

Szigeti, can be obtained; for s^2 we get

$$s^2 = 1 - (1+f)t + ft^2, \quad (\text{A10})$$

where

$$t = \frac{\frac{n_+}{k_+} - \frac{n_-}{k_-}}{\frac{Z}{A} + \frac{Zf}{k_+} + \frac{Zf}{k_-}}. \quad (\text{A11})$$

If we compare these results with those of Hanlon and Lawson, it turns out that Eqs. (A8) and (A9) are the same as Eqs. (21) and (29) in their paper. However, for s

they obtained [Eq. (25)], in our notation,

$$s^2 = 1 - 2ft + f^2t^2 = (1 - ft)^2. \quad (\text{A12})$$

The reason for this difference is that they did not calculate the expression for the static polarizability, which is also altered by the change in the model.

That they obtained agreement between s values from Eq. (1) and those from Eq. (A12) is therefore no support for the model, but possibly also with Eq. (A10) a value of f can be selected that is in agreement with experimental data. However, as the more simple model of Dick and Overhauser already gives good results, we do not think it necessary to include this complication.

Vibrational Modes Near Impurities

HERBERT B. ROSENSTOCK AND CLIFFORD C. KLICK
U. S. Naval Research Laboratory, Washington, D. C.

(Received March 25, 1960)

In many cases, the interaction between the electronic state of an impurity in a solid and the motion of the atoms in the lattice is controlled by the relative motion of the impurity with respect to its nearest neighbors. We therefore examine the nature of the vibrations of the lattice near an impurity. In particular, two problems are considered: First, the direct absorption of light by the "localized" mode introduced by the presence of the impurity, and the relation of its frequency to that of the "reststrahlen" absorption; second, the relative importance of the "localized" modes and of the "lattice" modes in producing the observed broadening of the spectra due to electronic transitions of the impurity center. It is found that the large number of lattice modes together produce a mean displacement of the same order of magnitude as do the very few local ones. The implications for the "configuration coordinate" model for phosphors are examined; both theory and experiment suggest that if only one mode, or group of modes, are effective in producing broadening, their frequency is substantially lower than that of the localized modes which are optically active.

I. INTRODUCTION

WE wish to discuss here the nature of the vibrations of a lattice near an impurity. Many of the properties of impurities in a lattice depend on interaction of the electronic state of the impurity with that of the lattice vibrations; the mechanism of this interaction has been discussed by many people.¹ Here we shall not concern ourselves with the detailed nature of these interactions; we shall merely note that this interaction, whatever it is, will be the result, in many cases, of the relative motion of the impurity atom with respect to its nearest neighbors, and ask what our knowledge of the lattice vibrations can tell us about this.

Two problems in particular are considered: First, the optical absorption by impurity centers is considered and the relation of the frequency of this absorption to the mass of the imperfection is computed. Second, an

attempt is made to assess the relative importance of local vibrational modes and of lattice modes in producing the observed broadening of optical spectra. This leads to an examination of the rationale for the "configuration coordinate" model for phosphors.

In most cases we shall have to work with rather simplified models, since more realistic ones are mathematically too complicated. However, many of our conclusions can be taken over qualitatively to more physical situations, as we shall point out as we go along. The results of this analysis will be compared with experimental data on the optical properties of KCl containing F centers, hydride ions, and thallium.

II. "BREATHING" MODES

One assumption we shall make throughout is that introduction of the impurity atom does not change the force constants in any way. This is strictly correct only for impurities which are isotopes of the regular constituents of the lattice, but may be approximately true also for impurities chemically similar to them.

We shall also confine ourselves to a cubic lattice and

¹ For a review, see M. Lax, in the *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4-6, 1954*, edited by R. G. Breckenridge, B. R. Russell, and E. E. Hahn (John Wiley & Sons, New York, 1956), p. 111.

assume that the impurity is located at the center of it, so that the lattice is symmetrical about the impurity. This is likely to be a valid assumption for laboratory size crystals with a reasonably low density of impurities; it is similar in nature to the well-known approximation according to which the details of the boundary conditions are ignored (cyclic boundary conditions) in lattice dynamical problems. Concretely, we let the crystal extend from site $-N$ to site N in each direction, and whenever there is an impurity, we put it at the site $(0,0,0)$.

