Infrared Lattice Absorption of Ionic Crystals Containing Finite Impurity Concentrations

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A theoretical calculation of the effect of isotopic defects on the infrared lattice absorption of ionic crystals is presented. The main concern has been to establish the relative strength of the absorption by local vibrations in such a system as compared with that of the nonlocal modes. It has been found that, when a local mode exists, it may display a vastly enhanced absorption cross section as compared with that of a charged defect in a nonpolar host. This effect arises from the fact that the uniform external field interacts directly with the zero-wave-vector components of the normal modes of the imperfect crystal. This interaction induces transitions into states which are not true eigenstates of the lattice Hamiltonian, and in which there is an effective coupling between band and local modes that results in the scattering and absorption of band-mode phonons by the local vibrations. It has been shown that if the local-mode absorption frequency is close to that of the pure crystal, a small concentration of impurity is sufficient to shift the main absorption to the local-mode frequency, as has been observed in the case of Li(H,D) mixtures containing 5% D⁻ impurity. Furthermore, application of the theory to calculating the temperature dependence of the total vibrational absorption by the local modes of U centers (H⁻ or D⁻ ions substituted into an alkali halide) has shown that, even for single defects which produce highly localized vibrations, it is incorrect to regard the local-mode and host-lattice absorptions as independent.

1. INTRODUCTION

THE main part of this paper is concerned with a fuller presentation of the theoretical interpretation[1] of observations[2,3] on the absorption spectra of lithium hydride-deuteride (Li,H,D) mixtures, the principal object of this part of the work being an understanding of the anomalous shift of the fundamental absorption of LiH produced by the addition of ∼5% LiD. While the details of the full spectra are uncertain it has been clearly established that in such mixtures the strongest absorption occurs at or near the frequency characteristic of pure LiD.

A theoretical understanding of this result involves studying the dynamics of an ionic crystal containing a *finite* concentration of defects and the interaction of its normal modes with external radiation. This problem does not appear to have been studied previously for a three-dimensional lattice, although Maradudin and Wallis[4] have treated an ionic linear chain containing one or two defects.

To solve the present problem we shall use the more recent results of Dawber and Elliott.[5,6] While this work provides the means of treating isolated defects in a real crystal, it is not directly applicable to the present problem since these authors were interested in the

infrared absorption produced by charged defects in nonionic host lattices. We can, however, use some of their results as a starting point in the present work and our notation will be very similar to theirs.

2. THEORY

For a perfect crystal the normal modes are plane waves, each specified by **k** its wave vector, and j its branch index. In an ionic crystal only the transverse optic modes at **k**=**0** will interact with an external electromagnetic field. When the crystal contains defects the normal modes are no longer plane waves and all modes may have **k**=**0** Fourier components and thus absorb radiation. Fortunately, as we are concerned with an effect which occurs at low defect concentrations, we are able to avoid determining the true normal coordinates. This is possible because the majority of the photons are then absorbed in regions of perfect crystal as **k**=**0** phonons which are quasistationary states of the whole system. These phonons then interact with the defects and, as we shall show, resonance scattering of these phonons by local modes at the D⁻ ion sites produces the observed shift in the fundamental absorption frequency. The initial absorption still takes place in the host lattice, but the phonon produced is a virtual phonon and over-all energy conservation is maintained by its subsequent conversion to a real local-mode phonon.[1]

To demonstrate the existence of the local modes we apply the results of Ref. 5 to the H⁻ sublattice, and regard the Li⁺ ions as infinitely heavy. This is a reasonable approximation and very much simplifies the problem as we can then use the results appropriate to a monatomic cubic lattice.[7]

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[1] D. J. Montgomery and J. R. Hardy, International Conference on Lattice Dynamics, Copenhagen, 1963, to be published in Phys. Chem. Solids.

[2] W. B. Zimmerman and D. J. Montgomery, Phys. Rev. **120**, 405 (1960).

[3] R. H. Misho, W. B. Zimmerman, and D. J. Montgomery, International Symposium on Far Infrared Spectroscopy, Cincinnati, Ohio, August, 1962 (unpublished); TID-17203, Abstract 2947 (unpublished); Nucl. Sci. Abstr. **17**, 402 (1963).

