PHYSICAL REVIEW VOLUME 166, NUMBER 3 15 FEBRUARY 1968

Asymptotic Description of Localized Lattice Modes and Low-Frequency Resonances

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(Received 2 October 1967)

Point imperfections in crystals may produce localized modes of vibration with frequencies not allowed in the perfect crystal, or resonances with frequencies within the perfect-crystal frequency bands. In general, such frequencies depend both on parameters characteristic of the defect and on Green's functions characteristic of the dynamical properties of the perfect lattice. In the limits of frequencies, both very high and very low with respect to the maximum perfect-lattice frequency, simple equations, giving physical insight into the nature of the defect mode, are developed, and the results are compared with recent calculations on specific models and with experiment. It is shown that for a variety of situations the defect-mode properties are, to first order, very directly related to the mass and force-constant parameters in the center only.

1. INTRODUCTION

Point imperfections in crystals perturb the vibrational Hamiltonian of the crystal and modify the normal modes of vibration. At frequencies greater than the maximum host-lattice frequency, localized modes with large amplitudes in the neighborhood of the imperfection may result, or alternately, the defect may give rise to resonance effects within the normal-lattice spectrum.

Such phenomena have been established by a wide variety of experimental techniques; the relationship of these experimental results to established theory has recently been reviewed by Maradudin.[1,2]

The Green's-function approach to defect-lattice vibrations is now well established, at least for low defect concentrations, and general discussions of the methods developed are given, for example, by Lifshitz,[3] Maradudin,[4] and Elliot.[5] The theories express the properties of the localized modes or resonances, on the one hand, in terms of parameters characteristic of the perturbation by the imperfection (e.g., the changes in force and mass constants), and on the other, in terms of lattice response functions or Green's functions characteristic of the perfect crystal. Isotopic substitution in a lattice has received by far the most attention, but most point imperfections involve also changes in force constants. Though a formal solution of this case is easily found,[1] applications to realistic problems—by Sievers and Takeno,[6] Yussouff and Mahanty,[7] Patnaik and Mahanty,[8] Brice,[9] Benedeck and Nardelli,[10,11] Tseng,[12] and others—involve either highly simplified models or extensive computation.

Some of the interesting experimental situations correspond to localized modes with frequencies very large by comparison with the maximum frequency of the host lattice, e.g., the U center in the alkali halides[13] or sharp resonances at very low frequencies, e.g., the properties of Li^+ ions in KBr. Experimental evidence[14–16] on Li^+ in KCl and theoretical studies[17–19] suggest that the Li^+ ion is unstable on the defect-lattice site, resulting in the intrinsically nonharmonic behavior discussed by Bowen, Gomez, and Krumhansl.[20] The low-frequency resonance in lithium-doped KBr is very sensitive to stress and alloying effects,[21,22] suggesting that it may be

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* Supported in part by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-3699, Technical Report No. NYO-3699-14.

† Supported in part by the United Kingdom Atomic Energy Authority.

[1] A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, p. 273.

[2] A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 19, p. 1.

[3] I. M. Lifshitz, Nuovo Cimento Suppl. **3**, 716 (1956).

[4] A. A. Maradudin, Rept. Progr. Phys. **28**, 331 (1965).

[5] R. J. Elliot, in *Proceedings of the Scottish Universities Summer School, 1965* (Oliver and Boyd, Edinburgh, 1966), p. 377.

[6] A. J. Sievers and S. Takeno, Phys. Rev. **140**, A1030 (1965).

[7] M. Yussouff and J. Mahanty, Proc. Phys. Soc. (London) **85**, 1233 (1965).

[8] H. Patnaik and J. Mahanty, Phys. Rev. **155**, 987 (1967).

[9] D. H. Brice, Phys. Rev. **140**, A1211 (1965).

[10] G. Benedek and G. F. Nardelli, Phys. Rev. Letters **16**, 517 (1966).

[11] G. Benedek and G. F. Nardelli, Phys. Rev. **155**, 1004 (1967).

[12] R. Tseng, Ph.D. thesis, Cornell University, 1966 (unpublished).

[13] G. Schaefer, J. Phys. Chem. Solids **12**, 233 (1960).

[14] H. S. Sack and M. C. Moriarty, Solid State Commun. **3**, 93 (1965).

[15] G. Lombardo and R. O. Pohl, Phys. Rev. Letters **15**, 291 (1965).

[16] F. C. Baumann, J. P. Harrison, R. O. Pohl, and W. D Seward (to be published).

[17] J. A. D. Matthew, Solid State Commun. **3**, 365 (1965).

[18] G. J. Dienes, R. D. Hatcher, R. Smoluchowski, and W. Wilson, Phys. Rev. Letters **16**, 25 (1966).

[19] R. P. Quigley and J. P. Das, Solid State Commun. **5**, 487 (1967).

[20] M. Gomez, S. P. Bowen, and J. A. Krumhansl, Phys. Rev. **153**, 1009 (1967).

[21] I. G. Nolt and A. J. Sievers, Phys. Rev. Letters **16**, 1103 (1966).

[22] B. P. Clayman, I. G. Nolt, and A. J. Sievers, Phys. Rev. Letters **19**, 111 (1967).

possible to monitor continuously the transition from a resonance condition mainly harmonic in character (as probably exists in KBr:Li) to an unstable configuration characterized by tunnelling and other nonharmonic effects (as in KCl:Li). It is therefore essential to understand fully the predictions of harmonic-lattice dynamical theory for low-frequency resonances.

