John R. Hardy Papers   Research Papers in Physics and Astronomy

7-15-1968

Infrared Absorption Properties of LiH, LiD Mixed Crystals

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Infrared Absorption Properties of LiH, LiD Mixed Crystals*

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The normal modes of pure LiH and LiD, required in impurity mode calculations, have been computed on the basis of the deformation-dipole model. Neutron-scattering results of Verble, Warren, and Yarnell for Li^7D, along with some other experimental quantities, have been used to determine the various parameters involved. It is found that the frequency spectrum of LiH has a gap and that a substitutional D^- ion produces a local mode in this gap whose frequency has been computed, together with its amplitude at the impurity. The infrared absorption frequency associated with this local mode and its integrated absorption have been computed as functions of D^- content in the limit of low D^- concentration. Also, we find an in-band resonance in the amplitude of the substitutional D^- ion. Similar calculations have been carried out for H^- impurities in LiD. The present results are compared with those of other calculations and with experiment.

1. INTRODUCTION

FOR the purpose of studying impurity effects on lattice vibrations, mixed LiH-LiD systems are ideal, since they are true isotopic mixtures and the H, D mass difference is large enough to produce marked changes in the vibrational properties of these systems as the relative concentrations of the two components are varied. Some time ago, with this fact in mind, Misho[1] carried out infrared absorption measurements on thin films of such mixtures. He found that the addition of a small amount of D^- to LiH produces a large decrease in the main absorption frequency below the fundamental infrared dispersion frequency (ω_{TO}) of pure LiH.

Our main object in the present paper is to attempt to understand Misho's results theoretically, but, in order to do this, we first need an adequate theoretical treatment of the dynamics of both pure LiH and pure LiD.

Previously this has not been possible because of lack of knowledge of the necessary input parameters, e.g., experimental values[2,3] of the compressibility vary over a wide range. Recently, Benedek[4] reported some calculations on the lattice dynamics of LiH and LiD using the deformation-dipole (DD) model[5] but we believe that these are in error, since for both the alternative sets of input data he uses, we find that the lattice is unstable against certain normal-mode displacements within the reduced zone.

For example, for a compressibility $\beta = 2.55 \times 10^{-12}$ cm²/dyn and a H^- polarizability $\alpha^- = 1.9 \times 10^{-24}$, some of the frequencies are imaginary for reduced wave vectors **q** equal to $(0.2, 0.2, 0)$, $(0.3, 0.3, 0.1)$, $(0.4, 0.4, 0)$, $(0.4, 0.4, 0.2)$, $(0.4, 0.4, 0.4)$, $(0.5, 0.5, 0.3)$, and $(0.5, 0.5, 0.5)$. Also, his expression for ω_{TO} appears to be incorrect. When the short-range interactions are approximated by central forces between nearest neighbors only, the correct expression for ω_{TO} is

$$\omega_{TO}^2 = \frac{1}{\bar{M}} \frac{e^2}{v_a} \left[A + 2B - \tfrac{4}{3}\pi s^2 \frac{1}{1 - (4\pi/3v_a)(\alpha^+ + \alpha^-)} \right], \quad (1.1)$$

where v_a is the volume of a primitive cell, e is the electronic charge, $\bar{M}$ is the reduced mass of the positive and negative ions, A and B are the short-range force constants defined by Kellermann,[6] s is the ratio of the Szigeti charge[7] to the electronic charge, and α^+ and α^- are, respectively, the positive- and negative-ion crystal polarizabilities.

Montgomery and Hardy[8] explained the experimental results of Misho in terms of a local mode in a gap in the LiH frequency spectrum. They approximated the LiH lattice by a monatomic face-centered cubic lattice made up of H^- ions, and to estimate the frequency spectrum they used the neutron scattering data of Woods *et al.*[9] which give only the optical modes. More recently, Elliott and Taylor[10] made a more elaborate study of the LiH:D and LiD:H systems and calculated the local mode frequency and the integrated local mode absorption as functions of defect concentration. In this case, the optical mode frequency distribution of LiH

[1] R. H. Misho, Ph.D. thesis, Michigan State University, 1961 (unpublished).

[2] F. E. Pretzel, G. N. Rupert, C. L. Mader, E. K. Sturms, G. V. Gritton, and C. C. Rushing, J. Phys. Chem. Solids **16**, 10 (1960).

