac{1}{2} \sum_{l\kappa\alpha} M_{l\kappa} \dot{u}_\alpha^2(l\kappa) + \Phi^{(0)} + \frac{1}{2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \Phi_{\alpha\beta}(l\kappa, l'\kappa') u_\alpha(l\kappa) \\ & \times u_\beta(l'\kappa') + \frac{1}{6} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \sum_{l''\kappa''\gamma} \Phi_{\alpha\beta\gamma}(l\kappa, l'\kappa', l''\kappa'') u_\alpha(l\kappa) \\ & \times u_\beta(l'\kappa') u_\gamma(l''\kappa'') + \dots \quad (3) \end{aligned}$$

<sup>9</sup> P. G. Klemens (private communication).

<sup>10</sup> C. T. Sennett, thesis, Oxford University, 1964 (unpublished).

<sup>11</sup> A. A. Maradudin and R. F. Wallis Phys. Rev. **123**, 777 (1961).

Here  $l$  and  $\kappa$  ( $= +$  or  $-$ ) are the cell and sublattice indices, respectively, and  $M_{l\kappa}$  is the mass of the atom occupying the lattice site ( $l\kappa$ ). The first term on the right-hand side of Eq. (3) denotes the kinetic energy of the crystal and the following terms represent the expansion of the crystal potential energy in Taylor's series in powers of the atomic displacements.

The induction of the dipole moment by the lattice vibrations can also be described by expanding its components in a Taylor series in powers of the atomic displacements as

$$\begin{aligned} M_{\mu} &= M_{\mu}^{(0)} + \sum_{l\kappa\alpha} M_{\mu,\alpha}(l\kappa)u_{\alpha}(l\kappa) \\ &+ \frac{1}{2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} M_{\mu,\alpha\beta}(l\kappa,l'\kappa')u_{\alpha}(l\kappa)u_{\beta}(l'\kappa') + \dots \\ &= M_{\mu}^{(0)} + M_{\mu}^{(1)} + M_{\mu}^{(2)} + \dots \end{aligned} \quad (4)$$

We will evaluate Eq. (1) on the assumption of an isolated impurity ion, and will eventually multiply the result by  $n_d$ , the number of impurity ions.

#### A. Cubic Anharmonicity Mechanism

We first calculate, in this section, the contribution from the cubic anharmonicity mechanism to Eq. (1). Therefore, the Hamiltonian  $H$  is that of the anharmonic crystal, given by Eq. (3), in which we will retain only the cubic anharmonic terms. On the other hand, it is sufficient for our present purpose to take into account only the first-order terms in the expansion Eq. (4) of the dipole moment (assuming that the crystal has no permanent electric dipole moment), i.e.,

$$M_{\mu} = \sum_{l\kappa\alpha} M_{\mu,\alpha}(l\kappa)u_{\alpha}(l\kappa). \quad (5)$$

The harmonic Hamiltonian is diagonalized by a normal coordinate transformation

$$\begin{aligned} u_{\alpha}(l\kappa) &= \left( \frac{\hbar}{2M_{l\kappa}} \right)^{1/2} \sum_s \frac{B_{\alpha}^{(s)}(l\kappa)}{(\omega_s)^{1/2}} (b_s + b_s^{\dagger}) \\ &= \left( \frac{\hbar}{2} \right)^{1/2} \sum_s \frac{C_{\alpha}^{(s)}(l\kappa)}{(\omega_s)^{1/2}} A_s, \end{aligned} \quad (6a)$$

with

$$A_s = b_s + b_s^{\dagger} \quad (6b)$$

and

$$C_{\alpha}^{(s)}(l\kappa) = \frac{B_{\alpha}^{(s)}(l\kappa)}{M_{l\kappa}^{1/2}}, \quad (6c)$$

where  $b_s$  and  $b_s^{\dagger}$  denote the usual phonon destruction and creation operators, respectively, while  $\omega_s$  and  $B_{\alpha}^{(s)}(l\kappa)$  are the frequency and amplitude of the  $s$ th vibrational mode of the perturbed crystal.

For an alkali-halide crystal, the first-order dipole-moment coefficients  $\{M_{\nu,\alpha}(l\kappa)\}$  have the following

form<sup>12</sup>:

$$M_{\nu,\alpha}(l\kappa) = M_{\nu,\alpha}(0\kappa) = \delta_{\nu\alpha}\epsilon_{\kappa}, \quad (7a)$$

where

$$\epsilon_{+} = -\epsilon_{-} = \epsilon^{*}, \quad (7b)$$

$\epsilon^{*}$  playing the role of an effective charge.

Taking account of Eqs. (5)–(7), we can rewrite Eq. (1) as

$$\begin{aligned} \sigma_{\mu\nu}(\omega) &= \frac{1}{4V} \frac{\omega}{n(\omega)} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \delta_{\nu\alpha}\delta_{\mu\beta}\epsilon_{\kappa}\epsilon_{\kappa'} \sum_{ss'} \frac{C_{\alpha}^{(s)}(l\kappa)C_{\beta}^{(s')}(l'\kappa')}{(\omega_s\omega_{s'})^{1/2}} \\ &\times \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle A_s(t)A_{s'}(0) \rangle. \end{aligned} \quad (8)$$

The Fourier transform of the two-time correlation function appearing in Eq. (8) has previously been calculated by Maradudin.<sup>13</sup> The result is

$$\int_{-\infty}^{\infty} dt e^{-i\omega t} \langle A_s(t)A_{s'}(0) \rangle \cong 2n(\omega)\delta_{ss'}F_s(\omega). \quad (9)$$

The function  $F_s(\omega)$  has the same value for each of the triply degenerate localized modes<sup>13</sup> whose frequency we denote by  $\omega_0$ . If  $\omega_L$  is the maximum vibration frequency of the unperturbed crystal, then for the sideband frequency range  $\omega_0 - \omega_L < \omega < \omega_0 + \omega_L$ , we obtain, after substituting Eq. (9) into Eq. (8), carrying out the summations over  $\alpha$ ,  $\beta$ , and  $s'$ , and subsequently multiplying the result by  $n_d$ ,

$$\begin{aligned} \sigma_{\mu\nu}(\omega) &= \frac{n_d}{2V} \frac{\omega}{\omega_0} F_0(\omega) \sum_{l\kappa} \sum_{l'\kappa'} \epsilon_{\kappa}\epsilon_{\kappa'} \\ &\times \sum_{\sigma} C_{\nu}^{(\sigma)}(l\kappa)C_{\mu}^{(\sigma)}(l'\kappa'), \end{aligned} \quad (10a)$$

with

$$F_0(\omega) = \frac{4\omega_0^2\Gamma_0(\omega)}{[\omega^2 - \omega_0^2 - 2\omega_0\Delta_0(\omega)]^2 + 4\omega_0^2\Gamma_0^2(\omega)}, \quad (10b)$$

where  $\sigma$  runs over the localized modes only.

To the lowest order in the anharmonicity, the function  $\Delta_0(\omega_0)$  describes the shift of the frequency of the localized mode from its value in the harmonic approximation, while  $\Gamma_0(\omega_0)$  is the half-width at half-maximum of the peak contributed by the localized modes to the one-phonon absorption cross section.<sup>13</sup> Both  $\Delta_0(\omega)$  and  $\Gamma_0(\omega)$  are slowly varying functions around  $\omega = \omega_0$  and moreover their values are very small in comparison to  $\omega_0$ . We therefore approximate Eq. (10b) by

$$F_0(\omega) = 4\omega_0^2/(\omega^2 - \omega_0^2)^2\Gamma_0(\omega). \quad (10c)$$

<sup>12</sup> R. F. Wallis and A. A. Maradudin, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962* (The Institute of Physics and the Physical Society, London, 1962), p. 490.

<sup>13</sup> A. A. Maradudin, *Ann. Phys. (N. Y.)* **30**, 371 (1964).

Equation (10a) then becomes

$$\sigma_{\mu\nu}(\omega) = \frac{2n_d}{V} \frac{\omega_0\omega}{(\omega^2 - \omega_0^2)^2} \Gamma_0(\omega) \sum_{l\kappa} \sum_{l'\kappa'} \epsilon_{\kappa}\epsilon_{\kappa'} \times \sum_{\sigma} C_{\nu}^{(\sigma)}(l\kappa) C_{\mu}^{(\sigma)}(l'\kappa'). \quad (11)$$

Let us now consider the function  $\Gamma_0(\omega)$ . To the lowest order in the anharmonicity, it has the general expression<sup>13</sup>

$$\Gamma_0(\omega) = \frac{18\pi}{\hbar^2} \sum_{s_1 s_2} V^2(\sigma s_1 s_2) \{ (n_{s_1} + n_{s_2} + 1) \times [\delta(\omega - \omega_{s_1} - \omega_{s_2}) - \delta(\omega + \omega_{s_1} + \omega_{s_2})] + (n_{s_1} - n_{s_2}) \times [\delta(\omega + \omega_{s_1} - \omega_{s_2}) - \delta(\omega - \omega_{s_1} + \omega_{s_2})] \}, \quad (12a)$$

with

$$V(s_1 s_2 s_3) = \frac{1}{6} \left( \frac{\hbar}{2} \right)^{3/2} \sum_{ll'l''} \sum_{\kappa\kappa'\kappa''} \sum_{\alpha\beta\gamma} \frac{\Phi_{\alpha\beta\gamma}(l\kappa, l'\kappa', l''\kappa'')}{(\omega_{s_1}\omega_{s_2}\omega_{s_3})^{1/2}} \times \frac{B_{\alpha}^{(s_1)}(l\kappa) B_{\beta}^{(s_2)}(l'\kappa') B_{\gamma}^{(s_3)}(l''\kappa'')}{(M_{l\kappa} M_{l'\kappa'} M_{l''\kappa''})^{1/2}}. \quad (12b)$$

