

Localized Mode in an Anharmonic Crystal*†

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We consider a harmonic crystal with a single isotopic impurity whose coupling to its neighbors includes a cubic anharmonic term. The impurity is chosen to be light enough that a localized mode exists. The Hamiltonian for this system is truncated, in a physically reasonable way, so as to yield an exactly solvable Schrödinger equation. The solutions give a new insight into the nature of the localized mode, which in this approximation is exactly analogous to an unstable particle in the Lee model of field theory. The wave functions are exhibited and the lifetime is calculated for a light impurity in a simple cubic lattice at $T=0$.

I. INTRODUCTION

AN isolated impurity in a harmonic crystal gives rise to certain changes in the vibration spectrum¹⁻⁵ of the system. In particular, if the impurity is lighter than the host-crystal atoms and the impurity-mass to host-mass ratio is less than a certain critical number dependent on the atomic arrangement, then a so-called localized mode appears above the quasicontinuum of phonons. The characteristics of this mode are that when it is excited only the atoms near the impurity participate in the motion (the attenuation length decreases as the frequency increases); and that its frequency is higher than the maximum phonon frequency. The latter may be looked upon as the reason why the mode is localized; its frequency is too high to propagate in the lattice. The localized mode is a single normal mode of the system, with a sharp frequency.

It is the purpose of this note to investigate what happens to the localized mode when the interatomic force is allowed to contain certain anharmonic terms.⁶ The "single-particle" description of independent oscillators (harmonic forces only) then goes over into the analog of an interacting many-body system, and the physics and mathematics encountered is similar to that which occurs in a wide variety of problems. The localized mode state of the harmonic approximation becomes mixed with the multiphonon states whose energies lie nearby. The strength of the anharmonic interaction determines the width of the energy interval in which the mixing occurs; the energy width in turn governs the coherence of the localized mode (now only an approximate eigenstate) and therefore its lifetime.

Lowest order perturbation theory involves the calculation of the diagram shown in Fig. 1, with time increasing from left to right. The single localized mode which is present in the initial state (dashed line) decays into two phonons in the final state (wavy lines) through a cubic anharmonic interaction. The matrix element of the interaction operator

$$h = \sum_{lm} B_{klm} a_m^\dagger a_l^\dagger a_k \quad (1)$$

between a localized mode state (k) and a state in which two phonons (l and m) are present is all that is involved in the perturbation calculation. Such a calculation has been performed by Klemens,⁶ who used the phonon operators of the perfect crystal, and the localized mode operator⁷ of Montroll and Potts.²

The interaction Eq. (1) is one of the terms which arise from the expansion of a cubic anharmonic term in the lattice potential energy

$$H' = \sum_{ij} C_{ij} (\mathbf{x}_i - \mathbf{x}_j)^3 \quad (2)$$

in terms of the phonon and localized mode creation and annihilation operators. The cubic anharmonic term has no lower bound for large relative displacements; hence one would not expect any solutions of a problem in which it is the only perturbation. For our anharmonic interaction, however, we choose only a part of Eq. (2),

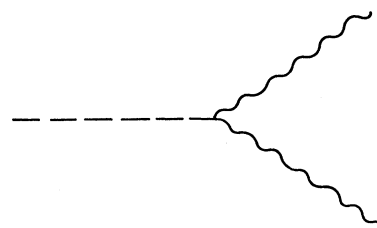


FIG. 1. Feynman diagram for decay of localized mode into two phonons.

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¹ I. M. Lifshitz, *Nuovo Cimento*, Suppl. **3**, 716 (1956).

² E. W. Montroll and R. B. Potts, *Phys. Rev.* **100**, 525 (1955).

³ Yu. Kagan and Ya. A. Iosilevskii, *Zh. Eksperim. i Teor. Fiz.* **42**, 259 (1962) [English transl.: *Soviet Phys.—JETP* **15**, 182 (1962)].

⁴ R. Brout and W. M. Visscher, *Phys. Rev. Letters* **9**, 54 (1962).

⁵ Yu. Kagan and Ya. A. Iosilevskii, *Zh. Eksperim. i Teor. Fiz.* **44**, 284 (1963) [English transl.: *Soviet Phys.—JETP* **17**, 195 (1963)].