[3] R. Weil and A. W. Lawson, J. Chem. Phys. **37**, 2730 (1962); F. F. Voronov, V. A. Goncharova, O. V. Slal'gorova, and T. A. Agapova, Fiz. Tverd. Tela **8**, 1643 (1966) [English transl.: Soviet Phys.—Solid State **8**, 1313 (1966)].

[4] G. Benedek, Solid State Commun. **5**, 101 (1967).

[5] J. R. Hardy, Phil. Mag. **7**, 315 (1962).

[6] E. W. Kellermann, Phil. Trans. Roy. Soc. (London) **A238**, 513 (1940).

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

[8] D. J. Montgomery and J. R. Hardy, J. Phys. Chem. Solids, Suppl. 1, 491 (1965).

[9] A. D. B. Woods, B. N. Brockhouse, M. Sakomoto, and R. N. Sinclair, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 487.

[10] R. J. Elliott and D. W. Taylor, Proc. Roy. Soc. (London) **A296**, 161 (1967).

was approximated by fitting two Gaussians to the experimental results of Woods *et al.*[9] Evidently, both theories are limited by lack of complete knowledge of the frequency spectrum of the perfect crystal.

Recently, Verble *et al.*[11] have obtained by neutron scattering most of the dispersion curves for Li⁷D along three symmetry directions. In the present work, we have computed the normal modes of LiH and LiD on the basis of the DD model and, in order to determine the various parameters involved, we have used these results along with other experimental quantities. With the help of the calculated eigenfrequencies and the eigenvectors of the pure crystals, we have carried out impurity-mode calculations for both LiH:D and LiD:H. The results of the present calculations are compared with the experimental data of Misho,[1] and Elliott and Taylor's[10] theoretical work. A preliminary report on the impurity-mode calculations in LiH:D has been given elsewhere.[12]

2. LATTICE DYNAMICS OF THE PURE SYSTEMS

We compute the normal modes of the pure systems on the basis of the DD model and within the harmonic approximation. The short-range interactions consist of central forces between nearest and next-nearest neighbors and an angle-bending force.[13] LiH has the NaCl structure, thus any two similar ions which are nearest neighbors of a dissimilar ion and lie along the positive directions of any two coordinate axes subtend a right angle at the dissimilar ion. The angle-bending force is proportional to the deviation from this right angle. The proportionality constant C is assumed to be the same with either kind of ion at the origin. In this approximation the contributions of the angle-bending force to various elements of the dynamical matrix D are as follows:

$$D_{xx}{}^B(KK':\mathbf{q}) = -(M_K M_{K'})^{-1/2}(e^2/v_a)4C$$
$$\times(\cos\pi q_y + \cos\pi q_z), \quad (2.1a)$$

$$D_{xy}{}^B(KK':\mathbf{q}) = 0, \quad (2.1b)$$

$$D_{xx}{}^B(KK:\mathbf{q}) = (1/M_K)(e^2/v_a)8C, \quad (2.1c)$$

$$D_{xy}{}^B(KK:\mathbf{q}) = (1/M_K)(e^2/v_a)2C \sin\pi q_x \sin\pi q_y, \quad (2.1d)$$

where K and K' label the two kinds of ions, $\mathbf{q}$ is the reduced wave vector, and C is the angle-bending force constant. These expressions are symmetric in the interchange of x, y, etc., and K and K'.

The next-nearest-neighbor (NNN) forces between positive-positive and negative-negative ions are not

FIG. 1. Phonon-dispersion curves in the three symmetry directions for Li⁷D.

[11] J. L. Verble, J. L. Warren, and J. L. Yarnell, Bull. Am. Phys. Soc. **12**, 557 (1957). (We should also like to thank these authors for private communication of a fuller account of this work.)

[12] S. S. Jaswal and J. R. Hardy, in Proceedings of the Irvine Conference on Localized Excitations in Solids (to be published).