The usual procedure in lattice dynamics is to write down the Newtonian equations of motion for the displacements u_l, v_l, w_l of particle $\mathbf{l} = (l_1, l_2, l_3)$ in the x, y , and z directions, and convert them into difference equations by inserting harmonic time dependence. The second assumption above then implies that these difference equations will be symmetrical about the origin, and from this we can deduce² that all solutions will be either even or odd in each of the variables l_1, l_2, l_3 . (In case of degeneracy, this is not strictly true, but linear combinations of solutions which are either even or odd can then be found.)

From the general theorem that all modes are either even or odd, we cannot conclude with certainty that some odd ones actually exist, at any rate not without examining the set of difference equations in each particular case. However, it seems very likely that, for every particular lattice, at least some of the very large number of modes should be odd in all three space variables. As an example we cite the simple monatomic cubic lattice (without any impurity) with free ends (i.e., correct boundary conditions) and interaction between nearest neighbors only—a nontrivial problem if the forces have a noncentral component. In that case the modes are³

$$u_l = \cos(l_1 - \frac{1}{2})\phi_1 \cos(l_2 - \frac{1}{2})\phi_2 \cos(l_3 - \frac{1}{2})\phi_3,$$

if the l 's run from 1 to $2N+1$; and similarly for v_l and w_l . If the indices \mathbf{l} run from $-N$ to $+N$, as we have stipulated, the first of the three factors becomes

$$\begin{aligned} (-)^{l_1/2} \cos l_1 \phi_1 & \quad \text{if } j_1 \text{ is even,} \\ (-)^{(l_1+1)/2} \sin l_1 \phi_1 & \quad \text{if } j_1 \text{ is odd,} \end{aligned}$$

and similarly for the two other two factors. Here $\phi_1 = j_1\pi/(2N+1)$, $j_1 = 1, 2, \dots, 2N+1$. Thus in this example $1/8$ of the modes are odd in all three l 's (viz., the ones for which all three j 's are odd integers).

There are two reasons for the interest in "odd" modes expressed in the preceding paragraph. The first is the work on "configurational coordinate" models for phosphors^{4,5}; it is suggested there that the interaction between the impurity and the lattice can be

described in terms of only one vibration, namely, a "breathing" (i.e., totally odd) one in which the impurity is at rest and the neighboring atoms move in a radial direction. The second reason is that these modes are entirely unaffected by the presence of the impurity. This is easy enough to understand: According to the assumption in the first paragraph, the impurity differs from the atom it replaces only by its mass, and it can therefore affect the motion of the other atoms only if it itself is moving; but, being at the origin, it does not move in an odd mode. In other words, any modes that we can compute for the pure lattice and that have the property of being odd in all the l 's, will also be correct for a lattice with an impurity.

III. "LOCALIZED" MODES

Lax and Smith,⁶ Montroll and Potts,⁷ Bjork⁸ and others have discussed the existence of localized modes induced under certain conditions by impurities. In case of the one dimensional monatomic lattice, this situation is as follows.⁷ The equations of motion for all normal atoms of mass M are

$$M\ddot{u}_l = \alpha(u_{l-1} - 2u_l + u_{l+1}) \quad \text{if } l \neq 0, \quad (1a)$$

and

$$m\ddot{u}_0 = \alpha(u_{-1} - 2u_0 + u_1), \quad (1b)$$

for the impurity atom of mass m at location $l=0$. Since the perfect lattice, described by the system (1) with m replaced by M , is known (or easily determined using, for example, cyclic boundary conditions) to have odd solutions of the form

$$u_l = U_j \sin l \phi_j e^{i\omega t}, \quad \phi_j = j\pi/N, \quad j = 1, 2, \dots, N, \quad (2)$$

with

$$\lambda = 2(1 - \cos \phi_j), \quad (3)$$

we can conclude from the previous section that these modes are solutions for the impure lattice (1) as well. Here λ has been written for the dimensionless squared frequency,

$$\lambda \equiv M\omega^2/\alpha. \quad (4)$$

The median frequency of these "breathing" modes around an impurity is given by $\lambda=2$.

