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Lattice-Vibration Effects Due to Impurities in an Alkali Halide*†

LEON GUNTHER
Physics Department, Massachusetts Institute of Technology, Cambridge, Massachusetts

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The Green's-function approach to the study of impurity effects on lattice vibrations is applied to alkali halides. Due to the strong phonon-photon interaction, some care must be taken in the application of the results for the pure crystal. A simplified approach for obtaining the impurity contribution to the lattice thermal conductivity is presented which leads to a phonon lifetime having resonance dips. Numerical calculations for NaI:Li$^+$, using a simple model for the interionic forces (which took into account the electronic polarization but not dipole deformation) and the "mass-defect approximation," revealed resonances at the frequencies 2.2, 2.5, 2.8, and 3.0×10^{13} sec^{-1}. An expression for the optical absorption is derived which reveals a peak of first order in the impurity concentration at the localized-mode frequency and peaks at the resonance frequencies proportional to the square of the impurity concentration. In the mass-defect approximation and in the above model, the localized-mode frequency of NaI:Li$^+$ lay at 4.28×10^{13} sec^{-1}, while that of NaI:K$^+$ lay at 1.76×10^{13} sec^{-1}. Using estimates of phonon and impurity-mode lifetimes, we conclude that these peaks should be easily observed.

I. INTRODUCTION

THE basic theory of lattice vibrations rests on the Born-Oppenheimer expansion.[1] Owing to the smallness of the ratio of the mass of the electron to that of an ion, the electrons are assumed to "follow" the nuclear motion. To first order, we obtain the harmonic approximation, which leads to normal modes of vibration, commonly referred to as phonons. Higher order, anharmonic terms (which will not be considered in formal detail) lead to finite phonon lifetimes and play a vital role in thermal conductivity, the maintenance of thermal equilibrium, and nonzero optical-absorption widths. The use of the harmonic approximation requires a knowledge of the two-body forces. The latter is provided by the "force-constant" matrix. The eigenvalues and eigenvectors of the "dynamical matrix" **D** are the phonon frequencies and amplitudes, respectively. With these quantities, we can form a Green's function, with which we can determine the behavior of the crystal in the presence of impurities.

The Green's-function approach to the lattice-vibration impurity problem was introduced by I. M. Lifshitz.[2] Later on, work was done on the related problem of impurity levels in electron bands by Koster and Slater.[3] Soon after, many theoretical papers appeared on the subject, dealing with increasingly complex crystal models and investigating various phenomena due to impurities.[4] All the works listed used the Green's-function technique.

Experimentally, impurities play big roles in many lattice-vibration phenomena observed in solids. One of the more important ones is lattice thermal conductivity. Here, the impurities can be viewed as phonon scatterers, with the phonons serving as the carriers of the energy. Recently, careful measurements of the thermal conductivity κ of some alkali halides at low temperatures has revealed a dip in the κ versus T curves.[5] It was suggested that the dip may be due to an impurity resonance mode.

Impurities can also play an important role in the infrared absorption of ionic crystals. Sharp absorption peaks in the infrared have been observed for some alkali halides doped with H^{-1} ions (U centers).[6] The peaks are attributed to a mode of vibration localized about the impurity ions. Due to the fact that, in this case, the frequency of the localized mode is more than twice the maximum phonon frequency, no three-phonon scattering can take place, and this mode has an unusually long lifetime and therefore yields a very sharp absorption peak.

The Green's-function technique will be applied to an ionic crystal, where, in particular, long-range Coulomb forces exist. Two simple models for the interionic forces will be used in the calculations for NaI:Li$^+$ and NaI:K$^+$. One of the reasons for choosing NaI was that it has a gap between the acoustic and optical bands, thus making it possible to have a localized mode in the case of NaI:K$^+$. However, the main reason for choosing the couples NaI:Li$^+$ and NaI:K$^+$ is that, to a good approximation, we have to take account only of the mass change at the impurity site—we get what will be referred to as the "mass-defect approximation" (MDA). In Table I, we list the physical constants used in the calculations. We see that the changes in the electronic

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[1] M. Born and K. Huang, *Dynamics of Crystal Lattices* (Oxford University Press, New York, 1956), 1st ed.

[2] I. M. Lifshitz, Zh. Eksperim. i Teor. Fiz. **12**, 117 (1942).

[3] G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954); G. F. Koster, *ibid.* **95**, 1436 (1954).

[4] E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955); R. F. Wallis and A. A. Maradudin, Progr. Theoret. Phys. (Kyoto) **24**, 1055 (1960); R. Brout and W. M. Visscher, Phys. Rev. Letters **9**, 54 (1962); I. M. Lifshitz, Nuovo Cimento Suppl. **4**, 716 (1956); P. G. Dawber and R. J. Elliot, Proc. Phys. Soc. (London) **81**, 453 (1963); S. V. Maleev, Zh. Eksperim. i Teor. Fiz. **39**, 891 (1960) [English transl.: Soviet Phys.—JETP **12**, 617 (1961)]; A. A. Maradudin and P. A. Flynn, Phys. Rev. **126**, 2059 (1962).

[5] C. T. Walker and R. O. Pohl, Phys. Rev. **131**, 1433 (1963).

[6] G. Schaefer, J. Phys. Chem. Solids **12**, 233 (1960); B. Fritz, *ibid.* **23**, 375 (1962); D. W. Mirlin and I. I. Reshina, Fiz. Tverd. Tela **5**, 3352 (1963) [English transl.: Soviet Phys.—Solid State **5**, 2458 (1964)].

TABLE I. Room-temperature data.

1. Atomic weights[a]	Li:	6.940	K:	39.100
	Na:	22.991	I:	126.91
2. Ionic radius[b] (in Å)	Li^+:	0.78	K^+:	1.33
	Na^+:	0.98	I^-:	2.20
3. Nearest-neighbor distance[b] (in Å)	LiI:	3.02		
	NaI:	3.23		
	KI:	3.53		
4. Compressibility[b]	LiI:	6.01×10^{-12} cm²/dyn		
	NaI:	7.07×10^{-12} cm²/dyn		
	KI:	8.54×10^{-12} cm²/dyn		
5. Reststrahlen frequency of NaI[b]	ω_T:	$=2.20\times10^{13}$ sec⁻¹		
6. Electronic polarizability[b]	Na^+:	0.28×10^{-24} cm³		
	I^-:	6.41×10^{-24} cm³		
	K^+:	1.13×10^{-24} cm³		
	Li^+:	0.045×10^{-24} cm³		
7. Madelung constant of NaI[b]	α:	$=1.7476$		

[a] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957).
[b] Reference 1.

polarizability, compressibility, and nearest-neighbor distances are small in comparison with the mass changes. This holds especially well for NaI:Li^+. "Complete" theoretical results will be obtained only in the MDA. Theoretical results in the cases when other changes are taken into account are straightforward though more complicated. In addition, they require a better knowledge of the interionic forces.