[13] A. A. Maradudin (private communication). We should like to thank Professor Maradudin for access to this unpublished work.
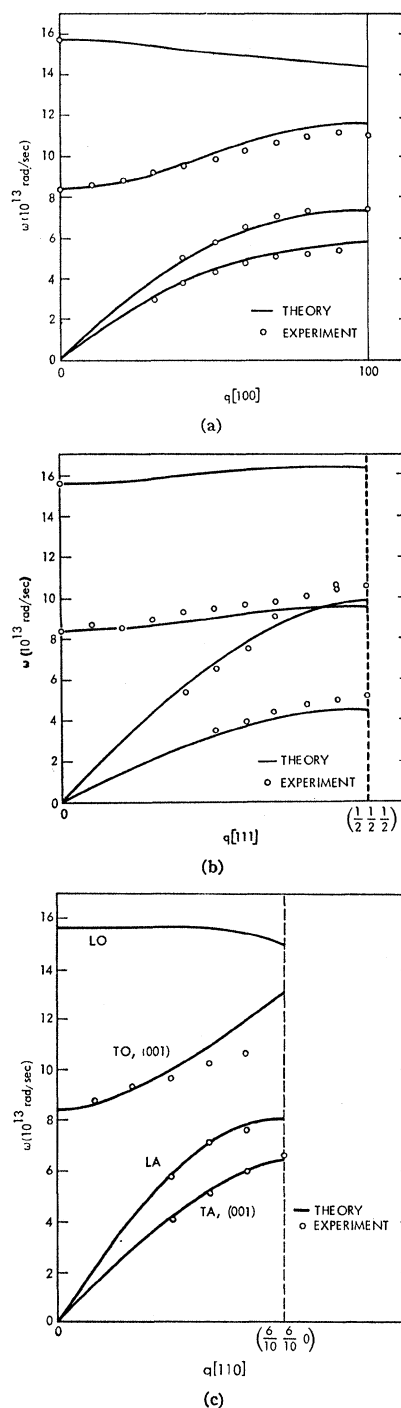
treated independently, since their ratio is assumed to be a constant which is used as an adjustable parameter.

The monopole charge Z is allowed to vary and the positive and negative ion polarizabilities are adjusted so that their sum is equal to 1.893×10^{-24} cm⁻³, the value obtained from the Clausius-Mossotti relation.
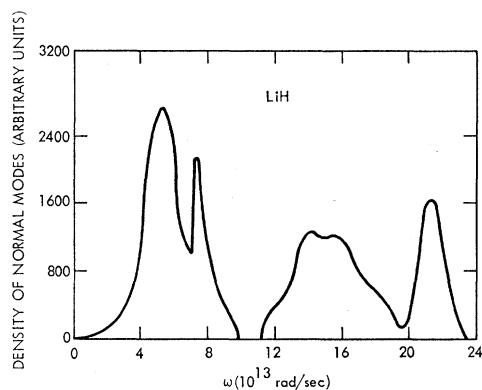
FIG. 2. Frequency distribution for LiH.

To adjust the various parameters involved, we first computed the normal modes of Li^7D. In addition to using the measured phonon dispersion curves of Verble *et al.*[11] as a guide in our calculations, we also used the lattice parameter r_0,[2] the infrared dispersion frequency ω_{TO},[14] the Szigeti charge $s = 0.52$,[14] and the elastic constants C_{11} and C_{44} derived from the longitudinal acoustic and transverse acoustic branches of the experimental phonon dispersion curves of Li^7D in the symmetry direction [100].

Thus with elastic constants

$$C_{11} = 6.63 \times 10^{11} \text{ dyn/cm}^2,$$

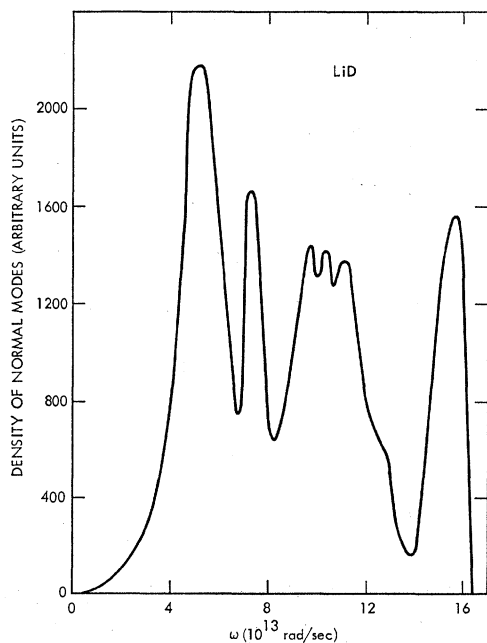$$C_{44} = 4.83 \times 10^{11} \text{ dyn/cm}^2,$$

FIG. 3. Frequency distribution for LiD.