In the present case, the frequency  $\omega$  is positive. On the other hand, both the indices  $s_1$  and  $s_2$  should run over all the normal modes of the perturbed crystal. However, we assume that  $\omega_0 > 2\omega_L$  which is true for most alkali-halide crystals (in particular for potassium iodide) containing  $H^-$  or  $D^-$   $U$  centers. In that case, the only nonvanishing contributions to  $\Gamma_0(\omega)$  come from the terms where one of the indices  $s_1$  and  $s_2$  refers to a localized mode, while the other refers to a continuum mode. Taking account of the complete symmetry in  $s_1, s_2,$  and  $s_3$  of the coefficient  $V(s_1 s_2 s_3)$  given by Eq. (12b) and denoting  $\omega - \omega_0$  by  $\Omega$ , we obtain

$$\Gamma_0(\omega) = \frac{36\pi}{\hbar^2} \sum_{\sigma\sigma'} V^2(\sigma\sigma's) \times \{ (n_s + n_0 + 1) \delta(\Omega - \omega_s) + (n_s - n_0) \delta(\Omega + \omega_s) \} = \frac{24\pi}{\hbar^2} \text{sgn}\Omega [n(\omega_0) + n(\Omega) + 1] \times \sum_{\sigma\sigma's} V^2(\sigma\sigma's) \omega_s \delta(\Omega^2 - \omega_s^2). \quad (13)$$

According to Eq. (12b), we have that

$$\sum_{\sigma\sigma'} V^2(\sigma\sigma's) \omega_s \delta(\Omega^2 - \omega_s^2) = \frac{1}{36} \left( \frac{\hbar}{2} \right)^3 \frac{1}{\omega_0^2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \sum_{l''\kappa''\gamma} \sum_{l_1\kappa_1\alpha_1} \sum_{l_1'\kappa_1'\beta_1} \sum_{l_1''\kappa_1''\gamma_1} \Phi_{\alpha\beta\gamma}(l\kappa, l'\kappa', l''\kappa'') \Phi_{\alpha_1\beta_1\gamma_1}(l_1\kappa_1, l_1'\kappa_1', l_1''\kappa_1'') \times \sum_{\sigma} C_{\alpha}^{(\sigma)}(l\kappa) C_{\alpha_1}^{(\sigma)}(l_1\kappa_1) \sum_{\sigma'} C_{\beta}^{(\sigma')}(l'\kappa') C_{\beta_1}^{(\sigma')}(l_1'\kappa_1') \sum_s \frac{B_{\gamma}^{(s)}(l''\kappa'') B_{\gamma_1}^{(s)}(l_1''\kappa_1'')}{(M_{l''\kappa''} M_{l_1''\kappa_1''})^{1/2}} \delta(\Omega^2 - \omega_s^2). \quad (14)$$

In this equation, the indices  $\sigma$  and  $\sigma'$  run over the localized modes while the index  $s$  runs over the continuum modes only. However, in the frequency range  $0 < |\Omega| < \omega_L$  in which we are interested, the function  $\delta(\Omega^2 - \omega_s^2)$  vanishes identically for  $\omega_s = \omega_0$ . Consequently, the index  $s$  can be considered as running over all the normal modes of the perturbed crystal including the localized modes. The sum over  $s$  in Eq. (14) can therefore be written as

$$\sum_s \frac{B_{\gamma}^{(s)}(l''\kappa'') B_{\gamma_1}^{(s)}(l_1''\kappa_1'')}{(M_{l''\kappa''} M_{l_1''\kappa_1''})^{1/2}} \delta(\Omega^2 - \omega_s^2) = \frac{1}{\pi} \text{Im} U_{\gamma\gamma_1}(l''\kappa'', l_1''\kappa_1''; \Omega^2 - i0), \quad (15)$$

where  $U$  is the Green's-function matrix for the harmonic perturbed crystal whose general element is given by<sup>8</sup>

$$U_{\alpha\beta}(l\kappa, l'\kappa'; \omega^2) = \frac{1}{(M_{l\kappa} M_{l'\kappa'})^{1/2}} \sum_s \frac{B_{\alpha}^{(s)}(l\kappa) B_{\beta}^{(s)}(l'\kappa')}{\omega^2 - \omega_s^2}. \quad (16)$$

Taking account of Eqs. (10c) and (13)–(15), Eq. (10a) becomes

$$\sigma_{\mu\nu}(\omega) = \frac{\hbar n_d}{54V} \frac{\omega}{\omega_0} \frac{\text{sgn}\Omega}{(\omega^2 - \omega_0^2)^2} [n(\omega_0) + n(\Omega) + 1] \left\{ \sum_{l\kappa} \sum_{l'\kappa'} \epsilon_{\kappa}\epsilon_{\kappa'} \sum_{\sigma} C_{\nu}^{(\sigma)}(l\kappa) C_{\mu}^{(\sigma)}(l'\kappa') \right\} \times \left\{ \sum_{l_1\kappa_1\alpha} \sum_{l_2\kappa_2\beta} \sum_{l_3\kappa_3\gamma} \sum_{l_1'\kappa_1'\alpha'} \sum_{l_2'\kappa_2'\beta'} \sum_{l_3'\kappa_3'\gamma'} \Phi_{\alpha\beta\gamma}(l_1\kappa_1, l_2\kappa_2, l_3\kappa_3) \Phi_{\alpha'\beta'\gamma'}(l_1'\kappa_1', l_2'\kappa_2', l_3'\kappa_3') \sum_{\sigma_1} C_{\alpha}^{(\sigma_1)}(l_1\kappa_1) C_{\alpha'}^{(\sigma_1)}(l_1'\kappa_1') \right. \\ \left. \times \sum_{\sigma_2} C_{\beta}^{(\sigma_2)}(l_2\kappa_2) C_{\beta'}^{(\sigma_2)}(l_2'\kappa_2') \text{Im} U_{\gamma\gamma'}(l_3\kappa_3, l_3'\kappa_3'; \Omega^2 - i0) \right\}. \quad (17)$$

This equation is general. It applies to any crystal containing isolated substitutional impurities which are light enough or cause a sufficient stiffening of the force constants between the impurity site and each of its nearest neighbors, so that they give rise to localized vibration modes whose frequency is higher than  $2\omega_L$ .

The evaluation of  $\sigma_{\mu\nu}(\omega)$  as given by Eq. (17) is rather complicated because it requires the explicit knowledge of the eigenvectors  $\{\mathbf{C}^{(\sigma)}(lk)\}$  of the perturbed crystal whose determination, in the general case, is itself a difficult task. Moreover, the various index pairs  $(lk)$  in this equation must in principle run over all the lattice sites of the crystal. Fortunately, the amplitudes of vibration  $\{\mathbf{C}^{(\sigma)}(lk)\}$  in a localized mode decrease very rapidly when the distance from the site  $(lk)$  to the impurity site increases, so that in general, a good approximation is obtained by considering that  $\mathbf{C}^{(\sigma)}(lk)$  is zero at any lattice site which is not in the near neighborhood of the impurity. For our present purpose, we therefore seek to simplify the expression Eq. (17) of the real part of the conductivity tensor by making the following assumptions:

(a) We first assume that only the nearest neighbors to the impurity and the impurity itself are affected by

its presence. This means that  $\mathbf{C}^{(\sigma)}(lk)$  is nonzero only when it refers to the impurity site or any of its nearest neighbors.

(b) We also assume that the anharmonic force constants which, in alkali-halide crystals, arise mainly from short-range overlap forces<sup>14</sup> have appreciable values only between the impurity and any of its nearest neighbors and are negligible between the nearest neighbors themselves.

As a consequence of the first assumption, the index-pairs  $(lk)$  and  $(l'k')$  on the one hand and the pairs  $(l_3k_3)$  and  $(l'_3k'_3)$  on the other hand, now run over the impurity and its nearest neighbors only. This together with the second assumption forces at least one of the pairs  $(l_1k_1)$  and  $(l_2k_2)$  to refer to the impurity site. Considering that the amplitudes of vibration  $\mathbf{C}^{(\sigma)}(lk)$  of any of the nearest-neighbor ions are themselves very small in comparison to that of the impurity ion, we can make a further approximation for the total sum inside the last curly brackets of Eq. (17) which contain products of four  $C$ 's by restricting both the index pairs  $(l_1k_1)$  and  $(l_2k_2)$  to the impurity site. Of course, the same argument applies to the pairs  $(l'_1k'_1)$  and  $(l'_2k'_2)$ . With these approximations made, Eq. (17) is simplified into

$$\begin{aligned} \sigma_{\mu\nu}(\omega) = & \frac{\hbar n_a \omega}{54V \omega_0} \frac{\text{sgn}\Omega}{(\omega^2 - \omega_0^2)^2} [n(\omega) + n(\Omega) + 1] \left\{ \sum_{lk} \sum_{l'k'} \epsilon_k \epsilon_{k'} \sum_{\sigma} C_{\nu}^{(\sigma)}(lk) C_{\mu}^{(\sigma)}(l'k') \right\} \\ & \times \sum_{l_3k_3\gamma} \sum_{l'_3k'_3\gamma'} \sum_{\alpha\beta} \sum_{\alpha'\beta'} \Phi_{\alpha\beta\gamma}(0-, 0-, l_3k_3) \Phi_{\alpha'\beta'\gamma'}(0-, 0-, l'_3k'_3) \left\{ \sum_{\sigma_1} C_{\alpha}^{(\sigma_1)}(0-) C_{\alpha'}^{(\sigma_1)}(0-) \right\} \\ & \times \left\{ \sum_{\sigma_2} C_{\beta}^{(\sigma_2)}(0-) C_{\beta'}^{(\sigma_2)}(0-) \right\} \text{Im} U_{\gamma\gamma'}(l_3k_3, l'_3k'_3; \Omega^2 - i0). \quad (18) \end{aligned}$$

This expression of  $\sigma_{\mu\nu}(\omega)$  involves the localized-mode vibration amplitudes  $\{\mathbf{C}^{(\sigma)}(lk)\}$  and the Green's-function matrix  $\mathbf{U}$  for the perturbed crystal. These quantities depend on the lattice dynamical model for the harmonic perturbed crystal.