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

[5] P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) **A273**, 222 (1963).

[6] P. G. Dawber and R. J. Elliott, Proc. Phys. Soc. (London) **81**, 453 (1963).

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[7] While this approximation may seem too drastic for Li(H,D) mixtures, it would obviously be very much better for Na(H,D) or any other alkali hydride-deuteride mixture. For any of the last salts the error would be negligible.

Then the perturbed eigenfrequencies (indexed by f) are determined by the integral equation:

$$1+\frac{\epsilon\omega^2(f)}{3N}\sum_{\mathbf{k},j}\frac{1}{\omega_j^2(\mathbf{k})-\omega^2(f)}=0, \qquad (1)$$

where $\epsilon\equiv(M_H-M_D)/M_H$, and N is the number of H⁻ ions/unit volume.

Or

$$1+\epsilon Z\int_0^{\mu m}\frac{\nu(\mu)}{\mu-Z}d\mu=0, \qquad (1a)$$

where $Z=\omega^2(f)$ and $\omega_j^2(\mathbf{k})=\mu_j(\mathbf{k})=\mu$, and $\nu(\mu)$ is the normalized frequency distribution [i.e., $\int_0^{\mu m}\nu(\mu)d\mu=1$].

The neutron-scattering data of Woods et al.[8] suggest that $\nu(\mu)$ can be approximated by two delta functions with amplitudes in the ratio $2:1$; the first, representing the transverse optic (TO) modes, placed at $\mu_1=\omega_0^2$ (ω_0 being the TO frequency at $\mathbf{k}=0$) and the second at $\mu_2=3.5\omega_0^2$ corresponding to the longitudinal optic-mode frequency at $\mathbf{k}=0$.

Equation (1a) then has a solution $Z=0.6\omega_0^2$ corresponding to a triply degenerate local mode lying in the observed[8] gap between the optic and acoustic modes of LiH. There is also a second root lying between μ_1 and μ_2, but this is spurious as the true spectrum has a finite density of states in this region and the delta-function approximation can only be used to derive the frequencies of modes lying outside the range of the band modes. The resultant Z value is somewhat uncertain, but is nonetheless sufficiently accurate for the

present work and is not greatly influenced by the use of more refined frequency spectra.

We also have from Ref. 5 an expression for the eigenvectors $X_\beta(f,l)$ of the dynamical matrix for the imperfect crystal:

$$X_\beta(f,l)=-\frac{\epsilon}{N}\sum_{\alpha\mathbf{k}j}\frac{\sigma_\beta^{*j}(\mathbf{k})\sigma_\alpha^{j}(\mathbf{k})\omega^2(f)X_\alpha(f,0)}{\omega_j^2(\mathbf{k})-\omega^2(f)}e^{-i\mathbf{k}\cdot\mathbf{R}_l}. \qquad (2)$$

The unperturbed eigenvectors are

$$X_\beta^{j}(\mathbf{k},l)=\sigma_\beta^{*j}(\mathbf{k})(NM)^{-1/2}e^{i\mathbf{k}\cdot\mathbf{R}_l},$$

$M=M_H$, and the branch index $j=1$, 2, or 3. l specifies a particular unit cell at a position $\mathbf{R}_l$ relative to the defect site $l=0$.[9]

Evidently we can write the perturbed eigenvectors in terms of the unperturbed eigenvectors thus:

$$X_\alpha(f,l)=\sum_{\beta j\mathbf{k}}X_{\alpha\beta}^{\mathbf{k}j}(f)X_\alpha^{j}(\mathbf{k},l), \qquad (3)$$

where

$$X_{\alpha\beta}^{\mathbf{k}j}(f)=-\epsilon\left(\frac{M}{N}\right)^{1/2}\frac{\sigma_\beta^{j}(\mathbf{k})X_\beta(f,0)\omega^2(f)}{\omega_j^2(\mathbf{k})-\omega^2(f)}. \qquad (3a)$$