[14] D. J. Montgomery and K. F. Yeung, J. Chem. Phys. **37**, 1056 (1962).

the best fit was given by $C \times (e^2/2r_0^4) = 0.841 \times 10^{11}$ cgs units; $A_1 = 3.85$, $B_1 = -0.69$, $A_2^{++} = 0.24$, $A_2^{--} = 0.36$, $B_2^{++} = 0.025$, $B_2^{--} = 0.037$ (all in Kellermann's units[6]; the subscripts 1 and 2 refer to NN and NNN, respectively) $|Z| = 0.7 |e|$.

$$\frac{\text{NNN potential for positive ions}}{\text{NNN potential for negative ions}} = \frac{2}{3},$$

α^+ (positive ion polarizability) $= 0.229 \times 10^{-24}$ cm^{-3},

α^- (negative ion polarizability) $= 1.664 \times 10^{-24}$ cm^{-3}.

Our computed phonon dispersion curves in the three symmetry directions are compared with the experimental results in Fig. 1. In all three cases, the agreement between theory and experiment at low q is very good, but the deviation increases toward the zone boundary. However, except for the transverse optical branch at the zone face along the [110] direction and the transverse acoustic branch at the zone face along the [111] direction, where the disagreement is $\sim 13\%$, this deviation is about 6% or less. Thus the overall agreement between the calculated and the experimental results is satisfactory from the point of view of defect calculations. We would like to remark that our longitudinal optical frequencies are consistently higher than those of Verble *et al.*[11] obtained from a shell model.

As regards the adjustable parameters given above, we think they are quite realistic. The value of monopole charge is less than the free-electron charge, since lithium hydride is not as ionic as the alkali halides,[2] while the ratio of the NNN potentials of the two ions is comparable with that of their ionic radii. While it is probable that we could have improved the agreement between calculated and experimental dispersion curves by least-squares fitting the resultant model parameters would be less realistic (e.g., the high-frequency dielectric constant would be in error) and we have chosen to obtain the best fit we can without varying the input parameters beyond reasonable limits.

The parameters obtained for Li^7D are then used to compute the normal modes of LiH and LiD. The experimental values of ω_{TO} and s for these systems are
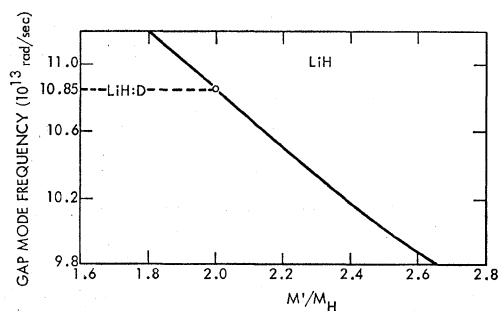
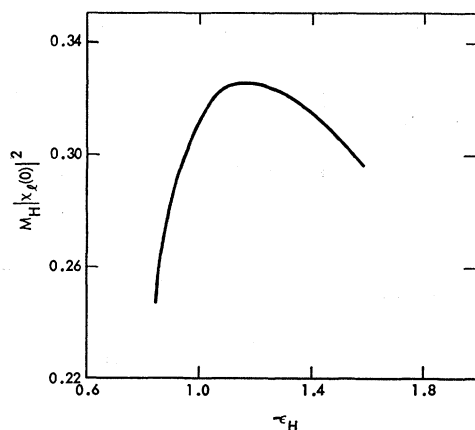FIG. 4. Gap-mode frequency in LiH as a function of impurity mass M'.

FIG. 5. Amplitude of vibration of the impurity
atom in LiH as a function of ϵ_H.

FIG. 6. Absorption frequency as a function of
D^- concentration in LiH.

those due to Zimmerman and Montgomery[15] and
Brodsky.[16] Our computed frequency distribution for
LiH is shown in Fig. 2. Our longitudinal optical peak
is at a somewhat higher frequency than that obtained
by incoherent neutron scattering by Woods *et al.*[9] It
can be seen that there is a gap in the frequency spec-
trum of LiH, bounded by the frequencies 9.83×10^{13}
and 11.2×10^{13} rad/sec. From the phonon dispersion
curves in Fig. 1, it is clear that the upper edge of the
gap is quite accurate, whereas the lower edge is un-
certain by about 10%. However, since the local mode
we are concerned with is near the upper edge of the
gap, our computed frequency spectrum should be
adequate to study its properties. Figure 3 shows the
computed frequency distribution of LiD which has no
gap, a fact consistent with the experimental results of
Verble *et al.*[11] Both frequency distributions have been
derived from samples of 8000 points within the first
Brillouin zone.