Let us denote by  $M_-'$  the mass of the impurity ( $\text{H}^-$  or  $\text{D}^-$ ) ion and by  $M_-$  that of the halogen ion which has been replaced by the impurity. The mass defect at the impurity site can be characterized by  $\epsilon = 1 - (M_-'/M_-)$ . We will also make use, in our present calculation, of a model for the  $U$  center very similar to that used by Fieschi, Nardelli and Terzi<sup>15</sup> and by Timusk and Klein.<sup>5</sup> In this model, the force-constant changes are assumed to be nonzero only at the impurity site. It can then be shown (see Appendix A) that such a model behaves formally in a localized mode of frequency  $\omega_0$  as a mass

defect whose effective value is given by

$$\epsilon' = \epsilon + (\Delta\Phi/\omega_0^2 M_-), \quad (19)$$

where  $\Delta\Phi$  is the scalar force-constant change at the impurity site for a displacement directed toward any of the nearest neighbors. In what follows, for the sake of definiteness, we will carry out the calculation for a  $U$  center described by a simple mass defect  $\epsilon$ . The result for a mass defect associated with a force-constant change will be eventually obtained by subsequently replacing the true mass defect  $\epsilon$  by the effective mass defect  $\epsilon'$ .

The sums in curly brackets in Eq. (18) are calculated in Appendix B and have the expressions Eqs. (B17) and (B7), respectively. Taking account of these, we can rewrite Eq. (18), after summing over  $\sigma_1, \sigma_2, \alpha'$ , and  $\beta'$ , as

$$\begin{aligned} \sigma_{\mu\nu}(\omega) = & \left\{ \frac{1}{[\omega_0^2 - \omega_l^2(\mathbf{0})]^2} \frac{k_{\mu} k_{\nu}}{k^2} + \frac{1}{[\omega_0^2 - \omega_l^2(\mathbf{0})]^2} \right. \\ & \left. \times \left( \delta_{\mu\nu} - \frac{k_{\mu} k_{\nu}}{k^2} \right) \right\} A(\omega), \quad (20a) \end{aligned}$$

<sup>14</sup> I. P. Ipatova, A. A. Maradudin, and R. F. Wallis, *Fiz. Tverd. Tela* **8**, 1064 (1966) [English transl.: *Soviet Phys.—Solid State* **8**, 850 (1966)].

<sup>15</sup> R. Fieschi, G. F. Nardelli, and N. Terzi, *Phys. Letters* **12**, 290 (1964).

with

$$A(\omega) = S^3 \epsilon^2 \omega_0^4 \epsilon^{*2} \frac{\hbar n_d \omega}{54V \omega_0 (\omega^2 - \omega_0^2)^2} \frac{\text{sgn} \Omega}{[n(\omega) + n(\Omega) + 1]} \\ \times \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \sum_{\mu\nu} \Phi_{\mu\nu\alpha}(0-, 0-, l\kappa) \Phi_{\mu\nu\beta}(0-, 0-, l'\kappa') \\ \times \text{Im} U_{\alpha\beta}(l\kappa, l'\kappa'; \Omega^2 - i0), \quad (20b)$$

where  $S$  is a constant given by Eq. (B8),  $\mathbf{k} \approx \mathbf{0}$  is the photon wave vector, and  $\omega_l$  and  $\omega_t$  are the frequencies of the zero wave-vector longitudinal and (doubly degenerate) transverse optical modes of the perfect-host crystal, respectively.

The real part of the conductivity tensor  $\sigma_{\mu\nu}(\omega)$  as given by Eq. (20a) can be separated into two parts representing the responses of the crystal to longitudinal and transverse electromagnetic waves, respectively, as

$$\sigma_{\mu\nu}(\omega) = \sigma_{\mu\nu}^{(l)}(\omega) + \sigma_{\mu\nu}^{(t)}(\omega), \quad (21a)$$

with

$$\sigma_{\mu\nu}^{(t)}(\omega) = \frac{1}{[\omega_0^2 - \omega_t^2(\mathbf{0})]^2} \frac{k_\mu k_\nu}{k^2} A(\omega), \quad (21b)$$

$$K^{(A)}(\omega) = \frac{2n_d \pi \hbar \epsilon^2 \epsilon^{*2} S^3}{3 c V \eta(\omega)} \frac{\omega_0^3 \omega}{(\omega_0^2 - \omega_t(\mathbf{0}))^2 (\omega^2 - \omega_0^2)^2} \text{sgn} \Omega [n(\omega_0) + n(\Omega) + 1]$$

$$\times \sum_{ll'} \sum_{\mu\nu} \sum_{\alpha\beta} \Phi_{\mu\nu\alpha}(0,0,l) \Phi_{\mu\nu\beta}(0,0,l') \text{Im} U_{\alpha\beta}(ll'; \Omega^2 - i0), \quad (23)$$

$$\mu, \nu, \alpha, \beta = x, y, z; \quad l, l' = 0, 1, 2, 3, 4, 5, 6.$$

We have put the superscript  $(A)$  in  $K^{(A)}$  to indicate that it refers to the anharmonicity contribution to the sidebands.

Assuming that the anharmonicity arises from a central potential, it can be shown<sup>16</sup> that there exists only two independent coefficients,  $\Phi_{\alpha\beta\gamma}(0,0,l)$ , represented by

$$\alpha = \Phi_{xxx}(0,0,1) \quad \text{and} \quad \beta = \Phi_{xyy}(0,0,1).$$

It remains to express the Green's-function matrix  $\mathbf{U}$  for the perturbed crystal in terms of the Green's-function matrix  $\mathbf{G}$  for the perfect-host crystal, whose general element is defined by<sup>8</sup>

$$G_{\alpha\beta}(l\kappa, l'\kappa'; \omega^2) = \frac{1}{N(M_\kappa M_{\kappa'})^{1/2}} \sum_{\mathbf{k}j} \frac{W_\alpha(\kappa|\mathbf{k}j) W_\beta^*(\kappa'|\mathbf{k}j)}{\omega^2 - \omega_j^2(\mathbf{k})} \\ \times \exp\{2\pi i \mathbf{k} \cdot [\mathbf{x}(l\kappa) - \mathbf{x}(l'\kappa')]\}, \quad (24)$$

where  $\mathbf{x}(l\kappa)$  is the lattice-site position vector and

<sup>16</sup> Nguyen X. Xinh (to be published).

$$\sigma_{\mu\nu}^{(t)}(\omega) = \frac{1}{[\omega_0^2 - \omega_t^2(\mathbf{0})]^2} \left( \delta_{\mu\nu} - \frac{k_\mu k_\nu}{k^2} \right) A(\omega) \\ = \left( \delta_{\mu\nu} - \frac{k_\mu k_\nu}{k^2} \right) \sigma^{(t)}(\omega), \quad (21c)$$

where  $\sigma^{(t)}(\omega)$  is a scalar. Light being a transverse wave, the response of the crystal to the incident light is given by the transverse real part of the conductivity  $\sigma^{(t)}(\omega)$ . This is related to the scalar infrared lattice absorption coefficient  $K(\omega)$  by<sup>14</sup>

$$K(\omega) = \frac{4\pi \sigma^{(t)}(\omega)}{c \eta(\omega)}, \quad (22)$$

where  $c$  is the speed of light and  $\eta(\omega)$  the index of refraction of the crystal.

From now on, we will let the cell index  $l$  take on the conventional values 0 for the impurity, and 1, 2, 3 and 4, 5, 6 for the six nearest neighbors (positive alkali ions) assumed to be located on the positive and negative branches of the coordinate axes, respectively. Whenever no confusion is possible, we will omit the sublattice index  $\kappa$ .

Substituting into Eq. (22) the expression Eq. (21c) of  $\sigma^{(t)}(\omega)$  and taking account of Eq. (20b), we obtain

$\omega_j(\mathbf{k})$  and  $\mathbf{W}(\kappa|\mathbf{k}j)$  are the frequency and eigenvector of the normal mode  $(\mathbf{k}j)$ , respectively.

We finally obtain the following expression for the contribution of the cubic anharmonic mechanism to the sidebands to the localized-mode peak in the infrared lattice absorption spectra of alkali-halide crystals containing  $U$  centers:

$$K^{(A)}(\Omega) = \frac{4\pi^2 \hbar \epsilon^2 \epsilon^{*2} S^3 n_d}{c V M_+ \omega_L^2 \eta(\omega)} \text{sgn} \Omega \frac{\omega \omega_0^3}{[\omega_0^2 - \omega_t^2(\mathbf{0})]^2 (\omega^2 - \omega_0^2)^2} \\ \times [n(\omega_0) + n(\Omega) + 1] \\ \times \{\alpha^2 A(x) + \alpha\beta C(x) + \beta^2 B(x)\}, \quad (25a)$$

where  $x = \Omega/\omega_L$ ,  $x_0 = \omega_0/\omega_L$ , and where the functions  $A$ ,  $B$ ,  $C$  are given by

$$A(x) = f_{xx}(11; x) - f_{xx}(41; x), \\ B(x) = -8f_{xy}(42; x), \\ C(x) = 2[3f_{xx}(11; x) - f_{xx}(41; x) \\ - 2f_{yy}(41; x) - 6f_{xy}(42; x)]. \quad (25b)$$

The function  $f_{\alpha\beta}(l'l'; x)$  is defined from the Green's function  $G_{\alpha\beta}(l'l'; \Omega^2)$  by the relation

$$G_{\alpha\beta}(lk, l'k'; \Omega^2 - i0) = \frac{1}{\omega_L^2 (M_{\kappa} M_{\kappa'})^{1/2}} \times [h_{\alpha\beta}(lk, l'k'; x) + i\pi f_{\alpha\beta}(lk, l'k'; x)].$$

## B. Second-Order Electric-Dipole-Moment Mechanism

We now proceed to calculate the contribution from the second-order electric-dipole-moment mechanism to Eq. (1). The analysis in the present case is simplified by the fact that the zero-wave-vector phonons do not play any special role as they did in the calculation of the one-phonon contribution to the absorption spectrum described in the preceding section. The infinite-wavelength photon can couple with any pair of phonons whose wave vectors add up to zero.