We wish to present a rather different treatment of the defect-lattice dynamical problem applicable for the cases of high-frequency localized modes and for very low-frequency resonances. In these limits, it is possible to derive useful asymptotic results which help to relate directly the properties of point imperfections to experimental observation, and to provide simple physical pictures of the resonance state. This work may be regarded as extensions of ideas introduced by Krumhansl[23] and Matthew.[24]

In Sec. 2 we consider the much-studied problem of isotopic substitution in a cubic lattice in the conventional Green's-function formalism of Brout and Visscher.[25] We derive asymptotic results for the high- and low-frequency case as a guide to the analysis of more general problems. In Sec. 3 we formulate the vibrational problem in a somewhat new way by dividing the crystal-basis space into two subspaces, one characteristic of the strongly perturbed region of the defect, the other characteristic of the rest of the crystal (the so-called "excavated lattice"). This technique is similar to those used by Krumhansl,[23] Wagner,[26] and Sitzman and Rozsa.[27] We compare the results with those derived from specific models in the conventional Green's-function formalism and with recent experiments. Very recently, Toyazawa, Inoue, Inui, and Hanamura[28] have developed a similar method to discuss coexistence of local and band character of both electronic and lattice excitations in impurity systems.

2. ASYMPTOTIC LIMIT FOR THE CASE OF ISOTOPIC SUBSTITUTION

If we consider a cubic Bravais lattice with host mass M and an isotopic impurity of mass M', the equation to determine the resonance or local-mode frequency ω_L is

$$1+\frac{M'-M}{M}\frac{1}{3N}\mathcal{P}\sum_{\mathbf{q},i}\frac{\omega_L^2}{\omega_L^2-\omega_{\mathbf{q},i}^2}=0\,, \tag{1}$$

where $\mathcal{P}$ denotes the principal value of the summation over all lattice frequencies $\omega_{\mathbf{q},i}^2$; and N is the number of unit cells in the crystal.

For the case $\omega_L \gg \omega_{\max}$, where $\omega_{\max}$ is the maximum perfect-lattice frequency, a straightforward expansion of (1) in powers of $\omega_{\mathbf{q},i}^2/\omega_L^2$ yields a series solution for ω_L^2 in powers of the small parameter M'/M:

$$\omega_L^2=\frac{M\langle\omega^2\rangle}{M'}+\frac{\langle\omega^4\rangle-\langle\omega^2\rangle^2}{\langle\omega^2\rangle}+\text{order}\left(\frac{M}{M'}\right)^{-1}, \tag{2}$$

where $\langle\omega_q^n\rangle$ is the mean value of $\omega_{\mathbf{q},i}^2$ (see, for example, Matthew[24] and Elliot[29]). It is difficult to prove the convergence of such an expansion in general, but it is interesting to note that for the case of the one-dimensional chain, which has the analytic solution[30]

$$\omega_L^2=\omega_{\max}^2/(1-\epsilon^2)\,, \tag{3}$$

where $\epsilon=1-(M'/M)$, the series is convergent for all values of M'/M for which a localized mode exists. In general, the series will converge for M'/M less than some critical value, but in considering modes of frequency very much greater than the maximum lattice frequency, i.e., $M'/M\ll 1$, such difficulties will be unimportant.

For resonant modes, similar expansions are possible in powers of $\omega_{\mathbf{q},i}^2/\omega_L^2$ for $\omega_{\mathbf{q},i}^2<\omega_L^2-\delta$, and $\omega_L^2/\omega_{\mathbf{q},i}^2$ for $\omega_{\mathbf{q},i}^2>\omega_L^2+\delta$, where δ is a small quantity. This is discussed in Appendix A. For $\omega_L\ll\omega_{\max}$ (i.e., $M'\gg M$), we obtain an expansion for ω_L^2 in terms of the small parameter M/M':

$$\omega_L^2=\frac{M}{M'\langle\omega^{-2}\rangle}+\text{order}\left(\frac{M}{M'}\right)^2+\cdots. \tag{4}$$

For a continuum Debye model,

$$\langle\omega^2\rangle=\tfrac{3}{5}\omega_{\max}^2$$

and (5)

$$1/\langle\omega^{-2}\rangle=\tfrac{1}{3}\omega_{\max}^2.$$

Using these values, Eqs. (2) and (4) are consistent with the results presented by Brout and Visscher.[25]

Thus, for both $M'\gg M$ and $M'\ll M$, the local frequency ω_L is given to first order by the relation

$$\omega_L^2=k/M'\,, \tag{6}$$

where k is an effective force constant independent of M'. It is of interest that the value of k is significantly different for localized modes and resonant modes:

$$\begin{aligned} k&=M\langle\omega^2\rangle=\tfrac{3}{5}M\omega_{\max}^2\ \text{(Debye model)}\,\omega>\omega_{\max}\,,\\ k&=M/\langle\omega^{-2}\rangle=\tfrac{1}{3}M\omega_{\max}^2\ \text{(Debye model)}\,\omega<\omega_{\max}\,. \end{aligned} \tag{7}$$

A generalization of such results and an insight into the meaning of such effective force constants is one of the objectives of this paper.

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[23] J. A. Krumhansl, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963* (Pergamon Press, Inc., New York, 1965), p. 523.

[24] J. A. D. Matthew, J. Phys. Chem. Solids **26**, 2067 (1965).