Of particular interest in optical problems is the so-called "reststrahlen" mode because it, and the ones near it, are the only modes in a pure lattice that have an oscillating dipole moment. In the other modes, individual cells usually do have dipole moments, but these can be shown to cancel when summed over the entire lattice—exactly if cyclic boundary conditions are assumed and approximately with more realistic boundary conditions or in presence of impurities.³

² See, e.g., L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, New York, 1955), 2nd ed., p. 39.

³ H. B. Rosenstock, *J. Chem. Phys.* **27**, 1194 (1957).

⁴ F. E. Williams, *J. Chem. Phys.* **19**, 457 (1951).

⁵ C. C. Klick, *Phys. Rev.* **85**, 154 (1952).

⁶ M. Lax, *Phys. Rev.* **94**, 1391 (1954).

⁷ E. W. Montroll and R. B. Potts, *Phys. Rev.* **100**, 525 (1955), particularly Sec. 3 and Appendix.

⁸ R. L. Bjork, *Phys. Rev.* **105**, 456 (1957).

The reststrahlen mode is

$$u_l = U(-)^l e^{i\omega t}, \quad (5)$$

$$\lambda = 4.$$

This is an even mode, not a solution of the impure lattice problem as it does not satisfy (1b), but it can be shown⁷ that the impurity will only slightly modify it. One would of course expect this on naive physical grounds, particularly a long distance away from the impurities. In particular, its finite dipole moment is retained.

Localized modes can be investigated by trying solutions of the form

$$u_l = U_{j*}(-)^l A^{-|l|} e^{i\omega t}, \quad (6)$$

with A and U_{j*} constants; one finds by substituting in (1) that

$$A = (2 - Q)/Q, \quad (7)$$

$$\lambda = 4/Q(2 - Q),$$

where

$$Q \equiv m/M. \quad (8)$$

This is physically acceptable if $A \geq 1$, hence $Q \leq 1$; otherwise the displacements diverge with l . It has been shown that this is the only localized mode for this model,⁷ and no local modes exist when the impurity atom is heavier than the lattice atoms. We note that (6) is even in l .

Examination of (6) shows that the local mode, when it exists, does have a dipole moment if even-numbered atoms have positive charge and odd-numbered ones negative charge ("one-dimensional KCl lattice"), for then the motion of all positively charged atoms will always be oppositely directed to that of all the negatively charged ones. The local mode, as well as the reststrahlen mode, should therefore be capable of absorbing light of its frequency and be directly observable optically. The ratio between the two observable frequencies, from (7) and (5) and (4), is

$$\omega_{loc}/\omega_{rest} = [Q(2 - Q)]^{-1/2}. \quad (9)$$

Such observations have actually been made by Schaefer⁹ on the U center, believed to be a H^- ion replacing a halide ion. For KCl, chosen because the masses of alkali and halide ion are nearly equal as in the model of this section, $M = 36$, $m = 1$, and $Q = 1/36$. The reststrahlen frequency for KCl is¹⁰ $\omega_{rest}/2\pi = 4.2 \times 10^{12}$ seconds⁻¹ and (9) thus gives a local frequency of $\omega_{loc}/2\pi = 17.5 \times 10^{12}$ seconds⁻¹. In view of the crudeness of our calculation (a three-dimensional crystal has been approximated by a one-dimensional one and

long-range forces have been ignored), this seems remarkably close to the observed value⁹ of $\omega_{loc}/2\pi = 15 \times 10^{12}$ seconds⁻¹, and the close agreement may well be partially fortuitous. Another vibrational frequency, which we call ω_{eff} , can be inferred from experimental data by observing the broadening, as a function of temperature, of the electronic absorption line of the U center. If, in accordance with the configuration coordinate model, the broadening is due to a single vibrational mode, then it should be given by¹ $\coth \hbar\omega/2k\theta$, θ being the temperature; measurements of Martienssen¹¹ then imply $\omega_{eff}/2\pi = 2 \times 10^{12}$ sec⁻¹. We observe that this is quite different from both the calculated and the observed value of the local mode in the infrared. One may therefore conclude that if the center-lattice interaction is due to one single mode, it is not the localized mode given by (9).