3. IMPURITY MODES IN LiH:D

On the basis of these results, we have studied the im-
purity modes in LiH containing low concentrations of
deuterium. Since LiH has a gap in its frequency spec-
trum, heavier impurities substituted for H^- will, in
general, give rise to localized modes in this gap. For
such substitutional mass defects, the solution of the
standard eigenvalue equation[17] gives the local-mode
frequency as a function of the relative change in mass.
The results for gap modes due to heavier impurities
substituted for an H^- ion in LiH are shown in Fig. 4,
where M' is the mass of the impurity. From this we find
that a substitutional deuterium gives rise to a local

mode in the gap at a frequency $\omega_1 = 10.85 \times 10^{13}$ rad/sec,
which is close to 11.21×10^{13} rad/sec, the value of
ω_{TO} for pure LiH.

Also, we have computed the amplitude[18] $|X_1(0)|^2$
of the impurity atom in these local modes and the
results are shown in Fig. 5, where $\epsilon_H = (M_H - M')/M_H$,
M_H being the mass of H^-. We see that the amplitude
as a function of ϵ_H goes through a maximum, whereas
the local mode frequency decreases monotonically as
the mass of impurity atom increases. For a deuterium
impurity, $M_H |X_1(0)|^2 = 0.312$.

Since these local modes are optically active, infrared
spectroscopy can be used to study them experimentally.
However, the infrared absorption frequency shifts
considerably with an increase in defect concentration p.
Various workers have studied this problem for low
defect concentrations.[17,10,19] According to Maradudin,[17]
the following equation gives the absorption frequency
as a function of p:

$$\omega_{TO}^2 - \omega^2 + \epsilon_H \mu p \omega_{TO}^2 A^{-1}(\omega) = 0, \qquad (3.1)$$

where ω is the frequency to be determined, $\mu = M_{Li}/$

FIG. 7. Integrated absorption in the gap mode as
a function of D^- concentration in LiH.

[15] W. B. Zimmerman and D. J. Montgomery, Phys. Rev. **120**,
405 (1960).
[16] M. Brodsky, Ph.D. thesis, University of Pennsylvania,
1965 (unpublished).
[17] A. A. Maradudin, in *1962 Brandeis University Summer
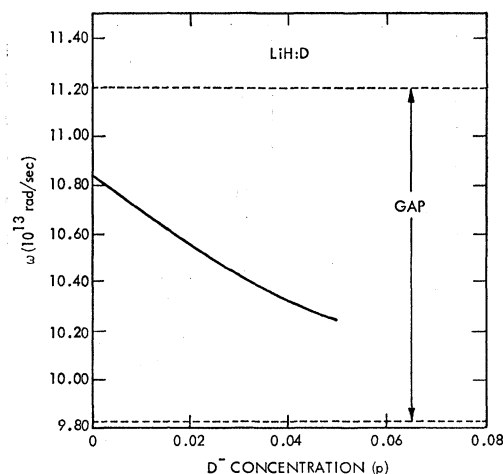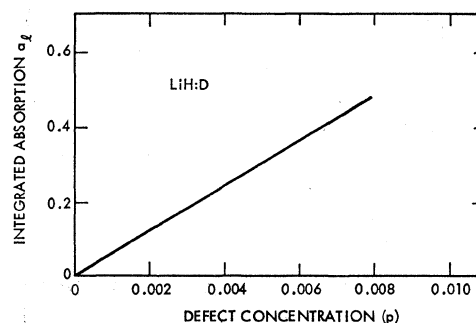Institute Lectures in Theoretical Physics* (W. A. Benjamin, Inc.,
New York, 1962), Vol. II.
[18] S. S. Jaswal, J. Chem. Phys. **46**, 4311 (1967).
[19] G. Benedek and G. F. Nardelli, Phys. Rev. **155**, 1004 (1967).
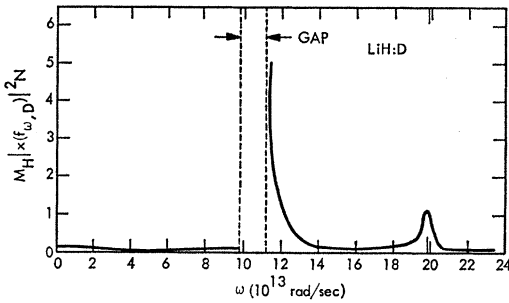
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FIG. 8. Amplitude of vibration of a D^- ion in LiH as a function of band-mode frequency.