[25] R. Brout and W. Visscher, Phys. Rev. Letters **9**, 54 (1962).

[26] M. Wagner, Phys. Rev. **131**, 2520 (1963).

[27] U. Sitzman and P. Rozsa, Proc. Phys. Soc. (London) **85**, 285 (1965).

[28] Y. Toyazawa, M. Inoue, T. Inui, M. Okazaki, and E. Hanamura, J. Phys. Soc. Japan **22**, 1337 (1967); **22**, 1349 (1967).

[29] R. J. Elliot, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963* (Pergamon Press, Inc., New York, 1965), p. 459.

[30] J. A. Krumhansl, J. Appl. Phys. Suppl. **33**, 307 (1962).

In the case of the resonant mode, the resonance response is damped to give a half-width $\Delta\omega_L$ which, for a Debye model, reduces to

$$\Delta\omega_L/\omega_L=(\pi/4\sqrt{3})(M/M')^{1/2}\,, \tag{8}$$

to lowest order in $(M/M')^{\frac{1}{2}}$; a general model will have the same mass dependence in the low-frequency limit.

3. FORMULATION OF THE GENERAL DEFECT DYNAMICAL PROBLEM

We wish to consider a crystal containing one point defect in which the displacement field $|\varphi)$ is described in terms of the Cartesian basis displacements of the atoms in the crystal. We divide the N-dimensional space $|\varphi)$ into two subspaces: $|\theta)$, which gives the displacement field of a local region at the defect; and $|\varphi-\theta)$, which gives the displacement field of the rest of the crystal. Let the reduced-mass potential-energy matrix of the crystal containing no point imperfection V be

$$V=\begin{bmatrix} L & a \\ a^T & C \end{bmatrix}, \tag{9}$$

and with a point imperfection by

$$V'=\begin{bmatrix} L' & a' \\ (a')^T & C' \end{bmatrix}, \tag{10}$$

where L and L' are symmetric square matrices which describe the interaction constants in the local subspace $|\theta)$ in the perfect and imperfect crystal, respectively, while C and C' describe the interaction constants in the rest of the crystal $|\varphi-\theta)$. The nonsquare matrices a and a', with their respective transposes a^T and $(a')^T$, describe the coupling between the space $|\theta)$ and the space $|\varphi-\theta)$.

The equation of motion of the imperfect crystal is given by

$$[V'-\omega^2]|\varphi)=0\,, \tag{11}$$

which yields

$$\begin{gathered}[L'-\omega^2 1]|\theta)+a'|\varphi-\theta)=0\,,\\ (a')^T|\theta)+(c'-\omega^2 1)|\varphi-\theta)=0\,.\end{gathered} \tag{12}$$

A quasi-equation-of-motion for the subspace $|\theta)$ may be readily obtained:

$$[L'-\omega^2-a'(c'-\omega^2 1)^{-1}(a')^T]|\theta)=0\,. \tag{13}$$

We may define a Green's-function matrix operator for the imperfect lattice such that

$$G[V'-\omega^2 1]=-1\,, \tag{14}$$

where

$$G=\begin{bmatrix} G_{\theta,\theta} & G_{\theta,\,\varphi-\theta} \\ G_{\varphi-\theta,\,\theta} & G_{\varphi-\theta,\,\varphi-\theta} \end{bmatrix}. \tag{15}$$

A formal solution of (11) yields

$$G_{\theta,\theta}=-[L'-\omega^2 1-a'(c'-\omega^2 1)^{-1}(a')^T]^{-1}\,. \tag{16}$$

For $\omega>\omega_{\max}$, $(c'-\omega^2 1)^{-1}$ will be a real operator, but for $\omega<\omega_{\max}$, the response operator will be a complex matrix operator of the form

$$(c'-\omega^2 1)^{-1}=\mathcal{P}(c'-\omega^2 1)^{-1}+iN(\omega)\,, \tag{17}$$

where $\mathcal{P}$ denotes the principal part of the response function and $N(\omega)$ the out-of-phase component.

If we are interested in the resonant response of the impurity region, the frequency of resonance ω_L will be given by

$$\mathrm{Re}\{\det[L'-\omega_L^2-a'(c'-\omega_L^2)(a')^T]\}=0\,. \tag{18}$$

Equation (18) is the equivalent of the resonance condition arising in the standard formalism, but we shall now manipulate Eq. (18) to give some useful and simple results in the high- and low-frequency limits.

The last term in brackets of (16) is the "shift-broadening" matrix of Toyazawa *et al.*[28] Its real part is $(a')\mathcal{P}(c'-\omega_L^2)(a')^T$, and the imaginary part is $(a')N(\omega)(a')^T$.

A. High-Frequency Localized Modes

For $\omega_L^2\gg\omega_{\max}^2$, we may choose the space $|\theta)$, such that ω_L^2 is much larger than all the elements of the matrix c'. Then $(c'-\omega_L^2 1)^{-1}$ may be approximated by

$$(c'-\omega_L^2 1)^{-1}\approx-(1/\omega_L^2)[1+(c'/\omega_L^2)]\,, \tag{19}$$

where the correction terms involve higher powers of ω_L^{-2}. Equation (18) now reduces to

$$\det[L'-\omega_L^2 1+(1/\omega_L^2)a'(a')^T]=0\,, \tag{20}$$

terms of order $1/\omega_L^4$ and higher having been neglected. It is of interest that, to this level of approximation, the frequency of the localized mode does not depend on the internal properties of the bulk of the crystal, i.e., it does not depend on c'.