It is also of interest to carry the application of (9) to the KCl lattice even further and use for m the value $1/1837$, hence $Q = 1/36 \times 1837$. The same three frequencies that one can find for the U center are also available here: the local frequency, first as calculated from the reststrahlen frequency and, second, as directly observed by absorption measurements; and, third, the frequency which is effective, according to the configuration coordinate model, in broadening the electronic absorption line of the F center. ω_{loc} describes the almost completely localized motion [see Eq. (7A)] of a particle of the mass of an electron; by (9) the frequency comes out $\omega_{loc}/2\pi = 7.7 \times 10^{14}$ sec⁻¹. The experimentally observed frequency to which this must be compared is the observed electronic absorption due to the F center itself, at $\omega_{loc}/2\pi = 5.2 \times 10^{14}$ sec⁻¹. In the case of the F center, we thus see that the "local" frequency becomes identical with the electronic absorption line. In addition to the previously stated assumptions, the electronic motion has been treated classically here, so that the close agreement seems remarkable indeed. The corresponding half-width measurements of the electronic absorption line for the purpose of determining the effective frequency for the configuration coordinate model have been made in this case by Russell and Klick.¹² They find $\omega_{eff}/2\pi = 2.6 \times 10^{12}$ sec⁻¹ showing very clearly, though not unexpectedly in this case, that the "localized" frequency, which in this case is identical with the optical electronic frequency itself, is not the one effective in the broadening in the configuration coordinate model here.

IV. RELATIVE DISPLACEMENTS

We have mentioned the "configuration coordinate" model^{4,5} for describing the interaction of an impurity center with the lattice by way of only one "breathing" vibration. The success of this model in accounting for

⁹ H. Pick, International Symposium on Color Centers in Alkali Halides, 1959, Corvallis, Oregon (unpublished); G. Schaefer, J. Phys. Chem. Solids **12**, 233 (1960).

¹⁰ C. Kittel, *Introduction to Solid-State Physics* (John Wiley & Sons, New York, 1953), 2nd ed., p. 114.

¹¹ W. Martienssen, Z. Physik **131**, 488 (1952).

¹² G. A. Russell and C. C. Klick, Phys. Rev. **101**, 1473 (1956).

many experimental facts has been somewhat puzzling, because not only one but many (three times the total number of atoms in the crystal—some 10^{23}) vibrational models are known to contribute to the atomic motion in the crystal, as well as for other reasons.¹³ More recently an explanation has been suggested by Bjork and Krumhansl¹⁸: Any existing localized mode was shown to have an amplitude, near the impurity, much larger than that of ordinary modes, and therefore it seemed reasonable to attribute the interaction to this one localized mode alone. We should like to examine this reasoning in some what more detail.

Any vibrating system described by coordinates u_l (regardless of its detailed nature, dimensionality, etc.) can be described by a kinetic energy function $T = \frac{1}{2} \sum_l \dot{u}_l^2 \times m_l$ and a potential energy function $\tilde{V} = \frac{1}{2} \sum_{ll'} \alpha_{ll'} \times u_l u_{l'}$ or, by a change of scale

$$v_l = m_l^{-\frac{1}{2}} u_l, \quad (10)$$

$$T = \frac{1}{2} \sum_l \dot{v}_l^2, \quad (11)$$

and

$$V = \frac{1}{2} \sum_{ll'} \alpha_{ll'} (m_l m_{l'})^{-\frac{1}{2}} v_l v_{l'}. \quad (12)$$