⁶ This question has been studied before by different methods. See P. G. Klemens, *Phys. Rev.* **122**, 443 (1961) and A. A. Maradudin, *1962 Brandeis Lectures in Theoretical Physics* (W. A. Benjamin and Company, Inc., New York, 1963), Vol. 2.

⁷ The localized mode displacements assumed by Klemens were those given by Montroll and Potts as asymptotic forms, except that he inadvertently omitted the alternation of sign with each successive lattice distance from the impurity. This omission tends to make Klemens' result for the width too large, as does the fact that he used phonon operators for the perfect harmonic crystal rather than those for the harmonic crystal with a single isolated impurity.

such that the resulting systems may easily be solved exactly. Our method exhibits the solutions for the wave function explicitly, hence has an esthetic advantage over a perturbation calculation, although the quantitative results should be taken only to lowest order in the anharmonicity parameters.

We shall keep only Eq. (1) and its Hermitian conjugate and consider their sum to be the anharmonic interaction and drop the rest of the terms in Eq. (2). The principal justification for this is that it allows an exact solution to be easily obtained, but it is possible to argue as follows that at least some of the dropped terms are unimportant. The anharmonic interaction is large only when the displacements are large, and the displacement of any atom in the crystal due to the excitation of a single phonon is proportional to $N^{-1/2}$, where N is the total number of atoms. On the other hand, the localized mode displacements do not vanish as one lets $N \rightarrow \infty$, but approach a finite limit which decreases more or less exponentially with distance from the impurity atom. It might therefore be reasonable to expect that the most important terms in the expansion of Eq. (2) are those which involve the creation or annihilation of one or more localized modes. Most of the terms in the expansion of Eq. (2) do not satisfy this criterion.

We therefore take

$$H' = h + h^\dagger \quad (3)$$

as our anharmonic interaction. The basic Feynman diagram is Fig. 1 and the time-reverse of it, and we have essentially defined a Lee model^{8,9} of the anharmonic crystal.

The total Hamiltonian for this model is

$$H = H_0 + H', \quad (4)$$

where H_0 is the harmonic Hamiltonian

$$H_0 = \sum_s \hbar \omega_s (n_s + \frac{1}{2}),$$

$$n_s = a_s^\dagger a_s.$$

II. EIGENSTATES AND EIGENVALUES

The ground state of H is the same as that of H_0 , and the one-phonon states are identical too. It is only when we get to the one localized mode state and the states containing two phonons that the effects of H' begin to be felt.

We therefore consider the localized mode state, which is mixed by H' with two phonon states, and let

$$\Psi = C_k \Phi_k + \sum_{lm} C_{lm} \Phi_{lm}, \quad (5)$$

where the C 's are constants subject to a normalization condition

$$|C_k|^2 + \sum_{lm} |C_{lm}|^2 = 1, \quad (6)$$

and

$$\begin{aligned} \Phi_k &= a_k^\dagger \Phi_0, \\ \Phi_{lm} &= 2^{-1/2} a_l^\dagger a_m^\dagger \Phi_0, \end{aligned} \quad (7)$$

with Φ_0 the ground state, and k always referring to the localized mode, l, m to phonons in the quasicontinuum.

By requiring that Eq. (5) be an eigenstate of H with eigenvalue E one immediately obtains

$$(E - \epsilon_k) C_k = 2^{1/2} \sum_{lm} B_{klm} C_{lm}, \quad (8)$$

$$(E - \epsilon_{lm}) C_{lm} = 2^{1/2} B_{klm} C_k,$$

where ϵ_k and ϵ_{lm} are eigenvalues of H_0 with Φ_k and Φ_{lm} , respectively. Therefore unless E happens to coincide with one of the ϵ_{lm} 's or C_k vanishes we must have

$$E - \epsilon_k = 2 \sum_{lm} \frac{|B_{klm}|^2}{E - \epsilon_{lm}}, \quad (9)$$

which has as many solutions $E = E_\lambda$ as there are terms in the sum, plus one. Equation (9) is very similar to that obtained by Glaser and Källén⁹ in their investigation of a Lee model⁸ for an unstable particle. A graph of the right- and left-hand sides of Eq. (9) appears in Fig. 2. The intersections define the set of eigenvalues E_λ .