$(M_{Li} + M_H)$, and

$$A(\omega) = 1 - \frac{\epsilon_H \omega^2}{3N} \sum_{qj} \frac{|W(-|q,j)|^2}{\omega^2 - \omega_j^2(q)}, \qquad (3.2)$$

where N is the number of unit cells in the crystal, $W(-|q,j)$ is the negative-ion eigenvector amplitude, and $\omega_j(q)$ is the eigenfrequency corresponding to wave vector q and branch index j.

We have solved Eq. (3.1) numerically for various concentrations of D^- impurities in LiH, and the resultant ω-versus-p curve is shown in Fig. 6. The absorption frequency decreases by about 6% as p goes from 0 to 5%. These results are in agreement with those of Elliott and Taylor's[10] calculations, based on their approximate form of the LiH frequency spectrum.

The relative integrated absorption a_1 in the local mode, i.e., the ratio of the absorption in the local mode to that at the transverse optic frequency of the perfect crystal, is equal to the ratio of the squares of the electric dipole moments of these two modes. The local-mode dipole moment μ_1 of the crystal is given by

$$\mu_1 = \sum_{Kl} e_K^* \chi(K|1,l), \qquad (3.3)$$

where e_K^* is an effective charge $(|e_+^*| = |e_-^*| = e^*)$ and

$$\chi(K|1,l) = -\frac{1}{N} \sum_{\alpha K'qj} \frac{W^*(K|q,j)W_\alpha(K'|q,j)}{\omega_j^2(q) - \omega_1^2}$$

$$\times \chi_\alpha(K'|1,0) e_{K'}(M_{K'}/M_K)^{1/2}\omega_1^2 \exp\left(-\frac{i\pi}{r_0}q \cdot R_l\right) \qquad (3.4)$$

is the amplitude[20] of Kth ion in the lth cell corresponding to the local mode 1. When the various summations in (3.3) are carried out, the only terms which survive on the right-hand side are those corresponding to transverse optical modes at $q=0$. The final result for the square of the dipole moment becomes

$$\mu_1^2 = e^{*2}\mu \epsilon_H^2 \frac{\omega_1^4}{(\omega_{TO}^2 - \omega_1^2)^2} \left|\frac{W(+|0,j)}{\sqrt{M_+}} - \frac{W(-|0,j)}{\sqrt{M_-}}\right|^2$$

$$\times M_H |\chi_1(0)|^2, \qquad (3.5)$$

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

where we have taken into account the threefold degeneracy of the local mode. Here j refers to the transverse optical branch. The corresponding result for the transverse optic mode of the perfect crystal is

$$\mu_{TO}^2 = e^{*2}N \left|\frac{W(+|0,j)}{\sqrt{M_+}} - \frac{W(-|0,j)}{\sqrt{M_-}}\right|^2. \qquad (3.6)$$

Thus, the relative integrated absorption for a low concentration of defects p is given by

$$a_1 = p\mu \frac{\epsilon_H^2 \omega_1^4}{(\omega_1^2 - \omega_{TO}^2)^2} M_H |\chi_1(0)|^2. \qquad (3.7)$$

This expression holds exactly only when the local modes centered on different defects do not interact, and p must be very low for this to be true.

Using this expression, we have computed a_1 as a function of p for LiH:D and the results are shown in Fig. 7. First of all we see that at very low concentrations of D^-, where our expression holds exactly, the absorption in the local mode forms a significant fraction of that in ω_{TO}. Secondly, even through our expression does not hold for higher defect concentrations, our results nonetheless indicate a rapid increase in the integrated absorption a_1 as p is increased further, e.g., for p as low as 0.01, $a_1 \sim 0.5$. Once again, our low concentration results are similar to those of Elliott and Taylor.[10] Also, they are in *qualitative* agreement with experiment,[1] i.e., the calculated integrated absorption of the so-called local mode becomes very large even for p as low as 0.02, but, even allowing for the shift with concentration, our computed absorption frequency is considerably higher than the experimental value,[1] of 8.49×10^{13} rad/sec for a crystal of LiH containing 5% LiD.