It is then known that there exists a transformation

$$v_l = \sum_j s_{lj} q_j, \quad (13)$$

which will put (11) (12) into the form

$$T = \frac{1}{2} \sum_j \dot{q}_j^2, \quad (14)$$

$$V = \sum_j \omega_j^2 q_j^2. \quad (15)$$

By putting (13) into (11) and comparing with (14) one finds

$$\sum_l s_{lj} s_{lj'} = \delta_{jj'}, \quad (16)$$

and in particular

$$\sum_l s_{lj}^2 = 1. \quad (17)$$

By multiplying (13) by $s_{lj'}$, summing over l and using (16) one gets

$$q_j = \sum_l s_{lj} v_l, \quad (18)$$

and by putting (18) into (14) and comparing with (11) one finds

$$\sum_j s_{lj} s_{l'j} = \delta_{ll'}, \quad (19)$$

and in particular

$$\sum_j s_{lj}^2 = 1. \quad (20)$$

Each of the oscillators q_j in the Hamiltonian (14), (15) can be quantized in the usual way,¹⁴ and upon computing the mean value of q_j^2 in any of its stationary states and taking an average over these states (using a Boltzmann distribution) we find

$$\langle q_j^2 \rangle = (\hbar/2\omega_j) \coth \hbar\omega_j/2k\theta, \quad (21)$$

θ being the temperature. By (13), and (12), the oscillator q_j contributes a quantity

$$u_l^{(j)} = m_l^{-\frac{1}{2}} s_{lj} q_j, \quad (22)$$

to the displacement u_l labeled by the index l ; and the mean value of this is therefore

$$\langle u_l^{(j)} \rangle = s_{lj} [(\hbar/2\omega_j m_l) \coth \hbar\omega_j/2k\theta]^{\frac{1}{2}}. \quad (23)$$

At this point it is convenient to return to the specific example of the monatomic one-dimensional lattice of Sec. III. In that case u_l means just the displacement of the l th atom and $\langle u_l^{(j)} \rangle$ the root means square value of the contribution of the j th mode to that displacement. What we are interested in is the mean relative displacement $\langle \Delta u^{(j)} \rangle$ of atom zero with respect to atom -1 or $+1$, $\langle \Delta u^{(j)} \rangle \equiv \langle u_0^{(j)} \rangle - \langle u_{\pm 1}^{(j)} \rangle$, which is

$$\langle \Delta u^{j(\text{odd})} \rangle = s_{0j} [(\hbar/2\omega_j M) \coth (\hbar\omega_j/2k\theta)]^{\frac{1}{2}}, \quad (24)$$

for any odd mode

$$\langle \Delta u^{j(*)} \rangle = (Q^{-\frac{1}{2}} s_{0j*} \pm s_{1j*}) \times [(\hbar/2\omega_{j*} M) \coth \hbar\omega_{j*}/2k\theta]^{\frac{1}{2}}, \quad (25)$$

for the local mode j^* . For (24) we have [Eq. (2)] $s_{0j} = U_{j0} \sin l\phi$, with $U_{j0} = N^{-\frac{1}{2}}$ resulting¹⁵ from the normalization condition (17), and ω_{j0} given by (3). For (25) we have $s_{1j*} = U_{j*}(-)^{lA-1} A^{-1/4}$ according to (6) with $U_{j*}^{-2} = 1 + [Q^2/(2-Q)]$ resulting from (17) with neglect of terms of order Q^{2N} , and ω_{j*} given by (7). Rather than just to substitute these values into (24) (25), let us write down the results of high- and low-temperature expansions. High temperature:

$$\langle \Delta u^{j(\text{odd})} \rangle = (k\theta/\alpha)^{\frac{1}{2}} N^{-\frac{1}{2}} \cos \phi_j/2 \times \left[1 + \frac{\sin^2 \phi/2}{6} \beta^2 - \frac{\sin^4 \phi/2}{40} \beta^4 \dots \right], \quad (26)$$