The contribution of the second-order electric dipole moment to the conductivity  $\sigma_{\mu\nu}(\omega)$  is obtained by substituting into the expression

$$\sigma_{\mu\nu}(\omega) = \frac{1}{2} \omega [n_a / \hbar V n(\omega)] \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle M_{\nu}(t) M_{\mu}(0) \rangle, \quad (26)$$

(where we have already introduced the number of impurities) the second-order terms in the expansion Eq. (4) of the crystal dipole moment operator:

$$M_{\mu}(t) = M_{\mu}^{(2)}(t) = \frac{1}{2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} M_{\mu,\alpha\beta}(l\kappa, l'\kappa') \times u_{\alpha}(l\kappa; t) u_{\beta}(l'\kappa'; t). \quad (27)$$

It is sufficient for our present purpose to calculate  $\sigma_{\mu\nu}(\omega)$  in the harmonic approximation for the crystal potential energy.

According to Eqs. (27) and (6a), we can write

$$\langle M_{\nu}(t) M_{\mu}(0) \rangle = \frac{1}{4} \sum_{ss'} \sum_{s_1 s_1'} M_{\mu}(ss') M_{\nu}(s_1 s_1') \times \langle A_s(t) A_{s'}(t) A_{s_1}(0) A_{s_1'}(0) \rangle, \quad (28a)$$

with

$$M_{\mu}(ss') = \frac{\hbar}{2(\omega_s \omega_{s'})^{1/2}} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} M_{\mu,\alpha\beta}(l\kappa, l'\kappa') \times \frac{B_{\alpha}^{(s)}(l\kappa) B_{\beta}^{(s')}(l'\kappa')}{(M_{l\kappa} M_{l'\kappa'})^{1/2}}. \quad (28b)$$

Using a generalization of the Wick's theorem due to Bloch and De Dominicis<sup>17</sup> to evaluate the thermal average in Eq. (28a), and noticing that  $M_{\mu}(s's) = M_{\mu}(ss')$  we obtain

$$\langle M_{\nu}(t) M_{\mu}(0) \rangle = \frac{1}{2} \sum_{ss'} M_{\mu}(ss') M_{\nu}(ss') \{ n_s n_{s'} e^{i(\omega_s + \omega_{s'})t} + n_s (n_{s'} + 1) e^{i(\omega_s - \omega_{s'})t} + n_{s'} (n_s + 1) e^{i(\omega_{s'} - \omega_s)t} + (n_s + 1)(n_{s'} + 1) e^{-i(\omega_s + \omega_{s'})t} \}. \quad (29)$$

The Fourier transform of this equation is given by

$$\chi_{\mu\nu}(\omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle M_{\nu}(t) M_{\mu}(0) \rangle = \frac{\pi \hbar^2}{4} \sum_{ss'} \frac{1}{\omega_s \omega_{s'}} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \sum_{l_1 \kappa_1 \alpha_1} \sum_{l_1' \kappa_1' \beta_1} M_{\mu,\alpha\beta}(l\kappa, l'\kappa') M_{\nu,\alpha_1 \beta_1}(l_1 \kappa_1, l_1' \kappa_1') \times \frac{B_{\alpha}^{(s)}(l\kappa) B_{\beta}^{(s')}(l'\kappa') B_{\alpha_1}^{(s)}(l_1 \kappa_1) B_{\beta_1}^{(s')}(l_1' \kappa_1')}{(M_{l\kappa} M_{l'\kappa'} M_{l_1 \kappa_1} M_{l_1' \kappa_1'})^{1/2}} \{ n_s n_{s'} \delta(\omega_s + \omega_{s'} - \omega) + n_s (n_{s'} + 1) \delta(\omega_s - \omega_{s'} - \omega) + n_{s'} (n_s + 1) \delta(\omega_{s'} - \omega_s - \omega) + (n_s + 1)(n_{s'} + 1) \delta(\omega_s + \omega_{s'} + \omega) \}. \quad (30)$$

We are only interested, in the present calculation, in the range of frequencies around the localized-mode frequency that we have assumed to be larger than twice the maximum frequency  $\omega_L$  of the unperturbed crystal. In that case, the only nonvanishing contributions to the sums over the mode indices  $s$  and  $s'$  in Eq. (30) come from the terms where either  $\omega_s$  or  $\omega_{s'}$  is equal to  $\omega_0$ .

Now, the coefficients  $\{M_{\mu,\alpha\beta}(l\kappa, l'\kappa')\}$  satisfy the symmetry relation<sup>16</sup>

$$M_{\mu,\beta\alpha}(l'\kappa', l\kappa) = M_{\mu,\alpha\beta}(l\kappa, l'\kappa'). \quad (31)$$

Equation (30) therefore reduces to

$$\chi_{\mu\nu}(\omega) = \frac{\pi \hbar^2 n_0}{2\omega_0} \sum_{s_0} \frac{1}{\omega_{s_0}} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \sum_{l_1 \kappa_1 \alpha_1} \sum_{l_1' \kappa_1' \beta_1} M_{\mu,\alpha\beta}(l\kappa, l'\kappa') M_{\nu,\alpha_1 \beta_1}(l_1 \kappa_1, l_1' \kappa_1') \times \frac{B_{\alpha}^{(s_0)}(l\kappa) B_{\alpha_1}^{(s_0)}(l_1 \kappa_1) B_{\beta}^{(s_0)}(l'\kappa') B_{\beta_1}^{(s_0)}(l_1' \kappa_1')}{(M_{l\kappa} M_{l'\kappa'} M_{l_1 \kappa_1} M_{l_1' \kappa_1'})^{1/2}} \{ n_{s_0} \delta(\omega_{s_0} + \omega_0 - \omega) + (n_{s_0} + 1) \delta(\omega_0 - \omega_{s_0} - \omega) \}. \quad (32)$$

<sup>17</sup> C. Bloch and C. De Dominicis, Nucl. Phys. **7**, 459 (1958).

The expression in curly brackets in this equation can also be written as

$$n(\omega_s)\delta(\Omega-\omega_s)+[n(\omega_s)+1]\delta(\Omega+\omega_s)=2\omega_s \operatorname{sgn}\Omega n(\Omega)\delta(\Omega^2-\omega_s^2). \quad (33)$$

Taking account of Eqs. (32) and (33), Eq. (26) becomes

$$\begin{aligned} \sigma_{\mu\nu}(\omega) = \operatorname{sgn}\Omega \frac{\pi\hbar n_d \omega}{2V \omega_0} \frac{n(\omega_0)n(\Omega)}{n(\omega)} \sum_{\sigma} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \sum_{l_1\kappa_1\alpha_1} \sum_{l_1'\kappa_1'\beta_1} M_{\mu,\alpha\beta}(l\kappa,l'\kappa') M_{\nu,\alpha_1\beta_1}(l_1\kappa_1,l_1'\kappa_1') \\ \times \frac{B_{\alpha}^{(\sigma)}(l\kappa)B_{\alpha_1}^{(\sigma)}(l_1\kappa_1)B_{\beta}^{(\sigma)}(l'\kappa')B_{\beta_1}^{(\sigma)}(l_1'\kappa_1')}{(M_{l\kappa}M_{l'\kappa'}M_{l_1\kappa_1}M_{l_1'\kappa_1'})^{1/2}} \delta(\Omega^2-\omega_s^2) = \operatorname{sgn}\Omega \frac{\hbar n_d \omega}{2V \omega_0} \frac{n(\omega_0)n(\Omega)}{n(\omega)} \\ \times \sum_{l\kappa} \sum_{l'\kappa'\beta} \sum_{l_1\kappa_1\alpha_1} \sum_{l_1'\kappa_1'\beta_1} M_{\mu,\alpha\beta}(l\kappa)M_{\nu,\alpha_1\beta_1}(l_1'\kappa_1') \sum_{\sigma} C_{\beta}^{(\sigma)}(l'\kappa')C_{\beta_1}^{(\sigma)}(l_1'\kappa_1') \operatorname{Im}U_{\alpha\alpha_1}(l\kappa, l_1\kappa_1; \Omega^2-i0). \quad (34) \end{aligned}$$

According to Eq. (26), the quantity  $\sigma_{\mu\nu}(\omega)$  transforms, under a symmetry operation  $\mathbf{S}$  which takes the crystal into itself leaving the impurity site fixed as the  $\mu\nu$  Cartesian component of a second-rank tensor. In the present case of a rock-salt lattice,  $\mathbf{S}$  belongs to the group  $O_h$ . Therefore,  $\sigma_{\mu\nu}(\omega)$  is diagonal and isotropic, i.e.,

$$\sigma_{\mu\nu}(\omega) = \delta_{\mu\nu}\sigma(\omega), \quad (35)$$

from which it follows from Eq. (22) that the absorption coefficient  $K(\omega)$  is given by

$$\begin{aligned} K(\omega) = \frac{2\pi\hbar n_d \operatorname{sgn}\Omega \omega}{cV\eta(\omega) \omega_0} [n(\omega_0)+n(\Omega)+1] \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \sum_{l_1\kappa_1\alpha_1} \sum_{l_1'\kappa_1'\beta_1} M_{\mu,\alpha\beta}(l\kappa,l'\kappa') M_{\mu,\alpha_1\beta_1}(l_1\kappa_1,l_1'\kappa_1') \\ \times \sum_{\sigma} C_{\beta}^{(\sigma)}(l'\kappa')C_{\beta_1}^{(\sigma)}(l_1'\kappa_1') \operatorname{Im}U_{\alpha\alpha_1}(l\kappa, l_1\kappa_1; \Omega^2-i0), \quad (36a) \end{aligned}$$

where  $\mu$  is either  $x$ ,  $y$ , or  $z$ .

This equation is general and gives the expression for the contribution from the second-order electric-dipole-moment mechanism to the sidebands to the localized-mode peak in the infrared lattice absorption spectra of alkali-halide crystals containing  $U$  centers. In this equation, the index-pairs  $(l\kappa)$ , . . . run over all the lattice sites of the crystal.