We know that the Hamiltonian of the imperfect crystal is given by

$$H=\tfrac{1}{2}\sum_f[\dot{d}(f)]^2+\omega^2(f)[d(f)]^2,$$

where $d(f)$ and $\dot{d}(f)$ refer to normal-mode amplitudes and their time derivatives. We can now express H in a different form if we use Eq. (3). Thus,

$$H=\tfrac{1}{2}\{\sum_{ff'\alpha\beta\mathbf{k}j}MX_{\alpha\beta}^{\mathbf{k}j}(f)X_{\alpha\beta}^{-\mathbf{k}j}(f')[\dot{d}(f)\dot{d}(f')+\omega_j^2(\mathbf{k})d(f)d(f')]\}+\tfrac{1}{2}\Delta M\sum_{ff'\alpha\beta}X_\alpha(f,0)X_\beta(f',0)\dot{d}(f)\dot{d}(f'),$$

where $\Delta M\equiv M'-M$; and if we now quantize and express H in terms of creation and destruction operators $a^+(f)$ and $a(f)$, we have

$$H=\frac{\hbar}{4}\sum_{ff'\alpha\beta\mathbf{k}j}MX_{\alpha\beta}^{\mathbf{k}j}(f)X_{\alpha\beta}^{-\mathbf{k}j}(f')$$

$$\times\left\{[\omega(f)\omega(f')]^{1/2}[a^+(f)-a(f)][a(f')-a^+(f')]+\frac{\omega_j^2(\mathbf{k})}{[\omega(f)\omega(f')]^{1/2}}[a(f)+a^+(f)][a(f')+a^+(f')]\right\}$$

$$+\frac{\Delta M\hbar}{4}\sum_{ff'\alpha\beta}[\omega(f)\omega(f')]^{1/2}X_\alpha(f,0)X_\beta(f',0)[a^+(f)-a(f)][a(f')-a^+(f')]. \qquad (4)$$

Our concern is with the absorption of radiation at normal incidence by a plate of crystal whose thickness≪wavelength of the photons. For convenience we shall consider a plane-polarized beam; and its interaction with the crystal is then given by the anti-Hermitian operator

$$H_e\propto\left(\frac{\hbar}{2MN}\right)^{1/2}i\sum_f\frac{X^0(f)}{\omega(f)^{1/2}}[a(f)+a^+(f)], \qquad (5)$$

where $X^0(f)\equiv\sum_{\beta j}X_{\beta\alpha}^{0j}(f)$, the α axis being chosen parallel to the direction of polarization. From the form of Eq. (5) it is evident that H_e operating on any given eigenstate of H produces a superposition of such eigenstates, which is not itself an eigenstate of H.

[8] A. D. B. Woods, B. N. Brockhouse, M. Sakomoto, and R. N. Sinclair, Inelastic Scattering of Neutrons in Solids and Liquids (International Atomic Energy Agency, Vienna, 1961), p. 487.
[9] Note the minus sign on the right-hand side of Eq. (2) which was omitted from the corresponding Eq. (3.8) of Ref. 5.

The normal approach in these circumstances is to use first-order perturbation theory to derive the absorption coefficient $\kappa(\omega)$.

This leads to the result

$$\kappa(\omega) \propto \sum_f [\chi^0(f)]^2 \delta[(\omega - \omega(f))]. \tag{6}$$

But we must remember that three of the indices f refer to local modes of frequency ω'; thus, we shall rewrite H in the form such that the band and local-mode parts are explicitly separated. Also, we confine our attention to the $\mathbf{k}=0$, $j=\alpha$ part of H, H_0.