$$\langle \Delta u^{j(*)} \rangle = \frac{\sqrt{2}}{2} (k\theta/\alpha)^{\frac{1}{2}} \times \left[\left(1 - \frac{Q}{2} \right)^{\frac{1}{2}} \left(1 \mp \frac{Q^{\frac{1}{2}}}{2-Q} \right) / \left(1 + \frac{Q^2}{2-Q} \right)^{\frac{1}{2}} \right] \times \left[1 + \frac{\beta^2}{6Q(2-Q)} - \frac{\beta^4}{40Q^2(2-Q)^2} \dots \right], \quad (27)$$

with $\beta^2 = \hbar^2 \alpha / M (k\theta)^2$. In each case the leading term can be obtained somewhat more easily by treating the system classically and evaluating the mean displacements by using the principle of equipartition of energy for each mode. Low temperature:

$$\langle \Delta u^{j(\text{odd})} \rangle = \frac{\hbar^{\frac{1}{2}}}{2(M\alpha)^{\frac{1}{2}}} N^{-\frac{1}{2}} (\sin \phi/2)^{\frac{1}{2}} \times \left[1 + e^{-2\beta \sin \phi/2} - \frac{1}{2} e^{-4\beta \sin \phi/2} \dots \right], \quad (28)$$

¹³ M. Lax, J. Chem. Phys. **20**, 1752 (1952).

¹⁴ L. Pauling and E. B. Wilson, *Quantum Mechanics* (McGraw-Hill Book Company, New York, 1935), Sec. 11.

¹⁵ H. B. Rosenstock, J. Chem. Phys. **23**, 2415 (1955), Appendix I.

$$\langle \Delta u^{(j^*)} \rangle = \frac{2^{\frac{1}{2}} \hbar^{\frac{1}{2}}}{2 (M/\alpha)^{\frac{1}{2}}} \times \left[\left(1 - \frac{Q}{2} \right)^{\frac{1}{2}} \left(1 \mp \frac{Q^{\frac{1}{2}}}{2-Q} \right) / Q^{\frac{1}{2}} \left(1 + \frac{Q^2}{2-Q} \right)^{\frac{1}{2}} \right] \times \left[1 + \exp \left(\frac{-2\beta}{[Q(2-Q)]^{\frac{1}{2}}} \right) - \frac{1}{2} \exp \left(\frac{-4\beta}{[Q(2-Q)]^{\frac{1}{2}}} \right) \right]. \quad (29)$$

The amplitude of the localized mode near the impurity thus exceeds that of any of the odd moments there by the very large factor of $N^{\frac{1}{2}}$. This is the essential conclusion of Bjork and Krumhansl,⁸ made somewhat more quantitative here. But their deduction that the coupling of the electronic state of the impurity to the lattice results mainly from this localized mode seems premature, since there exist N "odd" modes as compared to only one localized one.

The $\langle \Delta u^{j(\text{odd})} \rangle$ (26) and (28) are root mean square values, and the magnitude of any one displacement may be positive or negative with equal probability. The problem of finding the mean value of the sum of N unit steps is a random walk problem solved by Rayleigh¹⁶; the answer is known to be proportional to $N^{\frac{1}{2}}$; in our case the $\cos\phi/2$ term gives rise to a proportionality constant $\sqrt{2}/2$ (see Appendix).

The total mean relative displacement of atoms 0 and ± 1 due to all the odd modes thus turns out to be for high temperatures

$$\sum_{j(\text{odd})} \langle \Delta u^{j(\text{odd})} \rangle = \frac{\sqrt{2}}{2} (k\theta/\alpha)^{\frac{1}{2}} \left[1 + \frac{\sqrt{2}}{24} \beta^2 - \frac{(14)}{640} \beta^4 \dots \right], \quad (30)$$

and for low temperatures

$$\sum_{j(\text{odd})} \langle \Delta u^{j(\text{odd})} \rangle = \frac{\hbar^{\frac{1}{2}} \sqrt{2}}{2 (M\alpha)^{\frac{1}{2}}} [1 + O(e^{-2\beta})]. \quad (31)$$