We will assume that the impurity concentration $1/N$ is so small that we neglect the interaction between impurities. For the in-band modes, this consists in neglecting multiple scattering of phonons by impurities. Equivalently, we assume that we can treat the crystal as a collection of independent subcrystals, each with N ion pairs.

The program of the discussion is as follows. In Sec. II, we present the basic theory of lattice vibrations and impurity modes. In Sec. III, we present a new method of obtaining the contribution of impurity scattering to the thermal conductivity. In Sec. IV, we discuss two simple models for the lattice vibrations of ionic crystals, the point- (or rigid-) ion model of Kellermann,[7] (hereinafter referred to as the PIM), and a simple model which takes account of the electronic polarizability, referred to as the electronic-polarization model (EPM). For some modes of vibration, the ionic crystal interacts strongly with the electromagnetic field. We have attempted to clarify some aspects of this interaction which have sometimes been controversial. In Sec. V, we present a simple quantum-mechanical derivation of the contribution of the impurities to the optical absorption. In Sec. VI, we present and discuss the calculations and results made using the MDA for NaI:Li^+ and NaI:K^+. Finally, we reserve our summary, conclusions, and prospects for the future to Sec. VII.

II. BASIC THEORY OF IMPURITY MODES

In the MDA, with a single mass m_1' replacing m_1 at the origin of our lattice, all the properties of the impurity modes are determined by the Green's function[4]

$$G_{\alpha i\beta j}(\omega^2,n)=\sum\nolimits_k \frac{A_{\alpha i}{}^k(n)A_{\beta j}{}^{k*}(0)}{\omega^2(k)-\omega^2}, \tag{1}$$

where $\sum_k$ is a sum over the normal modes of the perfect crystal (hereinafter referred to as phonons); k is the phonon label $(\equiv\{\mathbf{k},s\})$; $\mathbf{k}$ is the wave vector; s is the branch index; $\omega^2(k)$ are the phonon frequencies; $A_{\alpha i}{}^k(n)$ are the normalized phonon amplitudes; n refers to the unit cell at $\mathbf{R}_n$; i refers to the ion of the cell; and α, β, $\cdots$ refers to components in x-y-z space. More explicitly,

$$A_{\alpha i}{}^k(n)=\frac{1}{(N)^{1/2}}\epsilon_{\alpha i}(k)e^{i\mathbf{k}\cdot\mathbf{R}_{ni}}, \tag{2}$$

where $\mathbf{R}_{ni}\equiv\mathbf{R}_n+\mathbf{R}_i$ is the position of the ith ion of the unit cell at $\mathbf{R}_n$. We have

$$\begin{gathered}\sum_{n\alpha i} A_{\alpha i}{}^k(n)A_{\alpha i}{}^{k'*}(n)=\delta_{kk'},\\ \sum_{\alpha i}\epsilon_{\alpha i}(\mathbf{k}s)\epsilon_{\alpha i}(\mathbf{k}s')=\delta_{ss'},\\ \sum\nolimits_s \epsilon_{\alpha i}(\mathbf{k}s)\epsilon_{\beta j}(\mathbf{k}s)=\delta_{\alpha\beta}\delta_{ij}.\end{gathered} \tag{3}$$

The Green's function can also be written as

$$G_{\alpha i\beta j}(\omega^2,n)=\frac{1}{N}\sum_{\mathbf{k}}\{\mathsf{D}(\mathbf{k})-\omega^2\mathsf{I}\}_{\alpha i\beta j}{}^{-1}e^{i\mathbf{k}\cdot\mathbf{R}_{nimj}}, \tag{4}$$

where $\mathbf{R}_{nimj}=\mathbf{R}_n+\mathbf{R}_i-\mathbf{R}_m-\mathbf{R}_j$. The local mode frequencies are determined by solving for ω

$$1=\epsilon\omega^2G(\omega^2), \tag{5}$$

where $G(\omega^2)=G_{x1x1}(\omega^2,0)$ and $\epsilon=m_1'/m_1-1$. The local-mode amplitudes are (for the x mode)

$$B_{\alpha i}{}^{LC}(n)=\epsilon\omega_{LC}{}^2B_{x1}{}^{LC}(0)G_{\alpha ix1}(\omega_{LC}{}^2,n). \tag{6}$$

The normalized amplitude is such that

$$B_{x1}{}^{LC}(0)=(\epsilon\omega_{LC}{}^2Z)^{-1}, \tag{7}$$

where

$$Z^2=W^2+(\epsilon\omega_{LC}{}^4)^{-1},$$

$$W^2=\sum_k\{|A_{x1}{}^k(0)|^2/[\omega^2(k)-\omega_{LC}{}^2]^2\}.$$

Actually, if we do not let our crystal become infinite, Eq. (5) has solutions for ω which lie in the phonon bands, differing from the phonon frequencies by amounts of order $1/N$.[8]

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

[8] See P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) **A273**, 222 (1963); A. A. Maradudin, *Phonons and Phonon Interactions* (W. A. Benjamin Inc., New York, 1964).

One usually replaces the sum over $\mathbf{k}$ by an integral. Then we have a singularity to avoid. In a sense, the certain presence of "external" perturbations such as anharmonic forces and genuine external fields "smears" the discrete spectrum (present as long as N is finite, however large it may be) into a continuous spectrum. We can write Eq. (5) as

$$1=\epsilon\omega^2\frac{v}{(2\pi)^3}\sum_s\int d\mathbf{k}\frac{\epsilon_{x1}{}^2(k)}{\omega^2(k)-\omega^2}, \tag{8}$$

where v is the volume of the unit cell.

Critical values of ϵ, corresponding to restrictions on the mass m_1' necessary to obtain a local mode, are gotten by setting ω equal to the frequency ω_m at the bottom/top edge of a band, in case $\epsilon \gtrless 0$.