Certain features of Fig. 2 deserve comment. One is that for a given size crystal it is always possible to have a single negative eigenvalue E_λ for the anharmonic coefficients B_{klm} large enough. However, because as it is defined in Eq. (1) B_{klm} should decrease as $N^{-1/2}$ in order to correspond with Eq. (2) with C_{ij} independent of N ; the point of appearance of the negative eigenvalue as a function of anharmonic-force strength will be independent of crystal size for large crystals. The negative eigenvalue appears only for very large B_{klm} . Its existence is due to the fact that our Hamiltonian is not positive definite. Another feature is that an eigenvalue pops up out of the quasicontinuum, reminiscent of the appearance of the localized mode in the harmonic case.

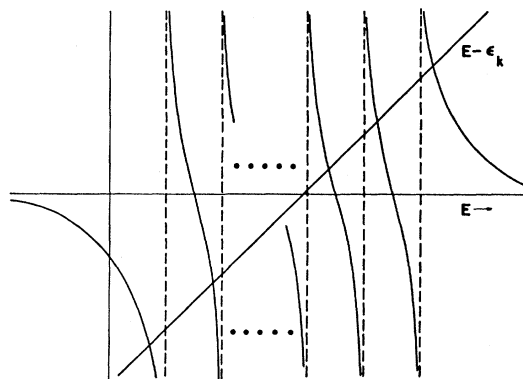


FIG. 2. Graphical solution of Eq. (9). The lowest asymptote will generally be at an energy of order $\hbar \omega_L / N$, the highest slightly below $2\hbar \omega_L$, where ω_L is the maximum phonon frequency.

⁸ T. D. Lee, Phys. Rev. **95**, 1329 (1954).

⁹ V. Glaser and G. Källén, Nucl. Phys. **2**, 706 (1956).

This state appears at a smaller, but still unphysically large, value of the anharmonic coupling. Like the negative eigenvalue, the critical-coupling parameter at which the positive energy state appears becomes independent of crystal size for large crystals.

III. COMPLETENESS

Since it is our purpose to study the evolution of the localized mode state as anharmonic forces are introduced, it behooves us to be sure that the set of states given by Eqs. (5) and (8) really spans that part of the Hilbert space which can be reached by operating repeatedly with the anharmonic Hamiltonian on the harmonic localized mode state Φ_k . To do this it is sufficient to show that

$$\sum_{\lambda} \Psi_{\lambda} \Psi_{\lambda}^{\dagger} = \Phi_k \Phi_k^{\dagger} + \sum_{lm} \Phi_{lm} \Phi_{lm}^{\dagger}, \quad (10)$$

where Ψ_{λ} is an eigenfunction of the Hamiltonian [Eq. (4)] with eigenvalue E_{λ} [a root of Eq. (9)], and which has the form of Eq. (5). The calculation is straightforward and proceeds as follows. Upon substitution of Eq. (5) into (10), we obtain

$$\begin{aligned} \sum_{\lambda} \Psi_{\lambda} \Psi_{\lambda}^{\dagger} &= \sum_{\lambda} C_k(\lambda) C_k^{\dagger}(\lambda) \Phi_k \Phi_k^{\dagger} \\ &+ \sum_{lm} C_{lm}(\lambda) C_{lm}^{\dagger}(\lambda) \Phi_{lm} \Phi_{lm}^{\dagger} \\ &+ \sum_{l'm' \neq lm} C_{l'm'}(\lambda) C_{l'm'}^{\dagger}(\lambda) \Phi_{l'm'} \Phi_{l'm'}^{\dagger} \\ &+ \sum_{lm} C_k(\lambda) C_{lm}^{\dagger}(\lambda) \Phi_k \Phi_{lm}^{\dagger} \\ &+ \sum_{lm} C_{lm}(\lambda) C_k^{\dagger}(\lambda) \Phi_{lm} \Phi_k^{\dagger}, \quad (11) \end{aligned}$$

and illustrate by calculating the coefficient of $\Phi_k \Phi_k^{\dagger}$.