If we are to assess the importance of the localized mode we must compare its effect [Eqs. (27) and (29)] with the total effect of all odd modes, (30) and (31), and not with that of a single odd mode. We see in the limit of small Q

$$\frac{\langle \Delta u^{(j^*)} \rangle}{\sum_{j(\text{odd})} \langle \Delta u^{j(\text{odd})} \rangle} = \begin{cases} 1 & \text{high temperature} \\ (2Q)^{-\frac{1}{2}} & \text{low temperature} \end{cases}. \quad (32)$$

We can thus conclude that the contributions by all the odd modes to the relative displacement of the impurity with respect to its nearest neighbors is about as large as that by the single local mode.

The argument in this section was general until after Eq. (23) we chose to proceed by considering a special example. Upon reviewing the development from there on down, we find that there seems little reason to confine the argument to this model or even to one dimensional lattices. In three dimensions, the "odd" modes, whose existence we have shown to be very plausible, have coefficients of the form $s_{1j} = U_j \sin l_1 \phi_{j1} \times \sin l_2 \phi_{j2} \sin l_3 \phi_{j3}$ and the normalization constant is found from the equation $\sum_j s_{1j}^2 = 1$ which is certainly valid, to be $\sim N^{-\frac{1}{2}}$, N^3 being the number of atoms in the crystal. The total number of modes is then $3N^3$, and perhaps 2^{-3} of them, or $3N^3/8$, will be odd in all three space variables. The total mean displacement due all these odd modes is then the resultant of a random walk of $3N^3/8$ steps, or $N^{\frac{3}{2}}$ (omitting trivial numerical constants), and the $N^{-\frac{1}{2}}$ in the normalization constant is cancelled out. The normalization constant for the localized mode, by contrast, is of order unity in the first place, and the displacement near the impurity due to all the odd modes is therefore roughly comparable to the displacement due to the local model. The argument remains valid even when the odd modes do not exist. In that case one must replace the word "odd" by "trigonometric" and abandon the simple picture of the impurity at rest with its nearest neighbors beating against it, and also the explicit use of the modes derived from the pure lattice; but one can retain the essential conclusions that the total displacement near the impurity due to all trigonometric modes is at least equal in order of magnitude to that of any of the few localized ones.

It seems therefore difficult to accept the suggestion that the remarkable success of the configuration coordinate model, which explains the interaction of the impurity with the lattice by considering only the one vibrational mode, can be simply explained by identifying this one mode with a "localized" mode induced in the lattice by the impurity. It seems likely that the combined contributions of some of the trigonometric modes must be at least as large. It may be that certain large groups of modes of similar frequency, as may arise near critical points in momentum space, may make a particularly large contribution. In this connection it is worth noting that Russell and Klick¹² have found the effective frequency for the configuration coordinate model in alkali halides to be substantially lower than that of most lattice modes. Our Eq. (21), where the term ω in the denominator suggests that low-frequency modes will make the largest contribution, is in qualitative agreement with this.

SUMMARY

Since some of the localized vibrational modes around a lattice imperfection are "even" they will give rise to optical absorption. The computed frequency of these modes is in good agreement with observed infrared and visible absorption bands in KCl with H^- centers and

¹⁶ Lord Rayleigh, Phil. Mag. 37, 321 (1919).