As we have done in the preceding section, and for the same reasons, we now make the approximation that only the impurity ion and its six nearest neighbors are affected by the presence of the impurity. In that case, the various index pairs in Eq. (36a) will be restricted to the sites of these seven ions only. We also make the same further approximation as in the preceding section that  $\mathbf{C}^{(\sigma)}(l\kappa)$  is nonzero only for the impurity ion. With these approximations made, Eq. (36a) becomes

$$\begin{aligned} K(\omega) = \frac{2\pi\hbar n_d \operatorname{sgn}\Omega \omega}{cV\eta(\omega) \omega_0} [n(\omega_0)+n(\Omega)+1] \sum_{l\kappa} \sum_{l_1\kappa_1\alpha_1} \sum_{\beta\beta_1} M_{\mu,\alpha\beta}(l\kappa, 0-) M_{\mu,\alpha_1\beta_1}(l_1\kappa_1, 0-) \\ \times \sum_{\sigma} C_{\beta}^{(\sigma)}(0-)C_{\beta_1}^{(\sigma)}(0-) \operatorname{Im}U_{\alpha\alpha_1}(l\kappa, l_1\kappa_1; \Omega^2-i0), \quad (36b) \end{aligned}$$

where  $(l\kappa)$  and  $(l_1\kappa_1)$  run over the impurity and its nearest neighbors.

If the sum over  $\sigma$  is carried out using the result expressed by Eq. (B7) and use is made of the property<sup>16</sup> that the coefficient  $M_{\mu,\alpha\beta}(l\kappa,l'\kappa')$  is symmetric with respect to the index-triples  $(l\kappa\alpha)$  and  $(l'\kappa'\beta)$ , we can finally rewrite Eq. (36b) as (using the same single-index convention to label the lattice sites as in the preceding section)

$$\begin{aligned} K^{(E)}(\omega) = \frac{2\pi\hbar S n_d \omega}{cV\eta(\omega) \omega_0} \operatorname{sgn}\Omega [n(\omega_0)+n(\Omega)+1] \\ \times \frac{1}{3} \sum_{\mu} \sum_{l'l'} \sum_{\alpha\beta\gamma} M_{\mu,\gamma\alpha}(0,l)M_{\mu,\gamma\beta}(0,l') \\ \times \operatorname{Im}U_{\alpha\beta}(ll'; \Omega^2-i0), \quad (37) \end{aligned}$$

where  $\mu$  runs over the coordinates  $x$ ,  $y$ , and  $z$  and the lattice-site indices  $l$  and  $l'$  run over the impurity and its six nearest neighbors. The superscript  $(E)$  in  $K^{(E)}(\omega)$  indicates that it refers to the contribution from the second-order electric dipole moment.

The symmetry and invariance properties of the coefficients  $\{M_{\mu,\alpha\beta}(0,l)\}$  have been discussed in.<sup>16</sup> Assuming that the second-order electric dipole moment has a central character (for instance, when it arises from the distortion of the electronic charge distribution due to overlap forces<sup>18</sup>), it is shown<sup>16</sup> that these coefficients

<sup>18</sup> M. Born and K. Kuang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1956), p. 113.



have only two independent elements represented by

$$a = M_{x,xx}(0,1) \quad \text{and} \quad b = M_{x,yy}(0,1).$$

We finally obtain

$$K^{(B)}(\Omega) = \frac{4\pi^2 \hbar S n_d}{c V M_+ \omega_L^2 \eta(\omega)} \frac{\omega}{\omega_0} \operatorname{sgn} \Omega [n(\omega_0) + n(\Omega) + 1] \\ \times \{a^2 A(x) + abC(x) + b^2 B(x)\}, \quad (38)$$

where the functions  $A$ ,  $B$ , and  $C$  are given by Eqs. (25b).

$K^{(B)}(\Omega)$ , whose expression is given by Eq. (38), represents the contribution of the second-order electric-dipole-moment mechanism to the sidebands to the localized-mode peak in the infrared lattice absorption spectra of alkali-halide crystals containing  $H^-$  or  $D^-U$  centers.

### III. APPLICATION TO A KI CRYSTAL

We have applied the results obtained in Sec. II to the case of a KI crystal containing  $U$  centers.

The lattice dynamical model for the harmonic perfect-host crystal used in the present calculations is the deformation dipole model of Hardy.<sup>19</sup> The normal-mode eigenfrequencies  $\{\omega_j(\mathbf{k})\}$  and eigenvectors  $\{\mathbf{W}(\mathbf{k}_j)\}$  at 4.3°K have been numerically computed by Jaswal<sup>20</sup> in the same way as for a KCl crystal described in Ref. 21. It been found<sup>20</sup> that  $\omega_L = 2.546 \times 10^{13}$  rad/sec and  $x_t = 0.7197$ . The functions  $\{f_{\alpha\beta}(l\kappa, l'\kappa'; x)\}$  have been computed as in Ref. 21.

If the impurity is considered as a simple mass defect, the equation for the localized-mode frequency  $x_0$  is<sup>22</sup>

$$1 = \epsilon x_0^2 g_0(x_0), \quad (39a)$$

where  $g_0(x)$  is the Green's function

$$g_0(x) = \frac{1}{N} \sum_{\mathbf{k}j} \frac{W_x(-|\mathbf{k}j)W_x(-|\mathbf{k}j)}{x^2 - x_j^2(\mathbf{k})}, \quad (39b)$$

with  $x_j(\mathbf{k}) = \omega_j(\mathbf{k})/\omega_L$ , and where  $\epsilon$  denotes the true mass defect. For an  $H^-$  impurity,  $\epsilon$  has the value 0.99206 and we have found that  $x_0 = 4.6$ , which is much higher than the experimental value  $x_0 = 2.84$ .<sup>3</sup> This is not surprising, as it is now well known that the simple-mass-defect model for  $U$  centers in alkali-halide crystals yields values of the localized-mode frequencies which are about 50% higher than the corresponding experimental values. This discrepancy can be reduced by taking into account the force-constant changes.

For most perfect alkali-halide crystals, the anharmonicity of the potential energy has been shown to

arise predominantly from the overlap potential.<sup>14</sup> We assume that this is also true for the anharmonic coupling between an  $H^-$  or  $D^-$  impurity and its nearest neighbors. We describe the overlap potential by a function of the form  $\lambda \exp[-r/\rho]$ , where  $\lambda$  and  $\rho$  are two constants and  $r$  is the interionic distance. Similarly, we assume<sup>16</sup> that the second-order electric dipole moment is induced by the distortion of the ionic charge distributions due to lattice vibrations and that the corresponding electric dipole moment has the form  $m \exp[-r/\rho]$ . We make a rough approximation by using the values of  $\lambda$  and  $\rho$  for the perfect-host crystal [Ref. 23, (a)]:  $\lambda = 4.60 \times 10^{-9}$  erg and  $\rho = 0.349 \times 10^{-8}$  cm. The corresponding cubic anharmonic force constants  $\alpha$  and  $\beta$  and the second-order electric-dipole-moment coefficients  $a$  and  $b$  have the following values<sup>16</sup>:

$$\alpha = -44.46 \times 10^{11} \text{ dyn/cm}^2; \quad \beta = 4.836 \times 10^{11} \text{ dyn/cm}^2; \\ a = -0.0266 \text{ statC/cm}; \quad b = 0.00289 \text{ statC/cm}.$$

The effective charge  $\epsilon^*$  is related to the Szigeti charge  $e_S$  and the high-frequency dielectric constant  $\epsilon_\infty$  by<sup>14</sup>

$$\epsilon^* = \frac{1}{3}(\epsilon_\infty + 2)e_S.$$

On the other hand, the Szigeti charge is related to the distortion factor  $s$  by  $e_S = se$ , where  $(-e)$  is the electronic charge. For KI [Ref. 23, (b) and (c)]:  $s = 0.69$  and  $\epsilon_\infty = 2.69$ . Therefore,

$$\epsilon^* = \frac{1}{3}s(\epsilon_\infty + 2)e = 1.078e.$$

If all the frequencies are expressed in units of  $\omega_L$ , we can rewrite Eqs. (38) and (25a), respectively, as

$$K^{(B)}(x) = K \operatorname{sgn} x \frac{x + x_0}{x_0} [n(x) + n(x_0) + 1] \\ \times \{a^2 A(x) + abC(x) + b^2 B(x)\}, \quad (40a)$$

$$K^{(A)}(x) = \frac{K'}{x^2(x + 2x_0)^2} K^{(B)}(x), \quad (40b)$$

where  $x = \Omega/\omega_L$ ,  $x_0 = \omega_0/\omega_L$ ,  $x_t = \omega_t/\omega_L$ ,  $S$  is given by Eqs. (B8) and (B5), and  $K$  and  $K'$  have the expressions

$$K = \frac{4\pi^2 \hbar S n_d}{c V M_+ \omega_L^2 \eta}, \quad K' = \left( \frac{\lambda \epsilon \epsilon^* S x_0^2}{\rho m \omega_L^2 (x_0^2 - x_t^2)} \right)^2.$$

In the expression for  $K$ , we have neglected the frequency dependence of the index of refraction  $\eta(\omega)$  in the infrared region and have considered it as a simple constant whose value<sup>24</sup> is 1.61.

The functions  $K^{(B)}(x)$  and  $K^{(A)}(x)$  have been calculated for the frequency range  $0 < x < 1$  and at 4.3°K in the following cases:

<sup>19</sup> J. R. Hardy, *Phil. Mag.* **7**, 315 (1962).

<sup>20</sup> S. S. Jaswal (private communication).

<sup>21</sup> Nguyen X. Xinh, A. A. Maradudin, and R. A. Coldwell-Horsfall, *J. Phys. (Paris)*, **26**, 717 (1965).

<sup>22</sup> A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963), p. 150.

<sup>23</sup> (a) Reference 18, p. 26; (b) *ibid.*, p. 112; (c) *ibid.*, p. 85.  
<sup>24</sup> *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1963), 2nd ed., pp. 6-33.

(a) The  $H^-$   $U$  center is first considered as a simple mass defect whose value is  $\epsilon = 0.99206$ . The localized-mode frequency  $x_0$  calculated from Eq. (39a) therefore has the value of 4.6. The impurity concentration ( $n_d/V$ ) is taken to be 1. The frequency dependence of the contributions to the higher-frequency sideband from the cubic anharmonicity and the second-order electric-dipole moment are plotted separately in Fig. 1. Some values of their ratio  $K^{(A)}(x)/K^{(B)}(x)$  are listed in Table I. The frequency dependence of the total absorption coefficient  $K(x) = K^{(A)}(x) + K^{(B)}(x)$  due to both mechanisms is shown in Fig. 2. The calculated absorption spectrum reproduces reasonably well the experimental one<sup>5</sup> represented by the smooth line of Fig. 4. However, the agreement is rather poor as far as the relative magnitudes of the main peaks are concerned.