Maradudin[8,9] has demonstrated that the localized mode amplitude behaves, for large $\mathbf{R}_n$, like a sum of terms which go like $\exp(-\alpha|\mathbf{R}_{ni}|)/|\mathbf{R}_{ni}|$, where α is, in general, a complex constant. That the amplitude should be localized is seen from the fact that $B_{\alpha i}{}^{LC}(n)$ is a superposition of all the phonon plane waves, each with nearly equal contributions. We have just another example (the superconductivity state is another) of a small perturbation leading to an "extraordinary" state. A good idea of the degree of localization can be obtained by looking at

$$|B_{x1}{}^{LC}(0)|^2/\sum_{n\alpha i}|B_{\alpha i}{}^{LC}(n)|^2=(\epsilon\omega_{LC}{}^2W)^{-2}. \tag{9}$$

For the in-band modes, one separates out a homogeneous part and takes the outgoing-wave solution for G:

$$B_{\alpha i}{}^k(n)=A_{\alpha i}{}^k(n)+\epsilon\omega^2\sum_\beta G_{\alpha i\beta 1}{}^+(\omega^2,n)B_{\beta 1}{}^k(0), \tag{10}$$

where

$$G_{\alpha i\beta j}{}^{\pm}(\omega^2,n)=G_{\alpha i\beta j}(\omega^2\pm i0,\,n)=G^p\pm iG^\delta.$$

The T matrix,[10] in this case, is

$$T_{\pm}=\epsilon\omega^2(1-\epsilon\omega^2G^{\pm})^{-1}; \tag{11}$$

and, in terms of T, we have

$$B_{\alpha i}{}^k(n)=A_{\alpha i}{}^k(n)+\sum_\beta T_+G_{\alpha i\beta 1}{}^+(\omega^2,n)A_{\beta 1}{}^k(0) \tag{12}$$

or

$$B=A+B_{\text{scattered}}\,.$$

Resonance modes occur for frequencies ω_R such that

$$1=\epsilon\omega_R{}^2G^p(\omega_R{}^2). \tag{13}$$

Corresponding to each of these resonances is a pole of T_+ just off the real axis of the complex ω^2 plane. Corresponding to the localized mode is a pole of T_+ on the real axis, but not in the unperturbed (phonon) spectrum. Since

$$B_{\alpha 1}{}^k(0)=(\epsilon\omega^2)^{-1}T_+A_{\alpha 1}{}^k(0), \tag{14}$$

at resonance

$$B_{\alpha 1}{}^k(0)=[i/\epsilon\omega_R{}^2G^\delta(\omega_R{}^2)]A_{\alpha 1}{}^k(0). \tag{15}$$

In the case of NaI:Li$^+$, $(1/\epsilon\omega_R{}^2G^\delta)\sim 10^2$. Finally, it is easily shown that the orthonormal in-band amplitudes are

$$C_{\alpha i}{}^k(n)=[m(ni)/m_i]^{1/2}B_{\alpha i}{}^k(n), \tag{16}$$

where $m(ni)=m_i$ for $R_{ni}\neq R_{01}$ and $m(01)=m_1'$. That they are orthogonal follows from the symmetry of the matrix for which they are eigenvectors.[11] That they are normalized (and orthogonal) is easily shown by carrying out $\sum_{n\alpha i}C_{\alpha i}{}^k(n)C_{\alpha i}{}^{k'*}(n)$.

We now express the above results on impurity modes in quantum-mechanical terms. The Hamiltonian for the perfect crystal is

$$H_0=\sum_{n\alpha i}\frac{p_{\alpha i}{}^2(n)}{2m_i}+\tfrac{1}{2}\sum_{\substack{nm\\ \alpha\beta ij}}V_{\alpha i\beta j}(n-m)x_{\alpha i}(n)x_{\beta j}(m), \tag{17}$$

where $x_{\alpha i}(n)$ and $p_{\alpha i}(n)$ are the ion positions and momenta, respectively. If we make the canonical transformation:

$$\begin{aligned}x_{\alpha i}(n)&=\textstyle\sum_k(\hbar/2m_i\omega(k))^{1/2}\{A_{\alpha i}{}^k(n)a(k)+\text{H.c.}\}\\ p_{\alpha i}(n)&=(1/i)\textstyle\sum_k(\hbar m_i\omega(k)/2)^{1/2}\\ &\qquad\times\{A_{\alpha i}{}^k(n)a(k)-\text{H.c.}\},\end{aligned} \tag{18}$$

where the $a(k)$ and $a^\dagger(k)$ obey the usual creation-annihilation commutation relations, the Hamiltonian is diagonalized:

$$H_0=\textstyle\sum_k\hbar\omega(k)[N(k)+\tfrac{1}{2}], \tag{19}$$

where $N(k)=a^\dagger(k)a(k)$.

In the case of a lattice with impurities, we can make an analogous transformation:

$$\begin{aligned}x_{\alpha i}(n)&=\textstyle\sum_k(\hbar/2m_i\Omega(k))^{1/2}\{B_{\alpha i}{}^k(n)b(k)+\text{H.c.}\}\\ p_{\alpha i}(n)&=(1/i)\textstyle\sum_k(\hbar m_i\Omega(k)/2)^{1/2}\\ &\qquad\times\{B_{\alpha i}{}^k(n)b(k)-\text{H.c.}\},\end{aligned} \tag{20}$$

where k is here an impurity-mode index, $\Omega(k)$ are the impurity-mode frequencies, and $b^\dagger(k)$ and $b(k)$ obey creation-annihilation commutation relations. Then, in the MDA,

$$\begin{aligned}H&=H_0+\sum_\alpha\left(\frac{1}{m_1'}-\frac{1}{m_1}\right)\frac{p_{\alpha i}{}^2(0)}{2}\\ &=\textstyle\sum_k\hbar\Omega(k)[b^\dagger(k)b(k)+\tfrac{1}{2}].\end{aligned} \tag{21}$$

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[9] A. A. Maradudin, *Astrophysics and the Many Body Problem* (W. A. Benjamin, Inc., New York, 1963).

[10] M. V. Klein, Phys. Rev. **131**, 1500 (1963).

[11] A. A. Maradudin, Westinghouse Res. Lab. Rept. No. 64–929–100–P1 (unpublished).

III. CONTRIBUTION TO THE LATTICE THERMAL CONDUCTIVITY

The bulk of the contribution to the lattice heat current is due to the phonons. The contribution of $B_{\text{scattered}}$ [see Eq. (12)] is of an order higher than $1/N$. Also, the contribution of certain "nondiagonal" terms which occur in some theories has been shown by Maradudin[12] to also be of an order higher than $1/N$. We thus use the following expression for the heat current J_α:

$$J_\alpha = \sum\nolimits_k v_\alpha \mathbf{v}\cdot\nabla T \tau C(k)\,, \tag{22}$$

where $v_\alpha(k)$ is the phonon group velocity, $\tau(k)$ the phonon lifetime (to be discussed later), $C(k)$ the phonon heat capacity, and ∇T the temperature gradient. Explicitly,

$$C(k) = \frac{\hbar^2\omega^2(k)}{V k_B T^2} \frac{\exp[\hbar\omega(k)/k_BT]}{\{\exp[\hbar\omega(k)/k_BT]-1\}^2}\,, \tag{23}$$

where k_B is Boltzmann's constant and V is the sample volume. Cubic symmetry leads to a thermal conductivity of the form

$$\kappa_{\alpha\beta} = \delta_{\alpha\beta}\kappa\,, \tag{24}$$

where

$$\kappa = \sum\nolimits_k C(k) v_x^2(k)\tau(k)\,. \tag{25}$$

We will assume that the theory of McLennan[13] and Schieve and Peterson[13] holds, and we will discuss only the contribution of impurity scattering to $\tau(k)$.