1. Isotopic Impurity in a Monatomic Cubic Lattice

We first test our formalism on the traditional proving ground of the isotopic impurity M' in a cubic lattice of host mass M. Let $\Phi(l,l';\alpha,\alpha')/M$ be the elements of the reduced-mass potential-energy matrix of the perfect crystal. Here l and l' label the atoms, while α, $\alpha'=x, y, z$ denote the components of the displacements; $\Phi(l,l;\alpha,\alpha)$ is independent of l and α.

We wish to study localized modes due to the impurity atom (set, for convenience, at the origin). We consider the space $|\theta)$ to be the three-dimensional space of the Cartesian basis displacements of the isotopic impurity, while $|\varphi-\theta)$ are the Cartesian basis displacements of the rest of the atoms in the crystal. Now, $L'=(M/M')L$, $a'=(M/M')^{1/2}a$, and $c'=c$. Because of the cubic symmetry, the determinantal condition (20) reduces to a single equation,

$$\frac{\Phi(l,l;\,\alpha,\alpha)}{M'}-\omega_L{}^2+\frac{1}{\omega_L{}^2}\sum_{l'\neq l}\sum_{\alpha'}\frac{1}{MM'}\Phi(l,l';\,\alpha,\alpha')^2=0\,, \quad (21)$$

which, on solving as a series in the small parameter M'/M, gives

$$\omega_L{}^2=\frac{\Phi(l,l;\,\alpha,\alpha)}{M'}+\sum_{l'\neq l}\sum_{\alpha'}\frac{\Phi(l,l';\,\alpha,\alpha')^2}{M\Phi(l,l;\,\alpha,\alpha)}$$
$$+\text{terms of order } (M'/M)\omega_{\max}{}^2. \quad (22)$$

From the properties of the perfect-lattice dynamical matrix V, it is easy to show that $M\langle\omega^2\rangle=\Phi(l,l;\,\alpha,\alpha)$, and $M^2\langle\omega^4\rangle=\sum_{l',\alpha'}\Phi(l,l';\,\alpha,\alpha')^2$. Equation (22) then reduces to Eq. (2) as required.

To first order, the localized mode frequency is given by the Einstein oscillator frequency of the isotopic impurity, and so the effective force constant k is just the restoring force on an atom when all the other atoms in the crystal are at rest. Dynamical correlation with the motion of other atoms in the crystal has no effect to this order of approximation. Equation (22) may be adapted to allow for force-constant changes, provided the isotopic perturbation is predominant as discussed by Matthew[24] and Gunther.[31]

2. *Impurity with a Large Nearest-Neighbor Interaction*

High-frequency localized modes may alternately be produced by point imperfections with very large nearest-neighbor force constants. Here, it is convenient to choose $|\theta)$ as the space of the basis displacements of the impurity atom and its nearest neighbors. Now the elements of L' are larger than those of either a' or c', and to first order, the possible localized modes may be calculated from the quasimolecular secular equation

$$\det[L'-\omega_L{}^2 1]=0\,. \quad (23)$$

Equation (23) may be solved by the usual methods of molecular dynamics to give a set of impurity modes classified according to the irreducible representations of the point group of the impurity, i.e., "pseudomolecule." Some of these solutions may not have frequencies which are higher, or at any rate much higher, than $\omega_{\max}$; such modes will not simulate realistic localized modes. Solutions of (23), which yield $\omega_L \gg \omega_{\max}$, will, however, be good approximations to the true localized modes both in frequency and eigenvector. If the components of a' are typical of force constants in the perfect lattice, the correction terms in Eq. (18) are of order $\omega_{\max}{}^4/\omega_L{}^2$, which results in corrections to the values of $\omega_L{}^2$ of order $(\omega_{\max}/\omega_L)^2\,\omega_{\max}{}^2$. Such molecular approximations have been applied—for example, by Litzman and Cely[32] and Lengeler and Ludwig[33]—to specific models.

B. Low-Frequency Resonances

We now consider the limit of $\omega_L \ll \omega_{\max}$. This implies that ω_L is very much less than the typical diagonal elements of c'. The operator $(c'-\omega^2 1)^{-1}$ may then be approximated by

$$(c'-\omega_L{}^2 1)\sim(c')^{-1}+(c')^{-1}(c')^{-1}\omega_L{}^2+\text{order } \omega_L{}^4\,,$$

and Eq. (18) reduces to

$$\det[L'-\omega_L{}^2-a'(c')^{-1}(a')^T]=0\,. \quad (24)$$

1. *Isotopic Impurity in a Monatomic Cubic Lattice*

Proceeding in a slightly different manner from the high-frequency case, we immediately exploit the cubic symmetry and confine ourselves to displacements that transform as a specific row of the T_{1u} representation, i.e., the only representation in which the impurity moves. Now we choose the $|\theta)$ subspace as a single-impurity basis displacement (say, x, y, or z), while $|\varphi-\theta)$ spans the crystal basis displacements which transform as the same row of T_{1u} as $|\theta)$.

Solving Eq. (24) to lowest order in M/M', we obtain

$$\omega_L{}^2=L'-a'c^{-1}(a')^T$$
$$=k/M'\,, \quad (25)$$

where

$$k=M[L-ac^{-1}a^T]\,. \quad (26)$$

This has still the same "mass-spring" form of the high-frequency case, but the effective force constant of the resonances is not the simple Einstein oscillator restoring force ML, but contains an additional component $MaC^{-1}a^T$. Let us attempt to understand how this extra effective force arises in the low-frequency case.