(b) One would expect a better result if the force-constant changes at the impurity site  $\{\Delta\Phi_{\alpha\beta}(0,0)\}$  are

TABLE I. The calculated frequency dependence of the ratio  $K^{(A)}(x)/K^{(B)}(x)$  for the high-frequency sideband due to  $H^-$  in KI. The quantity  $K^{(A)}(x)$  is the contribution to the total absorption coefficient from the anharmonicity phonon-coupling mechanism and  $K^{(B)}(x)$  is that from the second-order electric-dipole-moment mechanism. (a) The  $U$  center is treated as a pure mass defect; (b) the  $U$  center is treated as a mass defect associated with a change in force constant.

Frequency $x$	$K^{(A)}(x)/K^{(B)}(x)$	
	(a) Mass-defect model	(b) Effective-mass- defect model
0.05	327	9385
0.15	35.5	1007
0.25	12.5	350
0.35	6.2	173
0.45	3.7	101
0.55		
0.65	1.7	45
0.75	1.2	33
0.85	0.96	25
0.95	0.75	19

taken into account. Actually, we need not calculate explicitly the force-constant changes  $\{\Delta\Phi_{\alpha\beta}(0,0)\}$ . We simply use the experimental value<sup>3</sup> of the localized-mode frequency and calculate the corresponding effective mass defect  $\epsilon'$  with the help of Eq. (39a). It has been found that  $\epsilon'$  has the value 0.97902 for  $H^-$   $U$  centers in a potassium-iodide crystal. The frequency dependence of the total absorption coefficient  $K(x)$  is shown in Fig. 3. The discrepancy between the calculated and experimental data concerning the relative magnitudes of the various peaks has been substantially reduced while the frequencies of these maxima remain unchanged, in comparison with the case of a simple mass-defect model for the impurity (Fig. 2). The values of the ratio  $K^{(A)}(x)/K^{(B)}(x)$  as given in Table I show the predominance of the contribution from the anharmonicity mechanism in the whole frequency range of the higher-frequency sideband.

(c) In principle, the expressions Eqs. (40a) and (40b)

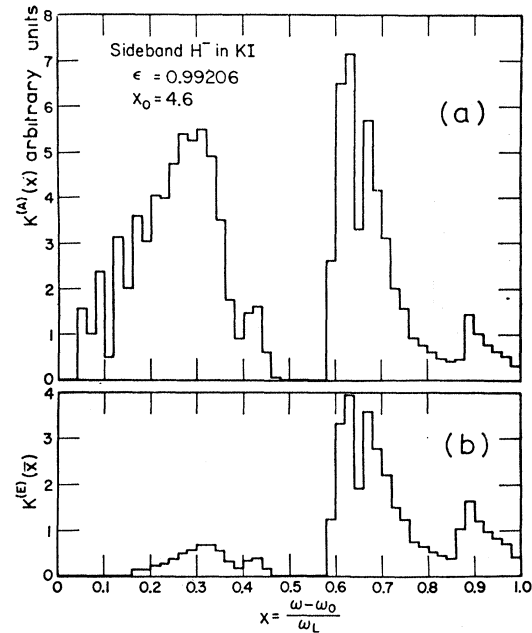


FIG. 1. The calculated frequency dependence of the contributions to the absorption coefficient in the high-frequency sideband due to  $H^-$  in KI treated as a pure mass defect: (a) from the cubic anharmonicity phonon-coupling mechanism; (b) from the second-order electric-dipole-moment mechanism.

of  $K^{(A)}(x)$  and  $K^{(B)}(x)$  give the absolute values of these absorption coefficients if the values of the cubic anharmonic force constants and the second-order electric dipole moment for the perturbed crystal are correctly known. In the present calculation, we have

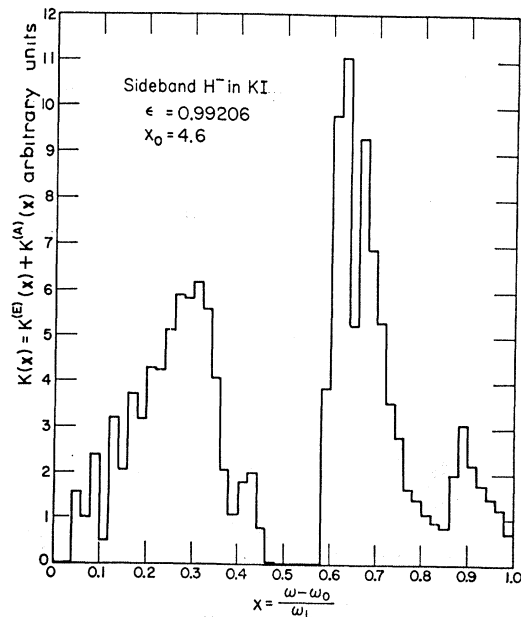


FIG. 2. The calculated frequency dependence of the total-absorption coefficient in the high-frequency sideband due to  $H^-$  in KI treated as a pure mass defect.

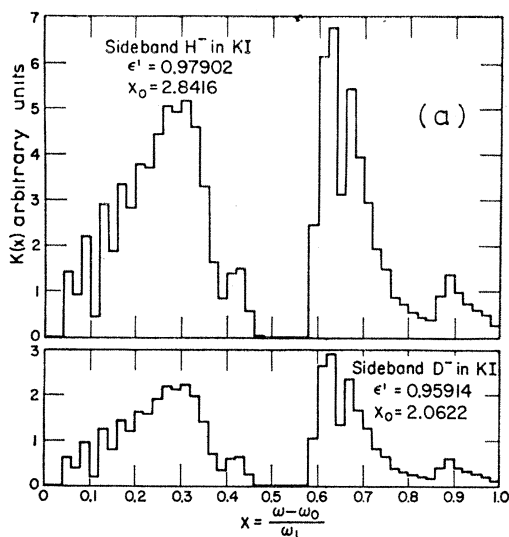


FIG. 3. The calculated frequency dependence of the total absorption coefficient in the high-frequency sideband due to  $H^-$  and  $D^-$   $U$  centers in KI treated as mass defects associated with force-constant changes (effective-mass-defect model).

used the values of these coefficients relevant to the perfect-host crystal. This is, of course, a very drastic approximation and it is not reasonable to expect that the absolute values of the absorption coefficient  $K(x)$  could be obtained in this way. In order to make a close comparison with the experimental spectrum obtained by Timusk<sup>5</sup> (Fig. 4), we have to multiply the theoretical values of  $K(x)$  calculated for an impurity concentration  $n_d/V = 6 \times 10^{17} \text{ cm}^{-3}$  by a factor of 10. As  $K(x)$  is proportional to the square of the constant  $\lambda$  which characterizes the overlap potential, this is equivalent to attributing to  $\lambda$  a value ( $\sqrt{10}$ ) times that corresponding to the perfect-host crystal.

(d) The same calculation as in (c) has been carried

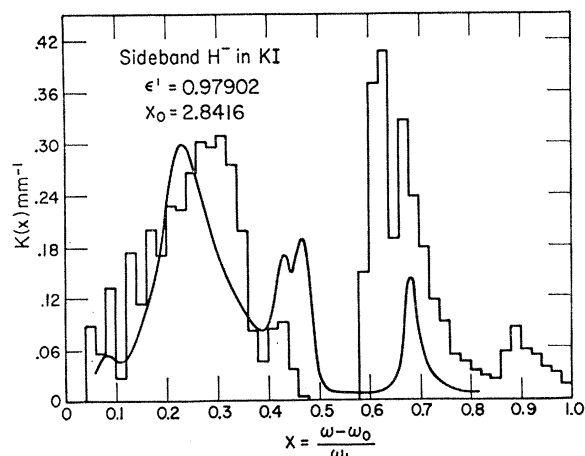


FIG. 4. The calculated spectrum of Fig. 3(a) is compared to the experimental one (smooth line) observed by Timusk (see Ref. 5) at 4.3°K for a concentration of  $6 \times 10^{17}$   $H^-$   $U$  centers per unit volume in KI.

out for  $D^-$   $U$  centers in KI. Using the experimental value for the localized-mode frequency  $\omega_0 = 278.6 \text{ cm}^{-1}$ ,<sup>25</sup> it has been found that the effective mass defect  $\epsilon'$  has the value  $\epsilon' = 0.95914$ . The calculated spectrum  $K(x)$  is shown in Fig. 3. It has exactly the same structure as that arising from  $H^-$   $U$  centers, in agreement with experiments.<sup>5</sup>

#### IV. DISCUSSION

We have presented in this paper a theory of the sidebands to the fundamental localized-mode peak in the infrared lattice absorption spectra of alkali-halide crystals containing isolated  $U$  centers. The results of the application of the theory to the case of a potassium-iodide crystal show clearly the nature of the sidebands as arising from two-phonon processes, the net result of which is the creation of one localized-mode phonon and the creation or destruction of a continuum-mode phonon. It has been shown in the present calculation that both the coupling mechanisms due to the anharmonicity of the crystal potential energy and the second-order electric dipole moment can contribute to these two-phonon absorption processes. As shown in Table I, the relative importance of the two mechanisms at a given frequency depends appreciably on the force-constant changes. Keeping in mind that the anharmonic force constants and the second-order dipole coefficients have been only roughly estimated one can nevertheless infer from the numerical results that in KI the anharmonic coupling would be more efficient than the coupling due to the second-order electric dipole moment.

The numerical results of the application of this theory to the case of a KI crystal present some discrepancies with the experimental data, particularly in the sideband region contributed by the optical phonons of the perfect-host crystal (Fig. 4). These discrepancies are likely due to the use of inaccurate phonon data and the effective-mass-defect approximation for the  $U$  center. As a matter of fact, according to a recent neutron scattering experiment by Dolling *et al.*, the deformation-dipole model for a KI crystal<sup>19,20</sup> which has been used in the present calculation yields values for the position of the gap between acoustical and optical vibrations that are about 10% lower than those given by the best model (whose data were not available to the author at the time the present calculation was carried out). This is reflected in the calculated sideband and is clearly visible on Fig. 4. According to the frequency spectrum of KI computed by Dolling *et al.*,<sup>26</sup> the gap lies between the frequencies  $2.09 \times 10^{12}$  cps and  $2.87 \times 10^{12}$  cps. The experimental sideband peak at  $x = 0.686$  ( $= 2.78 \times 10^{12}$  cps) in Fig. 4 would therefore lie inside the gap and would arise from a gap mode. However,

<sup>25</sup> W. C. Price and G. R. Wilkinson, U. S. Army Technical Report, 1960 (unpublished).