The lifetime $\tau(k)$ in the above theory is defined by the equation

$$\langle n|dN(k)/dt|n\rangle = [\tau(k)]^{-1}\langle n|N(k)|n\rangle\,, \tag{26}$$

where

$$dN(k)/dt = (1/i\hbar)[N(k),H]$$

and $|n\rangle$ is an eigenstate of H_0. The orthogonality relations of $A_{\alpha i}{}^k(n)$ lead to

$$\sum_{n\alpha i} A_{\alpha i}{}^{k*}(n) B_{\alpha i}{}^{k'}(n) = F^{kk'} = \delta_{k'k} + (\epsilon\cdot\epsilon'/N)[T_+'/(\omega'^2-\omega^2-i0)]\,, \tag{27}$$

where we have suppressed arguments, using primes instead, and have let

$$\epsilon\cdot\epsilon' \equiv \sum_\alpha \epsilon_{\alpha 1}(k)\epsilon_{\alpha 1}(k')\,. \tag{28}$$

Combining Eqs. (18), (20), and (27), we obtain

$$a(k) = \tfrac{1}{2}\sum_{k'} [1/(\omega\omega')^{1/2}][(\omega+\omega')F^{kk'}b(k') - (\omega-\omega')F^{-kk'*}b(k')]\,, \tag{29}$$

where $-k \equiv \{-\mathbf{k}, s\}$. To first order in $1/N$,

$$N(k) \equiv a^\dagger a = b^\dagger b + \sum_{k'} \frac{\epsilon\cdot\epsilon'}{2N(\omega\omega')^{1/2}} \left[\left(\frac{(\omega+\omega')T_-'b'^\dagger b}{\omega'^2-\omega^2+i0} + \frac{(\omega-\omega')T_-'b^\dagger b'^\dagger}{\omega'^2-\omega^2+i0}\right) + \text{H.c.}\right]. \tag{30}$$

Using

$$\frac{d(b'^\dagger b)}{dt} = \frac{1}{i\hbar}[b'^\dagger b, H] = \frac{1}{i}(\omega-\omega')b'^\dagger b\,, \tag{31}$$

we find

$$\langle n|dN/dt|n\rangle = \langle n|N|n\rangle/\tau_{\text{imp}}\,, \tag{32}$$

where

$$\tau_{\text{imp}}{}^{-1}(k) = \left\{\frac{\epsilon\cdot\epsilon}{\omega N}\right\} \text{Im}T_+\,. \tag{33}$$

The above expression for τ^{-1} was obtained by Maradudin,[12] for the case of a monatomic lattice for which $\epsilon\cdot\epsilon = 1$. (See also Elliott and Taylor.[14]) He used the Kubo expression for the thermal conductivity, many-body techniques, and approximations which amount to giving physical reality to the lifetime. However, the extreme simplicity of the above approach and the great amount of information derived suggest that the above approach may have general use in the investigation of the role of "localized perturbations" in irreversible phenomena. The approach is certainly applicable to the calculation of the contribution of point-defect scattering to the lifetime of electronic states.

To conclude this section, we should like to make a point concerning the McLennan expression for κ and one of Kubo's expressions for κ:

$$\begin{aligned} \kappa_{\text{Kubo}} &= \frac{V}{T}\int_0^\beta d\beta' \int_{-\infty}^0 dt \langle j(t-i\hbar\beta')j(0)\rangle_T\,, \\ \kappa_{\text{McLennan}} &= \frac{V}{k_BT^2}\int_{-\infty}^0 dt \langle j(t)j(0)\rangle_T\,. \end{aligned} \tag{34}$$

Above, $\beta = 1/k_BT$, $j(t)$ is heat-current-density operator $e^{iHt/\hbar}j(0)e^{-iHt/\hbar}$, and $\langle\ \rangle_T$ is a thermal canonical average using H. The Schieve-Peterson approximation replaces $\langle\ \rangle_T$ by a canonical average using H_0. The canonical average then becomes a sum over k of terms with a time dependence $\exp[t/\tau(k)]$ arising from $j(t)$. The lifetime $\tau(k)$ for alkali halides is at least 10^{-10} sec^{-1}, so that for $T > 10°$K, $\hbar/k_BT\tau \lesssim 10^{-2}$. Thus, in the Schieve-Peterson approximation, and to first order in the parameter $\hbar/k_BT\tau$, the two expressions for κ give the same result.

IV. LATTICE VIBRATIONS IN IONIC CRYSTALS

The application of the above theory on impurity modes to ionic crystals is not straightforward, due to

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[12] A. A. Maradudin, Westinghouse Res. Lab. Rept. No. 64–929–100–P4 (unpublished).

[13] J. A. McLennan, Phys. Rev. **115**, 1405 (1959); W. C. Schieve and R. L. Peterson, *ibid.* **126**, 1458 (1962).

[14] R. J. Elliott and D. W. Taylor, Proc. Phys. Soc. (London) **83**, 189 (1964).

the presence of macroscopic electric and magnetic fields produced by ionic vibrations. We have to deal with high dielectric constants and therefore with crystal-shape- and environment-dependent effects. In particular, theorists have concluded that the $\mathbf{k}=0$ optical modes consist of a longitudinal mode frequency ω_L and a doubly degenerate transverse mode frequency ω_T, with

$$\omega_T^2/\omega_L^2=\epsilon_\infty/\epsilon_0\,, \tag{35}$$

where ϵ_∞ and ϵ_0 are the high-frequency and zero-frequency dielectric constants of the crystal. This result is at first surprising, since cubic symmetry is expected to lead to the equality of ω_L and ω_T. Rosenstock,[15] besides bringing up this point, has recently claimed that the $\mathbf{k}=0$ modes and modes with $|\mathbf{k}|\gtrsim 0$ and $\mathbf{k}$ in the general direction have neither longitudinality nor transversality —with obvious justification. Rosenstock's arguments concerning cubic symmetry are true but are not applicable to ionic crystals because of depolarization fields and the strong phonon-photon interaction.