We consider a *static* displacement field $|\theta)$ of the impurity in the crystal: This produces a force field per unit mass of $-(a')^T|\theta)$ and causes a static relaxation $-C^{-1}(a')^T|\theta)$ of the rest of the crystal. The displacement of the crystal hence exerts a mass-reduced field $-a'C^{-1}(a')^T|\theta)$ on the impurity, in addition to the local force field $L'|\theta)$ induced if the lattice is not allowed to relax. The effective force constant which determines the resonance condition in Eq. (24) corresponds to the restoring force per unit mass exerted by the lattice if it is allowed to relax in a quasistatic manner, i.e., the lattice is responding to the motion of the heavy mass in an adiabatic way, just as the electrons in a crystal respond to the motion of the nuclei (Born-Oppenheimer approximation). For an isotopic impurity, the Einstein restoring force L' and the relaxation term $a'C^{-1}(a')^T$ are proportional to M/M': Though the correlated response of the lattice plays an important part in the

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[31] L. Gunther, J. Phys. Chem. Solids **26**, 1695 (1965).

[32] U. Sitzman and J. Cely, Czech. J. Phys. **118**, 320 (1961).

[33] B. Lengeler and W. Ludwig, Z. Physik **171**, 273 (1963).

resonance process, the isotopic dependence of the resonance frequency is the same as that of an Einstein oscillator.

In Appendix B we relate the effective force constant of Eq. (26) to the effective force constant of Eq. (5) deduced from the standard Green's-function formalism. The simple asymptotic descriptions of the isotopic localized mode, and the isotopic resonance derived from the Green's function $G_{\theta,\theta}$ of Eq. (16), help one to understand the discrepancies between the effective force constants in the high- and low-frequency cases.

The Green's function $G_{\theta,\theta}$ may alternately be used to discuss the natural harmonic breadth of the resonant response. From (16) and (17), it is clear that the imaginary part of the response function will be $(a')N(\omega)(a')^T$. If the resonance is sharp, the breadth at half-height $\Delta\omega_L$ will be approximately

$$\Delta\omega_L/\omega_L=(1/2\omega_L^2)[a'N(\omega_L)(a')^T]. \tag{27}$$

For the isotopic case, $C'=C$, i.e., C' is as for the perfect crystal, and the elements of $N(\omega)$ will be of the order of magnitude $\omega/\omega_{\max}^3$ by analogy with the analysis of Krumhansl,[23] while the elements of a' and $(a')^T$ are of order $(M/M')^{1/2}\,\omega_{\max}^2$. Remembering that

$$\omega_L\sim(M/M')^{1/2}\,\omega_{\max}\,,$$

we find that

$$\Delta\omega_L/\omega_L=A\,(M/M')^{1/2}\,, \tag{28}$$

where A is a number of the order of unity. This is in agreement with Eq. (8).

A basic limitation of the approach is that we cannot readily compute $N(\omega)$ exactly, but we can easily find the power-law dependence of the fractional breadth $\Delta\omega_L/\omega_L$ on the basic parameter M/M'. Extension of arguments of the type of Appendix B establishes the exact correspondence between Eqs. (28) and (8). For a Debye model, the value of A is 0.45, but the value will vary somewhat depending on the properties of C in a particular case.

2. *Impurity with a Very Weak Force Constant*

Very low-frequency resonances may alternately result from the weak dynamical force constants of the impurity. We therefore wish to discuss the case of an impurity atom where force constants are of the order of λ times the principal force constants in the perfect crystal ($\lambda\ll1$). We allow the impurity to have a mass M' as before, and let $|\theta)$ represent a basic displacement of the impurity.

Now $L'\approx\lambda(M/M')L$, and $a'\sim\lambda(M/M')^{1/2}a$. C' will no longer be the same as C of the perfect crystal, since the atoms near the impurity will have somewhat different force constants from corresponding atoms in the perfect crystal. However, these changes will not be as radical as those of the impurity, and we postulate $(C'-\omega^2)^{-1}\approx C'^{-1}$ in the frequency range of interest, i.e., we are considering resonances at frequencies much lower than any resonances characteristic of the neighbors. The range of validity of this assumption will be discussed at a later stage. Examining Eq. (24) and solving for ω_L^2 to first order in the small parameter λ which characterizes the impurity, we find

$$\omega_L^2=L'\,, \tag{29}$$

i.e., the simplest effective force constant of the resonance is just the Einstein oscillator force constant with the rest of the lattice rigid: $L'\sim\lambda(M/M')\omega_{\max}^2$. The extra force constant in higher order arising from the adiabatic response of the lattice is of order $\lambda^2(M/M')\times\omega_{\max}^2$, which is of higher power in λ and which may be neglected in lowest approximation.

The breadth of the resonance will likewise be given from (27), by

$$\Delta\omega_L/\omega_L\sim\lambda^{3/2}(M/M')^{1/2}. \tag{30}$$

We note that the breadth is much more sensitive to weakness of coupling (depending on λ to the power $\frac{3}{2}$) than to the mass parameter. This is seen to be a general feature, and the expression (30) has been obtained by simple arguments. It is not surprising that special models have arrived at similar results, though with considerably more algebraic effort.