<sup>26</sup> G. Dolling, R. A. Cowley, C. Schittenhelm, and I. M. Thorson, *Phys. Rev.* **147**, 577 (1966).

while gap modes have been observed<sup>27-32</sup> in KI crystals containing  $\text{Cl}^-$ ,  $\text{Tl}^+$ , or  $\text{NO}_2^-$  impurities, none has as yet been directly observed in the one-phonon absorption by KI crystals containing  $U$  centers. On the other hand, as has been pointed out by Bilz *et al.*, in a recent paper<sup>33</sup> in which a pertinent critical discussion is made of the theories of the sidebands, the use of the effective-mass-defect approximation in the present calculation would lead to a force-constant change at the impurity site larger than it should be, because of the neglect of the polarizability of the  $\text{H}^-$  (or  $\text{D}^-$ ) ion. They suggested that from such a strong force-constant change, one would expect the appearance of a gap mode—which has not as yet been observed—probably with the use of a better lattice dynamical model. In the opposite case, should a gap mode really occur near the low-frequency edge of the optical band as suggested by the comparison of Timusk's measured sideband spectrum (Fig. 4) and Dolling's computed frequency spectrum of KI, an over-estimation of the force-constant change at the  $\text{H}^-$  site would have the effect of shifting that gap mode toward higher frequencies into the optical band. Whether or not a gap mode does occur in a KI crystal containing  $\text{H}^-$  ions is therefore still an open question.

As far as the present calculation is concerned, it is also likely that better results would have been obtained if the overlap potential around the impurity could be better evaluated. On the other hand, one can, of course, consider the anharmonic force constants as well as the second-order dipole-moment coefficients as parameters to be determined by the best fitting of the calculated spectra to the experimental ones. However, unless the contribution to the sidebands from the second-order dipole moment is *a priori* neglected in comparison to that from the anharmonicity there will be at least three parameters which make the optimization procedure awkward and physically rather uninformative.

Let us also notice that the formal Eqs. (17) and (36a) are general, and in particular still valid if the polarizability and/or the coupling of the impurity with atoms located farther than its nearest neighbors are taken into account.

#### ACKNOWLEDGMENTS

I am most grateful to Professor A. A. Maradudin for suggesting the problem and for valuable critical discussions; and to Dr. R. R. Heikes for extending to me

<sup>27</sup> T. Timusk and W. Staude, *Phys. Rev. Letters* **13**, 373 (1964).

<sup>28</sup> A. J. Sievers, in *Proceedings of the International Conference on Low Temperature Physics, Columbus, Ohio, 1964* (Plenum Press, Inc., New York, 1965).

<sup>29</sup> A. J. Sievers and C. D. Lytle, *Phys. Letters* **14**, 271 (1965).

<sup>30</sup> K. F. Renk, *Phys. Letters* **14**, 281 (1965).

<sup>31</sup> A. J. Sievers, A. A. Maradudin, and S. S. Jaswal, *Phys. Rev.* **138**, A272 (1965).

<sup>32</sup> H. Bilz, K. F. Renk, and K. H. Timmesfeld, *Solid State Commun.* **3**, 223 (1965).

<sup>33</sup> H. Bilz, D. Strauch, and B. Fritz, *J. Phys. (Paris) Suppl.* **5**, C2 (1966); **6**, C3 (1966).

the hospitality of his directorate at the Westinghouse Research Laboratories. I would like to thank Miss B. J. Kagle for performing some of the numerical computations reported in this paper.

#### APPENDIX A

The general element of the perturbation matrix  $\delta l$  which describes a point-ion model for a negative impurity located at the lattice site  $(l\kappa) = (0-)$  has the expression<sup>34</sup>

$$\delta l_{\alpha\beta}(l\kappa, l'\kappa'; \omega^2) = \epsilon\omega^2 M_- \delta_{l0} \delta_{l'0} \delta_{\kappa-} \delta_{\kappa'-} \delta_{\alpha\beta} + \Delta\Phi_{\alpha\beta}(l\kappa, l'\kappa'), \quad (\text{A1})$$

where  $\epsilon = 1 - (M_-'/M_-)$  is the mass defect and  $\{\Delta\Phi_{\alpha\beta}(l\kappa, l'\kappa')\}$  are the force-constant changes. The latter, like the force constants  $\{\Phi_{\alpha\beta}(l\kappa, l'\kappa')\}$ , must satisfy the relation

$$\sum_{l'\kappa'} \Delta\Phi_{\alpha\beta}(l\kappa, l'\kappa') = 0, \quad (\text{A2})$$

which results from the requirement that the energy of the crystal be invariant under a rigid-body displacement, and which, in the present case, can be written explicitly as

$$\Delta\Phi_{xx}(0-, 0-) + 2\Delta\Phi_{xx}(0-, 1+) + 4\Delta\Phi_{yy}(0-, 1+) = 0, \quad (\text{A3})$$

where  $(1+)$  denotes the lattice-site nearest neighbor to the impurity on the positive  $x$  axis.

If all the force-constant changes  $\{\Delta\Phi_{\alpha\beta}(l\kappa, l'\kappa')\}$  are assumed to be zero, the right-hand side of Eq. (A1) reduces to its first term,

$$\delta l_{\alpha\beta}(l\kappa, l'\kappa'; \omega^2) = \epsilon\omega^2 M_- \delta_{l0} \delta_{l'0} \delta_{\kappa-} \delta_{\kappa'-} \delta_{\alpha\beta}, \quad (\text{A4})$$

and the corresponding matrix  $\delta l$  then describes a simple mass-defect model for the impurity.

One has a better description of a  $U$  center in alkali-halide crystals by considering that all the force-constant changes  $\{\Delta\Phi_{\alpha\beta}(l\kappa, l'\kappa')\}$  are zero except those associated with the impurity site only, namely  $\{\Delta\Phi_{\alpha\beta}(0-, 0-)\}$ . We know that, under a symmetry operation which takes the crystal into itself, leaving the impurity site fixed, the force constants and therefore the force-constant changes transform as the components of second-rank tensors. In an alkali-halide crystal, the impurity is at a site of  $O_h$  symmetry. It can therefore be easily shown that the tensor  $\Delta\Phi_{\alpha\beta}(0-, 0-)$  is diagonal and isotropic i.e.,

$$\Delta\Phi_{\alpha\beta}(0-, 0-) = \delta_{\alpha\beta} \Delta\Phi, \quad (\text{A5})$$

where  $\Delta\Phi$  is a scalar. The expression Eq. (A1) of the matrix  $\delta l$  therefore reduces to

$$\delta l_{\alpha\beta}(l\kappa, l'\kappa'; \omega^2) = (\epsilon\omega^2 M_- + \Delta\Phi) \delta_{l0} \delta_{l'0} \delta_{\kappa-} \delta_{\kappa'-} \delta_{\alpha\beta} + \epsilon' \omega^2 M_- \delta_{l0} \delta_{l'0} \delta_{\kappa-} \delta_{\kappa'-} \delta_{\alpha\beta}, \quad (\text{A6})$$

<sup>34</sup> See, for example, Ref. 8, p. 338.

where we have defined a frequency-dependent "effective-mass defect" by

$$\epsilon' = \epsilon + (\Delta\Phi/\omega^2 M_-). \quad (\text{A7})$$

In a localized mode of frequency  $\omega_0$ ,  $\epsilon'$  has the expression

$$\epsilon' = \epsilon + (\Delta\Phi/\omega_0^2 M_-). \quad (\text{A8})$$

Equation (A6) has the same form as Eq. (A4).

The "effective-mass-defect" model for the impurity just described obviously violates the invariance condition Eq. (A3). Its use can be justified crudely on the basis that in the expression Eq. (A1) of the perturbation matrix  $\delta l$ , the term in  $\omega^2$  which is nonzero for the impurity site only is, for the localized modes ( $\omega = \omega_0$ ), generally much larger than any force-constant change  $\Delta\Phi_{\alpha\beta}(lk, l'\kappa')$ . Therefore, although the force-constant changes  $\Delta\Phi_{xx}(0-, 1+)$  and  $\Delta\Phi_{yy}(0-, 1+)$  are not really very small in comparison to the force-constant change  $\Delta\Phi_{xx}(0-, 0-)$  at the impurity site, they are indeed small compared to the term in  $\omega^2$ .

## APPENDIX B

The sum  $\sum_{\sigma} C_{\alpha}^{(\sigma)}(0-)C_{\beta}^{(\sigma)}(0-)$  has been calculated for a Bravais crystal in Ref. 35. We are concerned here with a crystal of the rock-salt structure.

The vibrational eigenvectors  $\{\mathbf{C}^{(\sigma)}(lk)\}$  of the localized modes labeled by  $\sigma$  and whose frequency is  $\omega_0$  satisfy the following orthonormality relation:

$$\sum_{l\kappa\alpha} M_{l\kappa} [C_{\alpha}^{(\sigma)}(lk)]^2 = 1, \quad (\text{B1})$$

where  $(lk)$  runs over all the lattice sites of the crystal.

The amplitude  $\mathbf{C}^{(\sigma)}(lk)$  associated with any atom other than the impurity is related to the amplitude\* of the impurity atom itself (assumed to be located at the origin of the coordinate axes) by the relation<sup>35</sup>

$$C_{\alpha}^{(\sigma)}(lk) = \epsilon M_- \omega_0^2 \sum_{\beta} G_{\alpha\beta}(lk, 0-; \omega_0^2) C_{\beta}^{(\sigma)}(0-), \quad (\text{B2})$$

where the Green's function  $G_{\alpha\beta}(lk, l'\kappa'; \omega^2)$  is defined by Eq. (24).