The important fact to keep in mind is that all results concerning the $|\mathbf{k}|\gtrsim 0$ optical modes are crystal-shape- and environment-dependent. As Huang[16] shows, one obtains the frequencies ω_L and ω_T, corresponding to a longitudinal and two transverse modes, respectively, for the $\mathbf{k}\gtrsim 0$ optical modes, if one assumes that there is no transverse optical (TO) mode contribution to the macroscopic electric field ($E_{\mathrm{TO}}{}^m=0$). We will refer to such a crystal as an "isolated" crystal. Contrary to the statements of Lyddane and Herzfeld,[17] this result is independent of other boundary conditions (crystal shape and environment) and is independent of the direction of $\mathbf{k}$. In the case of nonelectromagnetic phenomena, such as thermal conductivity and neutron diffraction, it is assumed that the crystal is "isolated." Whether this is so may be questionable. For gross properties such as thermal conductivity, results are not observably affected by the actual conditions. In neutron diffraction, we might see a boundary condition effect in the TO branches near $\mathbf{k}=0$. In a calculation of the transverse susceptibility, the contribution to $E_{\mathrm{TO}}{}^m$ should just be removed from the dynamical matrix and be lumped together with the external transverse field. Then one can solve for the polarizability proportional to $E_T{}^m$, the total transverse macroscopic field. One should therefore use this modified dynamical matrix D to obtain the optical, local mode, characteristic frequency. We have used D in the calculation of the impurity contribution to the thermal conductivity lifetime—with the above-mentioned reservations. At $\mathbf{k}\equiv 0$, the condition $E_{\mathrm{TO}}{}^m=0$ leads to a singularity. Then, either $\omega=\omega_L$ and $D^m=E^m+4\pi P^m=0$, or $\omega=0$ and $D^m=\epsilon_0 E^m$. We neglect this fact and let $\mathsf{D}(\mathbf{k})$ be continuous at $\mathbf{k}=0$.

We now consider the computation of D. In the PIM, we use the $\mathbf{k}\neq 0$ elements obtained by Kellermann.[7] The elements for $\mathbf{k}=0$ (which he did not provide) are

$$\begin{aligned} D_{\alpha i\beta j}{}^K(0)&=\eta_i\eta_j\delta_{\alpha\beta}(C-Q)\,, \quad \alpha=x,\,y\,,\\ &=\eta_i\eta_j\delta_{\alpha\beta}(C+2Q)\,, \quad \alpha=z\,, \end{aligned} \tag{36}$$

where $\eta_i=e_i/\sqrt{m_i}$, $C=(A+2B)/v$, and $Q=4\pi/3v$—all in Kellermann's notation. We have also let $\alpha=z$ correspond to the longitudinal modes and, in the optical absorption calculation, will take the wave vector to be in the $\alpha=z$ direction.

In the EPM,[18] we include the fields due to an electronic polarization wave

$$\mu_{\alpha i}(n)=\mu_{\alpha i}e^{i\mathbf{k}\cdot\mathbf{R}_{ni}}\,. \tag{37}$$

We neglect overlap force effects on $\mu_{\alpha i}$, considering only the forces on $\mu_{\alpha i}$ due to the Kellermann active Coulomb field. The Coulomb contribution to D^K can be written as

$$D_{\alpha i\beta j}{}^{CK}=-\eta_i\eta_j R_{\alpha i\beta j}\,. \tag{38}$$

The active electric field is then in the PIM,

$$E_{\alpha i}{}^A=\textstyle\sum_{\beta j} R_{\alpha i\beta j}e_j x_{\beta j}+E_{\mathrm{TO}\alpha i}{}^m\,, \tag{39}$$

while in the EPM,

$$E_{\alpha i}{}^A=\textstyle\sum_{\beta j} R_{\alpha i\beta j}(e_j x_{\beta j}+\mu_{\beta j})+E_{\mathrm{TO}\alpha i}{}^m\,. \tag{40}$$

We assume

$$\mu_{\alpha i}=a_i E_{\alpha i}{}^A\,, \tag{41}$$

where a_i is the electronic polarizability of the ith ion. Solving for $\mu_{\alpha i}$, we have, in the EPM,

$$D_{\alpha i\beta j}{}^{CE}=\sum_{\gamma p}\left(\frac{1}{a}\mathsf{I}-\mathsf{R}\right)^{-1}_{\alpha i\gamma p}\left(\frac{1}{a_p}\right)D_{\gamma p\beta j}{}^{CK}\,, \tag{42}$$

where

$$\left(\frac{1}{a}\mathsf{I}\right)_{\alpha i\beta j}=\delta_{\alpha\beta}\delta_{ij}/a_i\,.$$

Then

$$\mathsf{D}^E=\mathsf{D}^{RK}+\mathsf{D}^{CE}\,, \tag{43}$$

where D^{RK} is the repulsive contribution to D^K. For $\mathbf{k}=0$, we obtain

$$D_{\alpha i\beta j}{}^E(0)=\eta_i\eta_j\delta_{\alpha\beta}\begin{cases} C-Q/d\,, & \alpha=x,\,y\\ C+2Q/d'\,, & \alpha=z\end{cases}\,, \tag{44}$$

where $d=1-(a_1+a_2)Q$ and $d'=1+2(a_1+a_2)Q$. In the absence of impurities, the equation of motion for $\epsilon_{\alpha i}(k)$ becomes

$$\begin{aligned} &\textstyle\sum_{\beta j} D_{\alpha i\beta j}{}^E(k)\epsilon_{\beta j}(k)-\omega^2(k)\epsilon_{\alpha i}(k)\\ &\qquad=(\eta_i/a_i)\textstyle\sum_{\beta j}(1/a\mathsf{I}-\mathsf{R})_{\alpha i\beta j}{}^{-1}E_{\mathrm{TO}\beta j}{}^m\,. \end{aligned} \tag{45}$$

The RHS is nonzero only for $\mathbf{k}\gtrsim 0$, when it equals $\eta_i E_{\alpha i}{}^m/d$. Removing the macroscopic field contribution of the LO mode amounts to taking the z components of $\mathsf{D}^K(0)$ and $\mathsf{D}^E(0)$ equal to the x, y components. In

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the absence of other perturbations, Huang's[16] macroscopic equation for the ion displacements is equivalent to the equation

$$\sum_j D_{\alpha i \alpha j}{}^E(0)\epsilon_{\alpha j}-\omega^2\epsilon_{\alpha i}=(\eta_i/d)E_\alpha{}^m. \tag{46}$$

The frequency spectrum obtained using the above theory is in gross disagreement with experiments. We assume, with Born and Huang, that the discrepancy is partly due to the fact that the ions do not carry a full unit charge. Rather, we should associate with them charges of magnitude $e^*=fe$. We have determined f so as to yield the experimental value of ω_T. We have

$$\omega_T{}^2=e^{*2}/\bar{m}\{C-Q/d\}, \tag{47}$$

where $\bar{m}$ is the reduced mass of the two ions. For NaI, with $\omega_T=2.20\times 10^{13}$ sec^{-1}, we find $f=0.69$. This is the only correction included in our calculations.