with F centers, respectively. A computation has been made of the relative effects of the localized mode and of the "odd" vibrational modes of the lattice in producing a net displacement of the center relative to its nearest neighbors. It is found that the lattice modes are at least as important as the localized modes. In the configuration coordinate model it is assumed that this net displacement gives rise to the variation of bandwidth with temperature seen in electronic transitions. An analysis of bandwidth data for electronic transitions in KCl with thallium, H^- centers, and F centers leads to effective vibrational frequencies of 4×10^{12} , 2×10^{12} , and 2.6×10^{12} , respectively. These values may be compared with the reststrahlen frequency, typical of lattice vibrations, which is 4.2×10^{12} . On the other hand the localized vibrations around these centers may also be computed. For thallium, which is heavier than potassium and chlorine, no localized mode exists for the simple model considered here. The H^- center has a frequency of 17.5×10^{12} and the F center has a frequency of 770×10^{12} . It is apparent that the effective frequency influencing electronic transitions is not strongly influenced by the frequency of the localized mode. Thus the localized modes around an imperfection give rise to optical absorption at their own frequency, but the modes influencing the bandwidth of electronic transitions in the impurity are more closely related to the "odd" modes of the pure lattice. The frequency of these "odd" modes varies from 0 to the reststrahlen frequency so that replacing this distribution by a single frequency, as is done in the configuration coordinate treatment, may not always be a valid approximation.

APPENDIX. COEFFICIENTS IN EQ. (30)

Consider three random walk problems.

(1) The two-dimensional problem in which the walker takes N successive steps of unit length and arbitrary direction.

(2) The two-dimensional problem in which the walker takes N successive steps of unit length in the directions $\pm\phi_j$, where $\phi_j = j\pi/N$, $j=1, 2, \dots, N$, the probability of $+$ or $-$ being $\frac{1}{2}$ for each step.

(3) The one-dimensional problem in which the walker takes N successive steps of length $\pm f(\phi_j)$, where ϕ_j and \pm are defined as in problem (2) and f is a continuous function.

In all cases N is assumed very large. What we desire is the mean square displacement in problem (3). We know the answer to problem (1)—this is Pearson's original random walk problem.¹⁶ We shall show (A)

that (2) and (1) are equivalent, and (B) that (3) can be obtained from (2).

(A) In problem (2), consider the range of ϕ_j broken up into increments $\Delta\phi$ such that $\Delta\phi$ is small enough to permit us to consider all angles within one increment to be the same (to whatever accuracy is desired), but large enough that each increment still contains a large number of steps. (Since we are dealing only with the limit of infinite N , this is possible.) In the first four pages of his paper,¹⁶ Rayleigh shows that the probability that the resultant lie between r and $r+dr$ which is obtained by considering only one increment $\Delta\phi$ is the same as that obtained for problem (1), and that the same is also obtained from considering all the $\Delta\phi$ together. This can be extended to the probability that the resultant lie between r and $r+dr$ and between ϕ and $\phi+d\phi$, merely by noting that both probabilities must actually be independent of ϕ , since both in problem (1) and in problem (2) no direction is preferred. The two distributions thus do not differ in r and cannot differ in ϕ , and are therefore in fact identical; and Rayleigh's equation (4) for the probability distribution of the resultant in problem (1),

$$P(r, \phi) dA = (\pi N)^{-1} \exp(-r^2/N) dA, \quad (A1)$$

therefore applies to problem (2) as well.

(B) The trick which enables us to use the solution (A1) in attacking the one-dimensional problem (3) is to formally identify the parameter ϕ_j there with the usual azimuthal angle in two-dimensional polar coordinates. Once this is done, problems (2) and (3) become essentially identical; the mean square value of f in (3) becomes just

$$\langle (rf)^2 \rangle = \int \int (rf)^2 P dA. \quad (A2)$$

The functions f that appear in (28) are $\cos\phi/2 \times \sin^{2k}\phi/2$, $k=0, 1, 2$. For $k=0$ we find

$$\langle (r \cos\phi/2)^2 \rangle = \langle \frac{1}{2} r^2 (1 + \cos\phi) \rangle.$$

From (A2) and (A1) we find $\langle r^2 \rangle = N$, $\langle r^2 \cos\phi \rangle = 0$. Therefore

$$\langle (r \cos\phi/2)^2 \rangle = N/2,$$

and similarly we find

$$\langle (r \cos\phi/2 \sin^2\phi/2)^2 \rangle = N/16,$$

$$\langle (r \cos\phi/2 \sin^4\phi/2)^2 \rangle = 7N/256.$$

The square roots of these values have been substituted into (28) to give (30).