We then have

$$H_0 = \hbar/4 \sum_{ff'} M \chi^0(f) \chi^0(f') \Big\{ [\omega(f)\omega(f')]^{1/2} [a^+(f) - a(f)][a(f') - a^+(f')]$$

$$+ \frac{\omega_0^2}{[\omega(f)\omega(f')]^{1/2}} [a(f) + a^+(f)][a(f') + a^+(f')] + \sum_L \hbar\omega'(a_L^+ a_L + \tfrac{1}{2}) \Big\}$$

$$+ \hbar M/2 \sum_L \sum_f' \chi^0(L)\chi^0(f) \Big\{ \Big[1 + \frac{\Delta M}{M} \frac{\chi(L,0)}{\chi^0(L)} \Big] [\omega'\omega(f)]^{1/2} [a_L^+ - a_L][a(f) - a^+(f)]$$

$$+ \frac{\omega_0^2}{[\omega'\omega(f)]^{1/2}} [a_L + a_L^+][a(f) + a^+(f)] \Big\}, \tag{7}$$

where the index $L = (1,2,3)$ refers to the local modes $\omega_0 = \omega_\alpha(0)$, and the primes on sums over f exclude the terms $f \equiv L$. Since the dominant terms in these sums arise from those in which $\omega(f) = \omega(f') = \omega_0$, we may write:

$$H_0 \approx \sum_f' \hbar |\chi^0(f)|^2 \omega_0 [a^+(f)a(f) + \tfrac{1}{2}] + \sum_L \hbar\omega'(a_L^+ a_L + \tfrac{1}{2}) + \hbar M/2 \sum_{Lf}' \chi^0(L)\chi^0(f)$$

$$\times \Big\{ [\omega(f)\omega']^{1/2} \Big[\Big(1 + \frac{\Delta M}{M} \frac{\chi(L,0)}{\chi^0(L)} \Big)(a_L^+ - a_L)(a(f) - a^+(f)) + \frac{\omega_0^2}{[\omega(f)\omega']}(a_L^+ + a_L)(a(f) + a^+(f)) \Big] \Big\}. \tag{8}$$

We can write the last term in Eq. (8), which we shall denote by $\sum_L V_L$, as

$$\sum_L V_L = \sum_{Lf}' \gamma_L(f)[a^+(f) + a(f)][a_L^+ + a_L] - \gamma_L'(f)[a^+(f) - a(f)][a_L^+ - a_L],$$

or

$$\sum_L V_L = \hbar \sum_{Lf}' \eta_L(f)[a^+(f)a_L^+ + a(f)a_L] + \eta_L'(f)[a^+(f)a_L + a(f)a_L^+], \tag{9}$$

where $\hbar\eta_L(f) = \gamma_L(f) - \gamma_L'(f)$; $\hbar\eta_L'(f) = \gamma_L(f) + \gamma_L'(f)$.

If we now compare Eqs. (5), (7), and (8) we see that the electromagnetic interaction H_e, defined by the first equation, induces transitions between the eigenstates of $H_0 - V_L$ which are also eigenstates of $H - V_L$. Consequently we must use these states when we calculate the matrix elements of H_e. An alternative way of regarding this result is to recognize that V_L would, in a classical theory, give rise to a generalized force on the local mode when a uniform external field stimulates the $\mathbf{k}=0$ mode of the whole crystal. Since this action on the local mode produces an equal and opposite reaction on the $\mathbf{k}=0$ mode, it follows that the response of the lattice is correspondingly reduced.

Let us characterize each eigenstate of H by two numbers thus: $|n(f), n_L\rangle$, where the first denotes the number of quanta present in a band mode (f) and the second the number present in a particular local mode L. Then, for simplicity, we shall consider that $n(f) = n_L = 0$ for the ground state.

Let us consider the following states $|1,0\rangle$, $|0,1\rangle$ and the ground state $|0,0\rangle$ and see how they are changed by the perturbation $-V_L$.

Thus

$$|1,0\rangle \to |A\rangle = |1,0\rangle + \sum_L \frac{\eta_L'(f)}{\omega' - \omega(f)}|0,1\rangle + \sum_L \frac{\eta_L(f)2^{1/2}}{\omega' + \omega(f)}|2,1\rangle, \tag{10a}$$

$$|0,0\rangle \to |B\rangle = |0,0\rangle + \sum_L \frac{\eta_L(f)}{\omega' + \omega(f)}|1,1\rangle + \sum_L \frac{\eta_L(f)\eta_L'(f)}{2^{1/2}\omega(f)[\omega' + \omega(f)]}, \tag{10b}$$

$$|0,1\rangle \to |0,1\rangle - \sum_L \frac{\eta_L'(f)}{[\omega' - \omega(f)]}|A\rangle, \tag{10c}$$

where we have included only those terms which influence the absorption coefficient.