To investigate the existence of in-band resonance modes associated with D^- impurities in LiH, we have computed the amplitude of the impurity atom as a
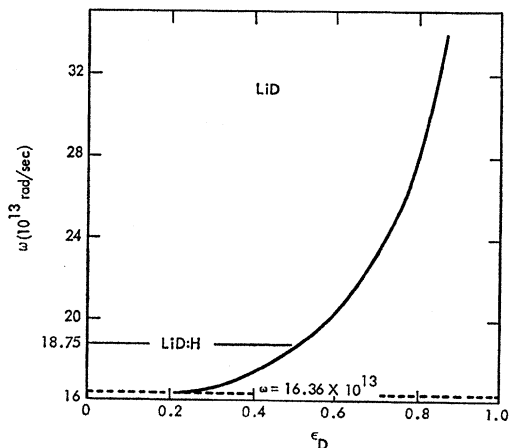

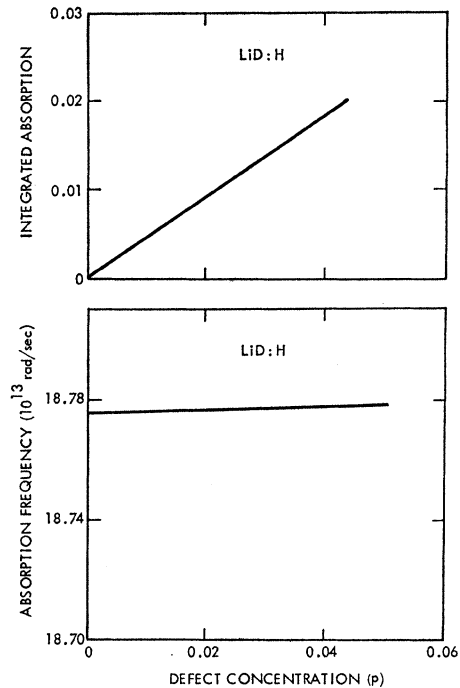FIG. 9. Local-mode frequency in LiD as a function of ϵ_D.

Fig. 10. Absorption frequency and integrated absorption in the local mode as functions of H⁻ concentration in LiD.

function of frequency within the ranges spanned by the spectrum of pure LiH, and the results are shown in Fig. 8. The large increase in the amplitude near the upper edge of the gap is due to the nearness of the local mode, and we also predict a resonance in the optical part of the frequency spectrum at 19.8×10^{13} rad/sec.

4. IMPURITY MODES IN LiD:H

Some of the impurity-mode calculations of Sec. 3 have been repeated for H⁻ impurities in LiD. Figure 9 shows the local mode frequency as a function of the mass defect ϵ_D when a lighter impurity is substituted for a D⁻ ion. From this we see that a substitutional H⁻ ion produces a local mode at a frequency $\omega_1 = 18.75 \times 10^{13}$ rad/sec, which lies above the maximum frequency of the pure crystal. This value is about 4% higher than

that obtained by Elliott and Taylor[10] for the same system.

Plots of the infrared absorption frequency and the integrated absorption against defect concentration are shown in Fig. 10. The absorption frequency increases slightly with increase in p, contrary to the results of Elliott and Taylor.[10] The integrated absorption in the local mode is quite small and increases linearly with p in the approximation we are using. For example, the integrated absorption is about 2% for $p = 0.05$, and this probably is the reason why Misho failed to see the local mode in his experiments on LiD:H. Moreover, our predictions with regard to the integrated intensity agree with those of Elliott and Taylor.[10]

5. CONCLUSIONS

We think that we now have a reasonably good representation of the normal modes of LiH and LiD, and hence our impurity-mode calculations are quite realistic. A low concentration of D⁻ in LiH gives a local mode in the gap whose frequency decreases with increase in defect concentration. The integrated absorption in the gap mode is quite large, even for low concentration of D⁻, but the absorption frequency is much higher than that measured experimentally by Misho.[1] Also, we find that the substitutional D⁻ has a resonance mode in the optical part of the frequency distribution of LiH.

A substitutional H⁻ in LiD gives rise to a local mode above the maximum frequency of the pure crystal whose frequency increases slightly with increase in H⁻ concentration. The integrated absorption in the local mode is small and increases linearly with the defect concentration. This absorption has not so far been seen experimentally.

To resolve the discrepancy between the calculated and the observed local mode absorption frequencies for D⁻ impurities in LiH, more experimental work is desirable. Also, it should be possible to observe the local mode produced by H⁻ impurities in LiD.

Finally, it is obvious that the behavior of truly mixed crystals, containing comparable amounts of H⁻ and D⁻, is very little understood either theoretically or experimentally.