V. CONTRIBUTION TO THE OPTICAL ABSORPTION COEFFICIENT

In this section, we let $B_{\alpha i}{}^k(n)$ be the impurity-mode amplitudes corresponding to $\mathbf{D}^K$ or $\mathbf{D}^E$, as the case may be. Then, in the presence of an external field yielding a macroscopic field

$$\mathbf{E}^m(\mathbf{r}t)=\mathbf{E}^m e^{i\kappa\cdot\mathbf{r}-i\omega t}, \tag{48}$$

we obtain for our total Hamiltonian, in the case of $\mathbf{D}^K$,

$$H_T=H-\mathbf{M}\cdot\mathbf{E}^m, \tag{49}$$

where

$$M_\alpha\equiv\sum_{ni} e_i x_{\alpha i}(n)=\sum_k m_\alpha(k)[b^\dagger(k)+b(k)]. \tag{50}$$

In Eq. (50), we have let $\kappa\to 0$, since $\boldsymbol{\kappa}\cdot\mathbf{R}_{ni}\ll 1$. We get three types of nonzero $m_\alpha(k)$: those due to the local modes, those due to the transverse optical modes at $\mathbf{k}=0$, and those which can be referred to as a background contribution $m_\alpha{}^B(k)$ due to in-band mode impurity scattering. We have

$$\begin{aligned} m_\alpha{}^{LC}&=\sum_i \eta_i(\hbar/2\omega_{LC})^{1/2}\{[\mathbf{D}(0)^K-\omega^2\mathbf{I}]_{\alpha i x1}{}^{-1}/Z\},\\ m_\alpha{}^T&=\sum_i \eta_i(N/2\omega_T)^{1/2}\epsilon_{\alpha i}=(\hbar N/2\bar{m}\omega_T)^{1/2}e,\\ m_\alpha{}^B(k)&=\frac{T_+}{N}\left(\frac{\hbar N}{2\bar{m}\omega_T}\right)^{1/2}\frac{e(\epsilon^T\cdot\epsilon(k))}{\omega_T{}^2-\omega^2(k)-i0},\end{aligned} \tag{51}$$

where $e=e_1$ and $\epsilon_i{}^T$ is the transverse, $\mathbf{k}\sim 0$, polarization vector.

Above, we have used the relations

$$\begin{aligned}(m_1)^{1/2}\epsilon_{x1}{}^T+(m_2)^{1/2}\epsilon_{x2}{}^T&=0,\\ (\epsilon_{x1}{}^T)^2+(\epsilon_{x2}{}^T)^2&=1.\end{aligned} \tag{52}$$

From cubic symmetry, the susceptibility $\chi_{\alpha\beta}$, satisfies

$$\begin{aligned}\chi_{\alpha\beta}&=\delta_{\alpha\beta}\chi,\\ P_\alpha{}^m&=\chi E_\alpha{}^m.\end{aligned} \tag{53}$$

First-order, time-dependent perturbation theory yields:

$$\chi=\sum\nolimits_k \chi(k), \tag{54}$$

where

$$\chi(k)=\frac{2\omega(k)}{\hbar N v}\left(\frac{|m_x(k)|^2}{\omega^2(k)-\omega^2+i(\Gamma^2(k)/2)}\right). \tag{55}$$

We have included a damping term due to the finite lifetime of the modes. The absorption coefficient is

$$a(\omega)=-(4\pi\omega/c)\,\mathrm{Im}\chi. \tag{56}$$

We find that

$$a(\omega)=a^T(\omega)+a^{LC}(\omega)+a^B(\omega), \tag{57}$$

with

$$\begin{aligned} a^T(\omega)&=\frac{4\pi e^2\omega}{\bar{m}vc}\left(\frac{\Gamma_T{}^2/2}{(\omega_T{}^2-\omega^2)+(\Gamma_T{}^2/2)^2}\right),\\ a^B(\omega)&=\frac{1}{N^2}\frac{4\pi e^2\omega}{\bar{m}vc}\sum_k\frac{|T_+\epsilon^T\cdot\epsilon(k)|^2\Gamma^2(k)/2}{\{[\omega_T{}^2-\omega^2(k)]^2+[\Gamma^2(k)/2]^2\}\{[\omega^2(k)-\omega^2]^2+[\Gamma(k)^2/2]^2\}},\\ a^{LC}(\omega)&=\frac{1}{N}\left(\frac{4\pi\omega}{vc}\right)\left(\frac{U^2}{Z^2}\right)\left(\frac{\Gamma_{LC}{}^2/2}{(\omega_{LC}{}^2-\omega^2)^2+(\Gamma_{LC}{}^2/2)^2}\right),\end{aligned} \tag{58}$$

where

$$U\equiv\sum\nolimits_i\eta_i[\mathbf{D}(0)^K-\omega_{LC}{}^2\mathbf{I}]_{xix1}{}^{-1}=\eta_1/(\omega_T{}^2-\omega_{LC}{}^2), \tag{59}$$

and we have inserted a width into the expression for $m_\alpha{}^B(k)$.

In the EPM, we have to use $\mathbf{D}^E$ instead of $\mathbf{D}^K$, use $e_i{}^*$ instead of e_i, use ω_{LC} resulting from $\mathbf{D}^E$, and divide the above expressions for χ and $a(\omega)$ by the factor d. An experimentally important quantity is

$$R_{LCT}\equiv\frac{a^{LC}(\omega_{LC})}{a^T(\omega_{LC})}=\frac{1}{N}\left(\frac{4\bar{m}}{m_1}\right)\cdot\left(\frac{1}{Z^2\Gamma_{LC}{}^2\Gamma_T{}^2}\right), \tag{60}$$

where we have let $U\to\eta_1/(\omega_T{}^2-\omega_{LC}{}^2+i\Gamma_T{}^2/2)$.

We see that, provided $|T_+|^2$ is sharply peaked at the resonance frequencies, and $\Gamma(\text{res})$ is large, we may see absorption peaks at resonance frequencies.

VI. CALCULATIONS AND RESULTS

The inputs for our calculations were the physical constants given in Table I and Kellermann's $\mathbf{D}^{cK}$. We were therefore restricted to his sampling mesh of the first Brillouin zone. We have sums such as

$$S_n=\frac{1}{N}\sum_k \frac{[\epsilon_{x1}(k)]^2}{[\omega^2(k)-\omega^2]^n}, \quad n=1,2$$

to perform. These were readily converted into sums over Kellermann's 1/48 section of the zone. All major computations were carried out using the IBM-709 of the Cooperative Computing Laboratory at MIT.