4. DISCUSSION

By examining the problem of resonances and localized modes in a particular representation, we have derived simple asymptotic results for which very little knowledge of the perfect-lattice response functions is needed. Further, the approach gives some physical insight into these phenomena. For a very high-frequency local mode due to an imperfection which is predominantly isotopic, the mode may be, to first order, simulated by an Einstein oscillator (the impurity vibrating in the field of the rest of the crystal static). It is interesting to note that in this limit, the result contains no information on the response functions of the perfect lattice, but depends only on the local properties of the defect. These results confirm previous interpretations by Matthew[24] and Gunther.[31] It is also possible to estimate simply the corrections to these leading terms [Eq. (22)].

In contrast, for low-frequency modes due to heavy impurities, the lattice is able to respond to the slow impurity motion by relaxing adiabatically. Here the accommodation of the lattice to the impurity motion significantly reduces the effective force constant of the center.

A particularly interesting case is that where the dynamical coupling between the impurity and its environment is very weak by comparison with the perfect-lattice coupling. As the impurity is largely decoupled, the extra restoring force arising from correlated lattice response becomes small compared with the Einstein oscillator contribution. Therefore, in the weak-coupling limit, the resonance once more closely resembles an Einstein oscillator. The effective-force constant of the resonance then can be simply interpreted in terms of the "local" force constant of the impurity; similarly, the dependence of the resonant frequency on $(M')^{1/2}$ is apparent. Most important, the weakness of coupling between the impurity and the lattice implies that resonances involving weak interactions with the lattice will tend to be much less damped and thus sharper than isotopic resonances having similar frequencies.

Let us now critically examine this low-frequency case by comparison with calculations on specific models, and relate them to recent experiments.

As discussed in Sec. 3, we are able to make an exact correspondence between our approach and the asymptotic results for the isotopic case derived from conventional theory. For the case of weak dynamical coupling, several studies have been carried out. Brice[9] considers resonances due to interstitials in silicon and germanium, on the assumption that the coupling of the interstitial atom is weak and that the dispersion of the perfect crystal is spherically symmetric. By extensive computation and graphical analysis, he infers empirically that the frequency and breadth of the resonance is given by equations of the type (29) and (30), up to a frequency of $\frac{1}{4}$ of the maximum transverse acoustic frequency. Further, he computes eigenvectors for the resonant mode, which support the Einstein oscillator picture. It may be noted that, because the weakly coupled atom is interstitial, the assumption that the properties of $(C'-\omega^2 1)^{-1}$ are comparable with those of $(C-\omega^2 1)^{-1}$ should be especially good in this case.

Sievers and Takeno[6] discuss a model of a cubic crystal with equal nearest-neighbor central and noncentral interactions: In the limit of weak coupling, they find the same result for the resonant frequency as that predicted here. Their expression for the breadth of the band does not agree in detail with the predictions of Eq. (30), and it has the quite nonphysical property that if $M'=M$, i.e., if the mass of the impurity is the same as the mass of the perfect-lattice atoms, the breadth of the resonance goes to zero: This result must be incorrect physically, and serves to raise considerable question of the model Green's function they use. Patnaik and Mahanty[8] consider a somewhat more complicated lattice model and obtain results for the frequencies of the resonances similar to those of Sievers and Takeno[6]; the breadths of the resonances are not derived.

Benedek and Nardelli[10,11] are the only workers to carry out calculations on ionic crystals, i.e., crystals with long-range force constants: Allowing for a local change of mass and short-range interaction, they compute in great detail the resonant response of the impurity and the host crystal; they compare their results with the experimental infrared absorption data on KBr:Li [6]and KBr:Ag.[34] The pattern which emerges differs somewhat from the predictions of Eqs. (29) and (30). To explain the very low-frequency resonances of Li^+ in KBr, a very weak local-interaction constant is inferred as required by Eq. (29) and by Sievers and Takeno.[6] Arguments by Matthew[17] and others[18,19] suggest that for a small ionic impurity, $L'\ll L$: If the ion is in a cubic site, there is no harmonic contribution to L' from Madelung forces, and the repulsive and polarization interactions can conspire to produce a very low value of L'. However, the off-diagonal coupling a' of the impurity to the lattice does contain electrostatic interactions, and a' may, as a result, be rather more comparable with a than the analysis of Sec. 3 B 2 might indicate. This suggests that in ionic crystals, the impurity interaction term $a'(C'-\omega^2 1)^{-1}(a')^T$ may play a more significant role in low-frequency resonances. The extreme sensitivity of the resonant frequencies to stress and alloying[21,22] could be explained entirely by the delicate balance between short-range repulsive and polarization in L', but this situation will also be highly sensitive to the terms $a'(C')^{-1}(a')^T$.

Nardelli and Benedek[10,11] find a smaller isotopic shift for the KBr:Li system than indicated by Eq. (29), and to obtain agreement with experiment, they must invoke large anharmonic effects. The implication of their result is that the ions around the impurity must also be sufficiently perturbed to contribute to the resonance in a dynamical way, in contrast to the adiabatic response of the lattice indicated for the heavy-mass impurity.

The breadth of the resonance which we find from Eqs. (29) and (30) by fitting λ to the resonance frequency in Li:KBr, is about one fifth of the experimental value, but the reservations with respect to either long-range forces (discussed above) or anharmonicity could modify the expression for the breadth considerably. The other purely harmonic models we have referred to also yield narrower theoretical widths than found experimentally.