For a finite defect concentration c we can generalize Eqs. (10) by summing the perturbation corrections in Eqs. (10a) and (10b) over all the defects, provided that c is small enough to allow us to neglect interdefect interactions. In this limit we must calculate all quantities correct to first order in c. This is the reason for including the final term in Eq. (10b) which, although it is of higher order for a *single* defect, produces effects of order c in an assembly.[10]

We can now calculate the absorption coefficient $\kappa(\omega)$ defined by

$$\kappa(\omega) = (\omega_j - \omega_i) |\langle i|He|j\rangle|^2 \delta[\omega - (\omega_j - \omega_i)]$$

using the corrected states $|i\rangle$ and $|j\rangle$ defined by Eqs. (10), except that we must normalize $|A\rangle$ and $|B\rangle$ everywhere. Thus, if

$$\langle A|A\rangle\langle B|B\rangle = X = 1 + \sum_{Li} \frac{\eta_{L}{}'(f)^2}{[\omega' - \omega(f)]^2} + \sum_{Li} \frac{3\eta_L(f)^2}{[\omega' + \omega(f)]^2}, \tag{11}$$

$$\kappa(\omega) = \sum_{f}{}' \frac{\Omega(f)}{\omega(f)X} \left\{ \chi^0(f) + \sum_{Li} \chi^0(L) \left(\frac{\omega(f)}{\omega'}\right)^{1/2} \left(\frac{\eta_{L}{}'(f)}{\omega' - \omega(f)} + \frac{\eta_L(f)}{\omega' + \omega(f)}\right) \right.$$

$$\left. + \sum_{Li} \frac{\eta_L(f)\eta_{L}{}'(f)\chi^0(f)\omega'}{\omega(f)[\omega'^2 - \omega(f)^2]} + \sum_{Li} \frac{2\chi^0(f)\eta_L(f)^2}{[\omega' + \omega(f)]^2} \right\}^2 \delta[\omega - \Omega(f)]$$

$$+ \sum_{Li} \left\{ \chi^0(L) - \left(\frac{\eta_{L}{}'(f)}{\omega' - \omega(f)} + \frac{\eta_L(f)}{\omega' + \omega(f)}\right)\left(\frac{\omega}{\omega(f)X}\right)^{1/2} \right\}^2 \delta(\omega - \omega'), \tag{12}$$

where $\hbar\Omega(f)$ is the energy difference between the perturbed states $|A\rangle$ and $|B\rangle$. Thus,

$$\Omega(f) = (1/\hbar)(E_A - E_B)$$

$$= \omega(f) - \sum_{Li} \left(\frac{\eta_{L}{}'(f)^2}{\omega' - \omega(f)} + \frac{\eta_L(f)^2}{\omega' + \omega(f)}\right), \tag{13}$$

where E_A and E_B are the corrected energies of states $|A\rangle$ and $|B\rangle$.

Here and elsewhere the sums over i refer to summations over all defects and, in Eq. (11) we retain only those terms up to order c.

If we now use Eq. (12) to evaluate $\int_0^\infty \kappa(\omega)d\omega$ we find that

$$\int_0^\infty \kappa(\omega) = \sum_{f}{}' |\chi^0(f)|^2 + \sum_{Li} |\chi^0(L)|^2 - 2\sum_{fLi} \frac{\chi^0(f)\chi^0(L)}{X[\omega'\omega(f)]^{1/2}}$$

$$\times [\eta_{L}{}'(f) - \eta_L(f)]\delta[\omega - \Omega(f)] \tag{14}$$

correct to first order in c.

Since the integrated absorption determines the difference between the static and high-frequency dielectric constants and this difference is unaltered by the presence of isotopic defects, it follows that $\int_0^\infty \kappa(\omega)d\omega = 1$ for the imperfect as well as the perfect crystal. It is not obvious from Eq. (14) that this constraint is satisfied and we must reexamine the derivation of Eq. (12) for $\kappa(\omega)$ from Eq. (5) which defines the photon-phonon coupling H_e to verify this point.