Substituting the expression Eq. (B2) for  $C_{\alpha}^{(\sigma)}(lk)$  in Eq. (B1), we have that

$$\begin{aligned} 1 = & -\epsilon M_- \sum_{\alpha} [C_{\alpha}^{(\sigma)}(0-)]^2 + \epsilon^2 \omega_0^4 M_-^2 \\ & \times \sum_{l\kappa} \sum_{\alpha\beta\gamma} M_{\kappa} G_{\alpha\beta}(lk, 0-; \omega_0^2) \\ & \times G_{\alpha\gamma}(lk, 0-; \omega_0^2) C_{\beta}^{(\sigma)}(0-) C_{\gamma}^{(\sigma)}(0-). \quad (\text{B3}) \end{aligned}$$

By expanding the Green's function according to Eq. (24), then subsequently making use of the orthonormality of the eigenvectors  $\{\mathbf{W}(\kappa|\mathbf{k}j)\}$  and the cubic

symmetry of the crystal at the impurity site (0-), we obtain

$$\sum_{l\kappa\alpha} M_{\kappa} G_{\alpha\beta}(lk, 0-; \omega_0^2) G_{\alpha\gamma}(lk, 0-; \omega_0^2) = \delta_{\beta\gamma} g / M_-, \quad (\text{B4})$$

where

$$g = \frac{1}{3N} \sum_{\kappa j} \frac{\mathbf{W}(-|\mathbf{k}j)\mathbf{W}^*(-|\mathbf{k}j)}{[\omega_0^2 - \omega_j^2(\mathbf{k})]}. \quad (\text{B5})$$

Taking account of Eq. (B4), we derive from Eq. (B3) that

$$\sum_{\alpha} [C_{\alpha}^{(\sigma)}(0-)]^2 = [\epsilon M_- (\epsilon \omega_0^4 g - 1)]^{-1}. \quad (\text{B6})$$

Because the  $\{\mathbf{C}^{(\sigma)}(0-)\}$  ( $\sigma = 1, 2, 3$ ) are the normalized eigenvectors of a  $3 \times 3$  real, symmetric matrix, it follows from Eq. (B6) that they must also satisfy the closure relation

$$\sum_{\sigma} C_{\alpha}^{(\sigma)}(0-) C_{\beta}^{(\sigma)}(0-) = \delta_{\alpha\beta} S, \quad (\text{B7})$$

with

$$S = [\epsilon M_- (\epsilon \omega_0^4 g - 1)]^{-1}. \quad (\text{B8})$$

We now turn to the calculation of the sum

$$\Sigma = \sum_{\sigma} \sum_{l\kappa l'\kappa'} \epsilon_{\kappa} \epsilon_{\kappa'} C_{\nu}^{(\sigma)}(lk) C_{\mu}^{(\sigma)}(l'\kappa'). \quad (\text{B9})$$

Let us first define a coefficient  $C_{\nu}$  by

$$C_{\nu} = \sum_{l\kappa} \epsilon_{\kappa} C_{\nu}^{(\sigma)}(lk). \quad (\text{B10})$$

According to Eqs. (B2) and (24), Eq. (B10) can be written as

$$\begin{aligned} C_{\nu} = & \frac{\epsilon M_- \omega_0^2}{NM_-^{1/2}} \sum_{l\kappa} \sum_{\kappa j\alpha} \frac{\epsilon_{\kappa}}{M_{\kappa}^{1/2}} \frac{W_{\nu}(\kappa|\mathbf{k}j) W_{\alpha}(-|\mathbf{k}j)}{\omega_0^2 - \omega_j^2(\mathbf{k})} \\ & \times e^{2\pi i \mathbf{k}' \cdot \mathbf{x}(lk)} C_{\alpha}^{(\sigma)}(0-). \end{aligned}$$

The summation over  $l$  and  $\mathbf{k}$  are straightforward; we obtain

$$C_{\nu} = \frac{\epsilon M_- \omega_0^2}{M_-^{1/2}} \sum_{j\kappa\alpha} \frac{\epsilon_{\kappa}}{M_{\kappa}^{1/2}} \frac{W_{\nu}(\kappa|\mathbf{0}j) W_{\alpha}(-|\mathbf{0}j)}{\omega_0^2 - \omega_j^2(\mathbf{0})} C_{\alpha}^{(\sigma)}(0-).$$

Writing explicitly the sum over  $\kappa$  and taking account of Eq. (7b), we have that

$$\begin{aligned} C_{\nu} = & \frac{\epsilon M_- \omega_0^2 \epsilon^*}{M_-^{1/2}} \sum_{j\alpha} C_{\alpha}^{(\sigma)}(0-) \frac{W_{\alpha}(-|\mathbf{0}j)}{\omega_0^2 - \omega_j^2(\mathbf{0})} \\ & \times \left[ \frac{W_{\nu}(+|\mathbf{0}j)}{M_+^{1/2}} \frac{W_{\nu}(-|\mathbf{0}j)}{M_-^{1/2}} \right]. \quad (\text{B11}) \end{aligned}$$

If  $j$  refers to an acoustic branch, the expression in brackets in Eq. (B11) vanishes.<sup>36</sup> Therefore the acoustic

<sup>35</sup> A. A. Maradudin, in *Phonons and Phonon Interactions*, edited by Thor A. Bak (W. A. Benjamin, Inc., New York, 1964), p. 424.

<sup>36</sup> This follows from Eqs. (2.1.32) and (2.1.35b) of Ref. 22, respectively.

modes do not contribute to the coefficient  $C_v$ . If  $j$  refers to an optical branch, we have that<sup>36</sup>

$$\left[ \frac{W_v(+|\mathbf{0}j)}{M_+^{1/2}} - \frac{W_v(-|\mathbf{0}j)}{M_-^{1/2}} \right] = - \left( \frac{M_-^{1/2}}{M_+} + \frac{1}{M_-^{1/2}} \right) W_v(-|\mathbf{0}j).$$

Therefore,

$$C_v = \sum_{l\kappa} \epsilon_\kappa C_v^{(\sigma)}(l\kappa) = -\epsilon\omega_0^2 \epsilon^* \left( \frac{M_+ + M_-}{M_+} \right) \times \sum_{j\alpha} C_\alpha^{(\sigma)}(0-) \frac{W_\alpha(-|\mathbf{0}j)W_v(-|\mathbf{0}j)}{\omega_0^2 - \omega_j^2(\mathbf{0})}, \quad (\text{B12})$$

where  $j$  runs over the optical branches only.

The sum Eq. (B9) can now be written as

$$\Sigma = \left( \epsilon\omega_0^2 \epsilon^* \frac{M_+ + M_-}{M_+} \right) \sum_{\sigma} \sum_{jj'} \sum_{\alpha\beta} C_\alpha^{(\sigma)}(0-) C_\beta^{(\sigma)}(0-) \times \frac{W_\alpha(-|\mathbf{0}j)W_v(-|\mathbf{0}j)}{\omega_0^2 - \omega_j^2(\mathbf{0})} \frac{W_\beta(-|\mathbf{0}j')W_\mu(-|\mathbf{0}j')}{\omega_0^2 - \omega_{j'}^2(\mathbf{0})}.$$

If the sum over  $\sigma$  is done using Eq. (B7) and the sum over  $\beta$  subsequently carried out, we obtain

$$\Sigma = S \left( \epsilon\omega_0^2 \epsilon^* \frac{M_+ + M_-}{M_+} \right)^2 \sum_{jj'\alpha} \frac{W_\alpha(-|\mathbf{0}j)W_v(-|\mathbf{0}j)}{\omega_0^2 - \omega_j^2(\mathbf{0})} \times \frac{W_\alpha(-|\mathbf{0}j')W_\mu(-|\mathbf{0}j')}{\omega_0^2 - \omega_{j'}^2(\mathbf{0})}, \quad (\text{B13})$$

where  $j$  and  $j'$  runs over the optical branches only.

For an ionic crystal of the rock-salt structure, it can be shown<sup>37</sup> that the eigenvectors of the optical modes satisfy the following orthogonality and closure relations:

$$\sum_{\alpha} W_\alpha^*(-|\mathbf{0}j)W_\alpha(-|\mathbf{0}j') = \mu \delta_{jj'}, \quad (\text{B14a})$$

$$\sum_j W_\alpha(-|\mathbf{0}j)W_\beta^*(-|\mathbf{0}j) = \mu \delta_{\alpha\beta}, \quad (\text{B14b})$$

where  $\mu = M_+/(M_+ + M_-)$  and  $j, j'$  refer to any of the optical branches. Using successively Eqs. (B14a) and (B14b) to carry out the sums over  $\alpha$  and  $j'$  in Eq. (B13), we obtain

$$\Sigma = \mu S \left( \frac{\epsilon\omega_0^2 \epsilon^*}{\mu} \right)^2 \sum_{j=\text{opt}} \frac{W_v(-|\mathbf{0}j)W_\mu(-|\mathbf{0}j)}{[\omega_0^2 - \omega_j^2(\mathbf{0})]^2}. \quad (\text{B15})$$

Let us denote by  $\omega_l(\mathbf{0})$  and  $\omega_t(\mathbf{0})$  the frequencies of the zero-wave-vector longitudinal and (doubly degenerate) transverse optical modes and label the corresponding branches by  $j=1, 2, 3$ . The eigenvector of the zero-wave-vector longitudinal optical mode as determined in Ref. 14 has the following expression:

$$\mathbf{W}(-|\mathbf{0}1) = -(\mu)^{1/2} \frac{\mathbf{k}}{|\mathbf{k}|}. \quad (\text{B16})$$

Making use of Eqs. (B14b) and (B16), we can finally write Eq. (B15) as

$$\Sigma = S(\epsilon\omega_0^2 \epsilon^*)^2 \left\{ \frac{1}{[\omega_0^2 - \omega_l^2(\mathbf{0})]^2} \frac{k_\mu k_\nu}{k^2} + \frac{1}{[\omega_0^2 - \omega_t^2(\mathbf{0})]^2} \left( \delta_{\mu\nu} - \frac{k_\mu k_\nu}{k^2} \right) \right\}. \quad (\text{B17})$$

<sup>37</sup> This follows from Eqs. (2.1.27a) and (2.1.35b) of Ref. 22.