These examples highlight the successes and failures of our simple approach to the resonance problem. We obtain good agreement with special models having short-range forces, and the simple pictures we have developed for the resonance state have very direct application there. The principal features of isotopic and coupling dependence of resonances are apparent. For more complicated systems with rather more subtle perturbation patterns, any model including ours must be interpreted with more care. In fact, the Lifshitz Green's-function method is inappropriate. The basic difficulty of any formulation is that one can establish experimentally only a very limited amount about the properties of the link term between the impurity system and the rest of the crystal; but even in the case of low-frequency resonances in ionic crystals, our analysis

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[34] A. J. Sievers, Phys. Rev. Letters 13, 310 (1964).

gives some general understanding of why significant differences may arise between calculations on simple models and more realistic simulations of the defect.

It would be useful to carry out further calculations on the lines of Nardelli and Benedek[10,11] in order to determine how sensitive their results are to the particular force-constant model used (i.e., to the perfect-lattice response functions), and to the precise form of the perturbation around the defect.

5. CONCLUSIONS

It has been shown that, independent of the model of crystal vibrations, localized modes with frequencies much greater than the maximum frequency of the lattice may be adequately described by the vibrations of the impurity region in the crystal, the rest of the crystal constrained to be static. Quite similarly, low-frequency resonances with very weak dynamical coupling can in some cases be described as Einstein oscillators; but for low-frequency resonances of very heavy-mass substitutions with force constants comparable to those of the host crystal, the lattice responds adiabatically to reduce the effective-force constant of the center to a value considerably less than that appropriate for an Einstein model. For impurities weakly coupled to the lattice, the behavior is again that of an Einstein oscillator, and the damping is strikingly small, $O(\lambda^{3/2})$, where λ is the coupling constant.

We consider that our model gives information complementary to that derived from large-scale machine computations using the conventional Green's-function formalism literally. Moreover, for interpretation of experimental data, our equations for frequencies and widths are probably as accurate as any lattice models computed numerically but based on special force-constant choices.

ACKNOWLEDGMENTS

One of us (J.A.D.M.) wishes to acknowledge the hospitality of the Theoretical Physics Division of the Atomic Energy Research Establishment, Harwell, England, where part of the manuscript was prepared. We both wish to thank a number of colleagues who have discussed these questions with us, particularly A. J. Sievers, R. J. Elliott, and S. Takeno.

APPENDIX A

Let us consider the properties of the function

$$G(\omega_L)=\frac{1}{3N}\mathcal{P}\sum_{\mathbf{q},i}\frac{\omega_L^2}{\omega_L^2-\omega_{\mathbf{q},i}^2} \tag{A1}$$

$$=\lim_{\delta\to 0}\,(1/3N)[R_-(\omega_L^2,\delta)-R_+(\omega_L^2,\delta)],$$

where

$$R_-(\omega_L^2,\delta)=\sum_{\mathbf{q},i}\frac{1}{[1-(\omega_{\mathbf{q},i}^2/\omega_L^2)]};\quad \omega_{\mathbf{q},i}^2<\omega_L^2-\delta,$$

$$R_+(\omega_L^2,\delta)=\sum_{\mathbf{q},i}\frac{\omega_L^2}{\omega_{\mathbf{q},i}^2[1-(\omega_L^2/\omega_{\mathbf{q},i}^2)]};\quad \omega_{\mathbf{q},i}^2>\omega_L^2+\delta.$$

Expanding, we obtain

$$G(\omega_L)=\lim(1/3N)\Big[\sum_{\mathbf{q},i}(1+\omega_{\mathbf{q},i}^2/\omega_L^2+\cdots)$$
$$-\sum_{\mathbf{q},i}{}'(\omega_L^2/\omega_{\mathbf{q},i}^2)(1+\omega_L^2/\omega_{\mathbf{q},i}^2+\cdots)\Big], \tag{A2}$$

where $\omega_{\mathbf{q},i}^2<\omega_L^2-\delta$ in the first summation and $\omega_{\mathbf{q},i}^2>\omega_L^2+\delta$ in the second summation. For small ω_L, we may conveniently express $G(\omega_L)$ as a series in powers of $\omega_L/\omega_{\max}$, where $\omega_{\max}$ is the maximum perfect-lattice frequency. We thus obtain

$$G(\omega_L)=-(1/3N)\sum_{\mathbf{q},i}(\omega_L^2/\omega_{\mathbf{q},i}^2)+A+B, \tag{A3}$$

where A and B are given by

$$A=\lim_{\delta\to 0}\,(1/3N)\sum_{\mathbf{q},i}(\omega_L^2/\omega_{\mathbf{q},i}^2+1+\omega_{\mathbf{q},i}^2/\omega_L^2+\cdots),\quad \omega_{\mathbf{q},i}^2<\omega_L^2-\delta \tag{A4}$$

$$B=-\lim_{\delta\to 0}\,(1/3N)\sum_{\mathbf{q},i}(\omega_L^4/\omega_{\mathbf{q},i}^4)(1+\omega_L^2/\omega_{\mathbf{q},i}^2+\cdots),\quad \omega_{\mathbf{q},i}^2>\omega_L^2+\delta.$$

The leading term of (A3) is of order $(\omega_L/\omega_{\max})^2$; since at low frequencies the density of phonon states must at least be proportional to ω^2, the terms in A and B can at most give contributions to $G(\omega_L)$ of order $(\omega_L/\omega_{\max})^3$. If the density of states $\sim\omega^2$ up to $\omega=\omega_L$, the terms in A and B to this order cancel exactly, and the first correction to the leading term is of order $(\omega_L/\omega_{\max})^4$. This is to be compared with the results of Brout and Visscher,[25] who assume a Debye distribution throughout the frequency range. $G(\omega_L)$ is then of the form

$$G(\omega_L)=-\omega_L^2\langle\omega^{-2}\rangle+O(\omega_L/\omega_{\max})^4. \tag{A5}$$

Applying Eq. (A5) to Eq. (1) and solving for ω_L^2 to lowest power in (M/M') yields Eq. (4).