When we formed the matrix element $\langle A|H_e|B\rangle$

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[10] For a finite concentration of defects, Eq. (10c) is not derived directly by perturbation theory, but by first correcting the states $|0,1\rangle$ and then orthogonalizing the states $|1,0\rangle$ to the states so corrected.

during the derivation of Eq. (12), in calculating the terms of zero order in c, we tacitly assumed that $H|A\rangle = \hbar\Omega(f)|A\rangle$ and that $(-H)|B\rangle = 0$, whereas in actual fact $H - \sum_{Li} V_L|A\rangle = E_A|A\rangle$ and $-(H - \sum_{Li} V_L)|B\rangle = -E_B|B\rangle$. Thus we must add to the zero-order terms a contribution of

$$\langle A| \sum_{Li} \frac{V_L H_e}{\Omega(f)X^{1/2}} |B\rangle,$$

which produces a change in $\kappa(\omega)$, $\Delta\kappa(\omega)$ given by

$$\Delta\kappa(\omega) = 2\sum_{fLi} \frac{\chi^0(f)\chi^0(L)}{X[\omega'\omega(f)]^{1/2}}$$

$$\times [\eta_{L}{}'(f) - \eta_L(f)]\delta[\omega - \Omega(f)], \tag{15}$$

which when integrated will cancel the final term in Eq. (14).

Thus,

$$\int_0^\infty [\kappa(\omega) + \Delta\kappa(\omega)]d\omega = \sum_{f}{}' |\chi^0(f)|^2 + \sum_{Li} |\chi^0(L)|^2.$$

However, since we know that $\chi(f,l) = \sum_{kj} \chi^{kj}(f)\chi^j(k,l)$, if we now multiply both sides of this equation by M_l, then sum over both l and f and finally square each side, we find that

$$\sum_{f}{}' |\chi^0(f)|^2 + \sum_{Li} |\chi^0(L)|^2 = 1,$$

which shows that the integrated absorption is indeed unchanged.

Our present results have been derived for a crystal at absolute zero, but it is also possible to demonstrate

that they are unchanged in $n(f)$ and $n_L \neq 0$ in the ground state.

In subsequent discussions we shall replace $\omega(f)$ by ω_0, the frequency of the $\mathbf{k}=0$ mode of the host crystal.

We can do this because the sum $\sum_f' |\chi^0(f)|^2$ is dominated by modes for which $\omega(f) \approx \omega_0$ and this sum is a common factor in all the terms of Eqs. (12) and (15). In this way we can obtain the integrated band-mode absorption correctly, but it is also evident that $\sum_f' |\chi^0(f)|^2$ is not strictly $\propto \delta[\omega(f) - \omega_0]$; consequently this absorption is spread over a finite range of frequencies.

3. APPLICATION TO Li(H,D) MIXTURES

We have already seen that a D^- ion substituted in LiH produces a triply degenerate local mode for which $\omega'^2 \approx 0.6\omega_0^2$ and we can now use Eq. (12) to derive the relative integrated absorption at $\omega = \omega'$ and $\omega = \bar{\Omega}(f)$, where $\bar{\Omega}(f)$ is given by Eq. (13) with $\omega(f) = \omega_0$. Thus the band-mode absorption will be of finite width but strongly peaked at $\omega = \bar{\Omega}(f)$. It will be quite sufficient to derive η_L and η_L' [which now refer to the values appropriate to $\omega(f) = \omega_0$] from the same approximations as those used to calculate ω' since these are such that they give lower limits to η_L and η_L'.

Moreover as $\eta_L/(\omega_0 + \omega') \ll \eta_L'/(\omega_0 - \omega')$ in this particular case, we can neglect the terms involving η_L altogether. We then find that for a concentration of only 5% of D^- ions the integrated local-mode absorption is nine times that of the band modes and that $\bar{\Omega}(f) = 1.35\omega_0$.

This proves conclusively that the principal minimum in the transmission of a thin film of Li(H,D) mixture will occur at the D^- local-mode frequency when the D^- concentration is $\sim 5\%$ or more.