In Subsec. A of this section, we discuss the results for the frequencies and eigenvectors of the dynamical matrix using the EPM, comparing the results with those obtained using the PIM[19] and DDM.[20] The EPM results were used to get an idea of the behavior of the impurity lifetime important in thermal conductivity. This subject is discussed in Subsec. B of the section. In Subsec. C, we discuss the results concerning the optical absorption. The dynamical matrices of the EPM were used. Table III summarizes the important numerical results.

A. Results for the EPM

In Table II, we compare the square frequencies along the ⟨100⟩ and ⟨111⟩ directions obtained with the PIM,[19] the EPM, and the DDM[20] with the results of neutron diffraction experiments carried out at 118°K.[21] The theoretical frequencies are those for the "isolated" crystal. We see that the longitudinal optical band of the PIM is completely out of line. For some points, the EPM does better than the DDM, but, all in all, the DDM yields more favorable results. There seems to be a tendency for the EPM to have a negative error along the ⟨100⟩ direction, which increases the closer we come to the zone face. The lower frequencies signify less binding. Woods *et al.*[22] have claimed that this is due to the neglect of dipole deformation. One may justify this claim simply by citing the good results of the DDM. But there is further confirmation. We note that acoustic modes along the ⟨100⟩ direction and with large $|\mathbf{k}|$ generally have a greater overlap of neighboring ions. If we do not permit the electron clouds to deform, we will get an added repulsive force.

TABLE II. Comparison of square frequencies for the isolated slab of NaI. LA = longitudinal acoustic; TA = transverse acoustic; LO = longitudinal optical; TO = transverse optical.

		Experiment[a]	EPM	PIM	DDM[a]
		⟨100⟩			
(000)	LA	0.0	0.0	0.0	0.0
	TA				
	TO	2.2	2.19	2.01	2.2
	LO	3.1	3.28	4.17	3.3
(200)	LA	0.6	0.58	0.52	0.6
	TA	0.2	0.17	0.27	0.2
	LO	3.0	3.16	4.09	3.1
	TO	2.2	2.18	2.05	2.2
(400)	LA	1.0	1.04	0.95	1.0
	TA	0.4	0.32	0.51	0.4
	LO	2.7	2.81	3.87	2.8
	TO	2.2	2.14	2.12	2.2
(600)	LA	1.2	1.25	1.25	1.1
	TA	0.6	0.37	0.69	0.5
	LO	2.4	2.32	3.61	2.6
	TO	2.3	2.09	2.23	2.3
(800)	LA	1.1	0.87	1.37	1.0
	TA	0.6	0.37	0.80	0.5
	LO	2.3	2.04	3.41	2.7
	TO	2.3	1.99	2.31	2.3
(1000)	LA	1.1	0.00	1.38	1.1
	TA	0.6	0.36	0.83	0.5
	LO	2.3	2.02	3.34	2.7
	TO	2.3	1.94	2.35	2.3
		⟨111⟩			
(111)	LA	0.5	0.37	0.43	0.5
	TA	0.3	0.30	0.26	0.3
	LO	···	3.27	4.13	3.3
	TO	2.2	2.22	2.01	2.2
(222)	LA	0.8	0.73	0.84	0.8
	TA	0.5	0.56	0.50	0.5
	LO	···	3.25	4.03	3.4
	TO	2.2	2.26	2.00	2.1
(333)	LA	1.1	1.01	1.20	1.0
	TA	0.7	0.76	0.69	0.6
	LO	···	3.22	3.89	3.5
	TO	2.2	2.31	2.00	2.1
(444)	LA	1.3	1.21	1.47	1.1
	TA	0.9	0.89	0.80	0.9
	LO	···	3.19	3.75	3.6
	TO	2.2	2.35	1.99	2.0
(555)	LA	1.4	1.28	1.57	1.1
	TA	0.9	0.93	0.85	0.9
	LO	···	3.18	3.70	3.6
	TO	2.2	2.37	1.99	2.0

[a] Estimated from graphs.

It is interesting to note that for all the cases considered, the amplitudes $\epsilon_{\alpha1}(k)$ were much greater for the optical modes than for the acoustic modes. This is a general result for the amplitude of the lighter ion in a diatomic crystal. From the orthogonality condition

$$\sum_s \epsilon_{\alpha i}(s)\epsilon_{\beta j}(s)=\delta_{\alpha\beta}\delta_{ij},$$

we have

$$\sum_s \epsilon_{\alpha1}(s)\epsilon_{\alpha1}(s)=\sum_s \epsilon_{\alpha2}(s)\epsilon_{\alpha2}(s)=1,$$

so that if $\epsilon_{\alpha1}$ is the larger for some s, $\epsilon_{\alpha2}$ must be the larger for other s. The dominance of $\epsilon_{\alpha1}$ over $\epsilon_{\alpha2}$ for the optical modes was so great, that, when combined with the ω^2 factors occurring in the equations for ω_{LC}^2, ω_{res}^2, and τ_{imp}, we found that the acoustic band played almost a negligible role in determining the effects of impurities (which replace the Na^+ ion) on the crystal.

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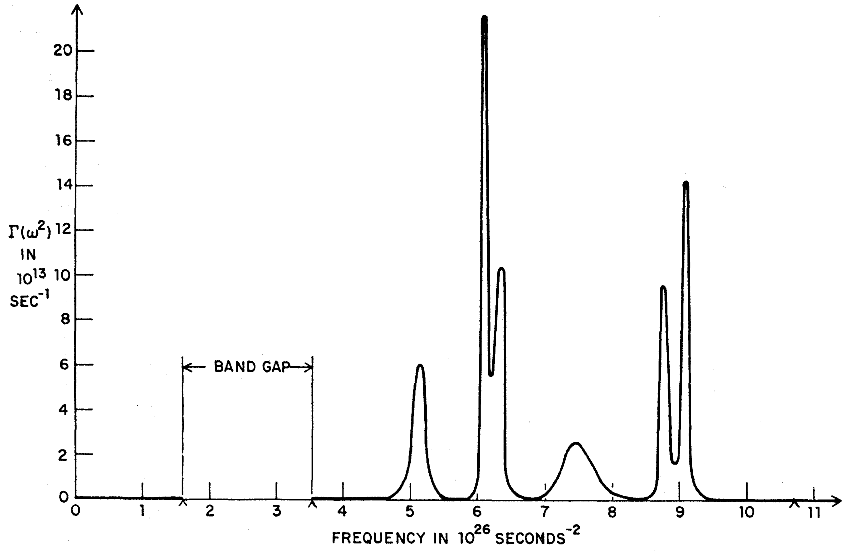

FIG. 1. Approximate behavior of the thermal conductivity inverse lifetime due to Li^+ in NaI. The carats at 1.63, 3.78, and 10.77 $\times 10^{26}$ sec^{-2} indicated the edges of the bands.