APPENDIX B

We wish to show that the effective force constant $M(L-aC^{-1}a^T)$ obtained in Eq. (26) is identical with the effective force constant $M/\langle\omega^{-2}\rangle$ obtained in the asymptotic limit of the standard Green's-function formalism, applied to a cubic crystal.

Consider a *static* reduced-mass force field $|F)$ applied to the *perfect* crystal: Then the induced displacement field $|\varphi)$ is given by

$$|\varphi)=V^{-1}|F), \tag{B1}$$

i.e., $(V^{-1})_{ii}$ is the induced displacement on the ith component of displacement due to unit force per unit mass applied to the ith basis direction. The effective restoring force on a unit mass (including the reaction force due to the other atoms in their new equilibrium configuration) is therefore

$$\alpha = 1/(V^{-1})_{ii}. \tag{B2}$$

But α is exactly the quantity $(L-aC^{-1}a^T)$ appearing in Eq. (26), i.e.,

$$L-aC^{-1}a^T = 1/(V^{-1})_{ii}. \tag{B3}$$

Now $\langle\omega^{-2}\rangle$ is given by the trace of the inverse reduced-mass potential-energy matrix (defined with care to eliminate zero-frequency modes) divided by the order of V. Since all atoms of the perfect cubic crystal are equivalent, all the diagonal elements will be equal, giving

$$\langle\omega^{-2}\rangle = (V^{-1})_{ii}. \tag{B4}$$

Therefore we have

$$M(L-aC^{-1}a^T) = M/\langle\omega^{-2}\rangle. \tag{B5}$$

This shows that Eq. (4) is equivalent to Eqs. (25) and (26).

PHYSICAL REVIEW VOLUME 166, NUMBER 3 15 FEBRUARY 1968

Optical Properties of Alkali-Halide Crystals*

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(Received 20 July 1967)

Reflectivity data from single crystals of alkali halides have been obtained in the ultraviolet region of the spectrum where excitonic and low interband transitions occur. Following recent calculations for the band structure of KCl and KI and basing our analysis on the experimental data, it has been possible to predict the properties of the band structure in other alkali halides and describe satisfactorily the low-lying transitions. Furthermore, a close relationship between the conduction band and the energy of the L bands of the F center has been established.

1. INTRODUCTION

Ultraviolet absorption from thin films and reflectivity from cleaved crystals are among the most direct methods for investigating the intrinsic optical properties related to the excitation of electron states of alkali halides. As far as the absorption measurements are concerned, there exist in the literature extensive data at room temperature,[1] liquid-nitrogen temperature,[1] and 10°K.[2] On the other hand, if we except the pioneering work of Hartman *et al.*,[3] the reflectivity of alkali halides has not been studied extensively. Yet the important work by Philipp and Ehrenreich,[4] although confined to room temperature, has fully shown the potentiality of these measurements. At present, no systematic analysis, comparable to that relative to the absorption, is available for the reflectivity from single crystals at low temperatures. Reflectivity measurements are expected to yield details characteristic of the crystal structure more easily than absorption data from thin films. In fact, one of the experimental results derived from this assumption has been the observation of structures which are presumably to be attributed to excited levels of the Wannier type. These structures had been previously observed, with certainty, in the absorption spectra of iodides only.[2,5]

Until recently, the theoretical interpretation of the optical spectra has been based on the use of simple models for the excited states[6] and limited generally to the lowest-energy peaks. An attempt to explain the rich structure above the edge was made, not long ago, by Phillips,[7] who based his analysis on a tentative band scheme for the alkali halides. A connection with the band structure of rare-gas solids has also been anticipated, since the alkali halides may be considered a slightly more complex version of the rare-gas solids.[8]

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* Preliminary data have been presented at the National Conference on Alkali Halides, Consiglio Nazionale delle Ricerche, Milano, Italy, 1966.

[1] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).

[2] K. J. Teegarden and G. Baldini, Phys. Rev. **155**, 896 (1967).

[3] P. L. Hartman, J. R. Nelson, and J. G. Siegfried, Phys. Rev. **105**, 123 (1957).

[4] H. R. Philipp and H. Ehrenreich, Phys. Rev. **131**, 2016 (1963).

[5] F. Fischer and R. Hilsch, Nachr. Akad. Wiss. Goettingen, II, Math. Physik. Kl. **8**, 241 (1959); F. Fischer, Z. Physik **160**, 194 (1960).

[6] For a review of the exciton models see R. S. Knox, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 5.

[7] J. C. Phillips, Phys. Rev. **136**, A1705 (1964); in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18.

[8] R. S. Knox and F. Bassani, Phys. Rev. **124**, 652 (1961); L. F. Mattheiss, *ibid.* **133**, A1399 (1964); J. C. Phillips, *ibid.* **136**, A1714 (1964); W. B. Fowler, *ibid.* **132**, 1591 (1963).