4. U-CENTER ABSORPTION

The U center is either an H^- or D^- ion substituted for a negative ion in an alkali-halide host crystal. These centers produce characteristic absorption spectra due to transitions between localized electronic and vibrational levels. Our present concern is with the second type of absorption which produces infrared absorption peaks at frequencies well above the *maximum* frequency of the host lattice. For small concentrations of H^- or D^- and at low temperatures there is a single sharp peak in each case.

As the temperature is raised this broadens strongly and the peak becomes ill defined. While one expects this as a result of anharmonic effects the *integrated* absorption should remain constant for a given number of defects.

Recent work by Smart and Wilkinson[11] has established that this is clearly not so since, the *total* absorp-

tion decreases by a factor of ~ 3 between 100 and 300°K for either H^- or D^- ions in KCl.

If we regard the U centers as isotopic impurities we can use our present theory to make qualitative predictions as to the behavior of the integrated local-mode absorption using Eq. (12). It is at once evident that this calculated absorption is independent of temperature, if we neglect anharmonic effects. If we include them then we shall see that they may affect not only the width of the local-mode absorption but also its total intensity. Before considering this further we must make certain modifications of the derivation of Eq. (12) since the ions of both sublattices have comparable masses. As we are going to be specifically concerned with KCl we shall assume that $M_+ = M_- = M$; this simplifies the results and their derivation somewhat, but is not a necessary assumption.

As before we need only consider one of the $\mathbf{k}=0$ optical modes polarized parallel to the α axis which is parallel to the faces of the specimen. If $M_+ = M_-$, $\sigma_+ = -\sigma_- = 1/\sqrt{2}$ as $\sigma_+^2 + \sigma_-^2 = 1$, and if we use the general form of Eqs. (2) and (3), we have

$$\chi_\pm^0(L)\sigma_\pm = \pm \frac{\epsilon\omega'^2}{2[\omega_0^2 - \omega'^2]} \left(\frac{M}{N}\right)^{1/2} \sum_L \chi(L,0), \quad (16)$$

where the upper and lower signs are to be taken together.

The derivation of Eq. (12) is almost unchanged, but we now have two sets of coupling parameters $\gamma_{L\pm}$ and $\gamma_{L\pm}'$. The important difference is that γ_{L-}' contains a factor.

$$\left[1 + \sigma_- \frac{\Delta M \chi(L,0)}{M\chi_-^0(L)}\right] \approx 0$$

[cf. Eq. (7)] while γ_{L+}' does not.

If we now set $\gamma_{L-}' = 0$ we find that the integrated local-mode absorption in Eq. (12) is now given by

$$I = \int_{\text{L.M.}} \kappa(\omega)d\omega = \frac{\chi^0(L)^2}{1}\left[1 + \frac{\omega_0 + \omega'/2}{2(\omega_0 - \omega')} - \frac{\omega_0 - \omega'/2}{2(\omega_0 + \omega')}\right]^2$$

$$= \frac{\chi^0(L)^2}{2}\left[1 + \frac{3}{2}\frac{\omega_0\omega'}{(\omega_0^2 - \omega'^2)}\right]^2, \quad (17)$$

where

$$\chi^0(L) = \chi_+^0(L) - \chi_-^0(L). \quad (17a)$$

This result is still independent of temperature and is also only valid for a true isotopic impurity. In actual fact a U center will carry an effective charge[12] e^* which differs from that of the Cl^- ion. A measure of this difference is provided by $\Delta e^* = e_{KCl}^* - e_{LiH}^* = (0.8 - 0.5)e$ ($e = |$electronic charge$|$) and we can include this by replacing 1 inside the square brackets on the right-hand

[11] C. Smart and G. R. Wilkinson, Proc. Roy. Soc. (London) (to be published).