B. Results Concerning the Thermal Conductivity

We computed a quantity related to the phonon lifetime important in thermal conductivity $\tau(k)_{\mathrm{imp}}$ given by Eq. (33):

$$\Gamma_{\mathrm{imp}}(\omega^2)=N[\epsilon(k)\cdot\epsilon(k)\tau(k)_{\mathrm{imp}}]^{-1}.$$

We used the dynamical matrix for the EPM and the isolated crystal. We have plotted Γ_{imp} in Fig. 1. We cannot rely heavily on the quantitative results for Γ_{imp} throughout its domain, since we had a principal value integral to perform without a fine enough mesh. However, varying the closeness of approach to the point for which the principal value was taken yielded changes in Γ_{imp} of usually about 1–5% and sometimes 50% ***but*** negligible change in the position and character of the peaks centered at

$$\omega_{\mathrm{res}}^2=6.1 \quad \text{and} \quad 8.9\times10^{26}\ \mathrm{sec}^{-2},$$

one smaller peak at

$$\omega_{\mathrm{res}}^2=4.8\times10^{26}\ \mathrm{sec}^{-2},$$

and an even smaller peak at

$$\omega_{\mathrm{res}}^2=7.6\times10^{26}\ \mathrm{sec}^{-2}.$$

TABLE III. Results concerning optical absorption.

	$\mathrm{NaI{:}Li^+}$	$\mathrm{NaI{:}K^+}$
$\omega_{LC}(10^{13}\ \mathrm{sec}^{-1})$	4.28	1.76
$W^2(10^{-52}\ \mathrm{sec}^4)$	0.00635	0.397
$\mathrm{Na}(\omega_{LC})(10^7\ \mathrm{cm}^{-1})$	3.25	1.60
$NR_{LCT}(10^4)$	16.3	0.91
$\lvert C_{x1}^{LC}(0)\rvert^2$	0.74	0.26
m_1'(amu)		
ω_{LC} above optical band	13.3	...
ω_{LC} in gap	...	33.1

According to Walker and Pohl,[5] a resonance frequency of $1.0\times10^{13}\ \mathrm{sec}^{-1}$ was able to account for a dip in κ at about 30°K, in the case of $\mathrm{KCl{:}I^-}$ (using a simple expression for τ). The above resonances can therefore be expected to be influential in this temperature region. In the range of the acoustic band, Γ_{imp} was, at most, $0.0085\times10^{13}\ \mathrm{sec}^{-1}$. It must be kept in mind that when other contributions to phonon lieftimes are added to τ_{imp}^{-1}, the effect of the sharp resonance peaks will be diminished. Moreover, if a peak is too sharp, it may not show up in the thermal conductivity. In the low-temperature range (0 to 50°K) that we are interested in, other contributions to τ^{-1} amount to 10^8–$10^9\ \mathrm{sec}^{-1}$.[5] Thus, our resonance peaks can still stand out, with magnitudes of about

$$(1/N)10^{14}=10^{10}\ \mathrm{sec}^{-1}$$

for $N=10^{+4}$. At low temperatures, we expect an error of a few percent to arise as a result of the use of room-temperature data. In any case, we can be prepared for some complex structure in the temperature dependence of κ for NaI doped with Li^+.

C. Results Concerning Optical Absorption

We now consider the results concerning optical absorption. In Table III, we list the results of our calculations. The figures for $\mathrm{Na}(\omega_{LC})$ and NR_{LCT} were gotten by assuming $\Gamma_T=\omega_T$ and $\Gamma_{LC}=\omega_{LC}/100$. Results of Barnes[23] show that Γ_T is of the order of magnitude of ω_T at room temperature. At lower temperatures ($\approx$50°K), Γ_T should be at least an order of magnitude

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[23] R. B. Barnes, Z. Physik **75**, 723 (1932).

lower. For monatomic crystals, Klemens[24] and Maradudin[11] have both obtained estimates of Γ_{LC} (due to anharmonic interactions) which are around $\omega_{LC}/100$ for temperatures around 10 to 50°K. We have neglected the shift in ω_{LC} due to the anharmonic interactions. This too, according to Maradudin,[11] is on the order of $\omega_{LC}/100$ at low T. All the above estimates may be incorrect by a factor of 10 either way. The acoustic band is so weakly "influential," that there exists *no* light mass ($\epsilon<0$) impurity with a localized mode in the gap. Finally, the results for $|C_{x1}{}^{LC}(0)|^2$ indicate that the length characterizing the localization of the NaI:Li$^+$ local mode is less than a lattice spacing.

VII. SUMMARY AND CONCLUSIONS

We have investigated two important effects due to impurities on the lattice vibrations of alkali halides. Having set up the basic theoretical machinery, we have obtained some idea of what to expect experimentally in the case of NaI:Li$^+$. We developed a simple approach to obtaining the impurity contribution to the phonon lifetime which is applicable in thermal conductivity. Numerical results indicate that we should observe a few dips due to resonance modes in the κ-versus-T curve of NaI:Li$^+$. It has been suggested by Visscher[25] that we may even be able to observe the virtual localized modes (resonances) directly by neutron-scattering experiments. It would therefore be worthwhile to calculate the contribution of impurities to the correlation function:

$$F(\mathbf{g},t)=\sum e^{i\mathbf{g}\cdot\mathbf{R}_{nmij}}\langle\{\exp[-i\mathbf{g}\cdot\mathbf{x}_i(n)]\}\times\{\exp[i\mathbf{g}\cdot\mathbf{x}_j(m,t)]\}\rangle,$$

where $\mathbf{x}_j(m,t)=e^{iHt/\hbar}\mathbf{x}_j(m)e^{-iHt/\hbar}$.

We should seek to improve on our numerical results by using a finer mesh. Then we could rely on results for G^p and obtain the group velocities, $\mathbf{v}(k)$, and finally, $\kappa(T)$. As far as optical absorption is concerned, we determined the localized mode frequency in the MDA for NaI:Li$^+$ and NaI:K$^+$; with estimates of the lifetime of the localized mode, we showed that one should be able to observe a localized mode absorption peak at a frequency of 4.28×10^{13} sec^{-1}, in the case of NaI:Li$^+$, and at a frequency of 1.76×10^{13} sec^{-1}, in the case of NaI:K$^+$. Resonance modes of NaI:K$^+$ and of NaI:Li$^+$ may also be optically observable.

In general, we should consider using better models for the interionic forces such as the DDM and others[26] which take account of dipole deformation. (The DDM has been applied to NaCl and KCl in the MDA by Jaswal and Montgomery.[27]) Furthermore, we should look into the effects and importance of impurity-impurity interactions, i.e., terms to second order in $1/N$. Finally, when possible, physical constants used in future calculations should correspond to the temperature around which experiments on the particular phenomenon of interest are carried out.

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