[12] B. Szigeti, Proc. Roy. Soc. (London) **A204**, 51 (1950).

side of Eq. (17) by

$$\left[1 + \frac{\Delta e^*}{e_{\mathrm{KCl}}^*} \frac{\chi(L,0)}{\chi_-^0(L)} \sigma_- \right] \approx 1.4 .$$

However, in the present situation we must also examine the effects of anharmonicity since, even in the harmonic approximation, we have found that the total photon-absorption cross section of the local mode is strongly affected by defect scattering of band-mode phonons. Anharmonicity provides additional possibilities for processes having the same effect.

If we consider those anharmonic terms of third order in the normal-mode amplitudes then there are two types of such terms which matter:

(a) those involving the product of three-band-mode amplitudes,
(b) those involving the product of one local-mode amplitude and two-band-mode amplitudes.

The terms (a) cause a $\mathbf{k}=\mathbf{0}$ band-mode phonon to split into two phonons of equal and opposite $\mathbf{k}$ vector while the terms (b) make it possible for this pair of phonons to be converted into a local-mode phonon. At finite temperatures, when phonon occupation numbers are nonzero, processes involving phonon annihilation must also be considered. A preliminary investigation of this effect has been made and will be reported fully elsewhere. The main conclusion is that one must substract from the expression inside the square brackets of Eq. (17) a temperature-dependent term which is of the correct order to explain the observed temperature dependence for the D^- impurity. For the H^- impurity this correction is too small, i.e., the calculated change in I is only about 25% of that actually observed. Since it is found that the correction is strongly dependent on $[\omega' - (\omega_1 + \omega_2)]^{-1}$ where ω_1 and ω_2 are the frequencies of the two intermediate band-mode phonons; and as Smart and Wilkinson's work[11] shows that $\omega'/\omega_0 = 3.36$ for H^- ions against 2.40 for D^- ions, it seems that virtual processes involving three intermediate phonons are likely to be more important for the H^- impurity because in this case $[\omega' - (\omega_1 + \omega_2 + \omega_3)]^{-1}$ will be of the same order as $[\omega' - (\omega_1 + \omega_2)]^{-1}$ for the local D^- vibrations. These processes will occur in a similar way to the (a) $\rightarrow$ (b) sequence described previously except that the coupling will be produced by the corresponding fourth-order terms in the anharmonic potential.

5. DISCUSSION

The effects we have been discussing are peculiar to systems in which the presence of a defect produces local vibrations; and to obtain the drastic effects observed in Li(H,D) mixtures, one needs both the presence of a local mode and an unperturbed frequency spectrum which is such that ω' is close to ω_0. This explains why ω_0 varies smoothly with concentration of Li^7 in $Li^{6,7}F$ mixed crystals,[3] since LiF has no gap in its frequency spectrum.[13] Also, even if a gap were present, the mass difference might well be too small to produce local modes.

In the case of an H^- ion substituted into pure LiD, it is possible that no local mode is produced,[14] but should one be present, it can only appear at a frequency greater than the maximum lattice frequency. Thus $(\omega' - \omega_0) \approx \omega_0$ and the scattering of band modes by the defect is drastically reduced as compared with that produced by a D^- ion in pure LiH. Consequently the anomalous shift of the fundamental absorption is only present for Li(H,D) mixtures.

One can suggest further tests of the present theory of isotopic mixtures:

(i) Measurements should be made on Li(H,D) mixtures containing $<5\%$ D^- designed to follow the shift of the fundamental absorption as a function of D^- concentration.
(ii) It is highly desirable to confirm that other alkali (H,D) mixtures display similar anomalous behavior, as one would expect from the present theory.
(iii) All possible alkali-halide mixed crystals should be subjected to similar measurements in the hope that, whenever the pure host has a gap in its frequency spectrum, the replacement of a few percent of the lighter of the two host ions by heavier impurity ions will produce an anomalously large shift in the principal lattice absorption.

[13] A. M. Karo and J. R. Hardy, Phys. Rev. **129**, 2024 (1963).
[14] The delta-function approximation to the frequency spectrum used in Sec. 2 predicts a local mode just above the upper delta function. This prediction is less reliable than that for the D^- ion in LiH since the calculated value of ω' can be brought into the range of band modes by a small variation of the position of the upper delta function. One can achieve the same result for the D^- impurity only by a large, completely implausible movement of the lower delta function.