We introduce a function $C_k(E)$ of the complex variable E , which has the property that it coincides with $C_k(\lambda)$ at $E=E_{\lambda}$, and is analytic in a small region surrounding each E_{λ} . Then

$$\sum_{\lambda} C_k(\lambda) C_k^{\dagger}(\lambda) = \frac{1}{2\pi i} \int_C C_k(E) C_k^{\dagger}(E) d \ln D(E), \quad (12)$$

where

$$D(E) = E - \epsilon_k - F(E), \quad (13)$$

and

$$F(E) = 2 \sum_{lm} \frac{|B_{klm}|^2}{E - \epsilon_{lm}}, \quad (14)$$

The contour C encircles the roots of $D(E)$ in a counterclockwise sense, and excludes any singularities of $C_k(E)$. Equation (12) follows from the fact that the eigenvalues E_{λ} are the roots of $D(E)$. Now, from Eqs. (6) and (8) we see that to within a phase factor

$$C_k(E) = [1 - F'(E)]^{-1/2} \quad (15)$$

has the properties we require for $C_k(E)$, and therefore

$$\sum_{\lambda} C_k(\lambda) C_k^{\dagger}(\lambda) = \frac{1}{2\pi i} \int_C \frac{dE}{E - \epsilon_k - F(E)} = 1, \quad (16)$$

which follows by expanding the contour to an infinite circle. Using some care in excluding the singularities of the C 's, the other coefficients in Eq. (11) can be similarly shown to be unity or to vanish, and Eq. (10) follows.

IV. LIFETIME OF LOCALIZED MODE

If we imagine that in the anharmonic crystal we can somehow excite the *harmonic* localized mode, its lifetime may easily be calculated. To do this it suffices to calculate

$$(\Psi(0), \Psi(t)) = (\Phi_k, \Psi(t)), \quad (17)$$

with

$$\Psi(t) = \sum_{\lambda} C(\lambda) \Psi_{\lambda} e^{-iE_{\lambda}t}, \quad (18)$$

and the C 's chosen so that

$$\Psi(0) = \Phi_k. \quad (19)$$

Equation (19) implies that

$$C(\lambda) = C_k^{\dagger}(\lambda), \quad (20)$$

and the scalar product of Eq. (17) is easily seen to be

$$(\Psi(0), \Psi(t)) = \frac{1}{2\pi i} \int_C e^{-iEt} \frac{1}{E - \epsilon_k - F(E)} dE. \quad (21)$$

Because of the presence of the exponential we can't evaluate the integral as easily as before, and must carefully study the denominator in the integrand.

If we are interested in times short compared to the longest periods of vibration of the crystal, then we may as well consider the infinite crystal. Therefore, we study the behavior of $F(E)$ in the limit $N \rightarrow \infty$. It will become an integral

$$F(E) = \int_0^{2\hbar\omega_L} \frac{\rho(k, \epsilon) d\epsilon}{E - \epsilon} \quad (22)$$

with $\rho(k, \epsilon)$ real and positive, of form similar to that encountered in many fields, but in particular in the theory of lattice-vibration spectra. $F(E)$ has acquired a cut in the locus of the poles it had before $N \rightarrow \infty$; the poles, in other words, have become dense along the real axis from 0 to $2\hbar\omega_L$. By analogy with similar integrals which have been calculated in other connections, we can sketch (Fig. 3) the real and imaginary parts of $F(E - i\delta)$, where δ is an infinitesimal positive number. The qualitative features of Fig. 3 which are certainly independent of the crystal model used are the general behavior of the real part for $E < 0$ and $E > 2\hbar\omega_L$; the fact that the imaginary part is positive for $0 < E < 2\hbar\omega_L$ and vanishes outside this range, and the rapid increase

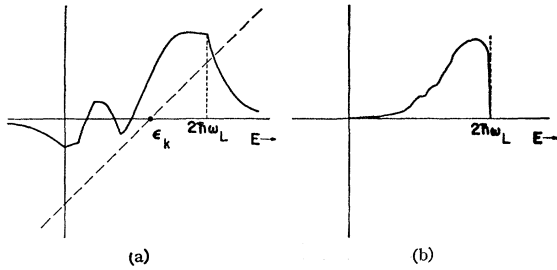


FIG. 3. Real (a) and imaginary (b) parts of $F(E-i\delta)$ for $N \rightarrow \infty$. The dashed line in (a) is $E - \epsilon_k$. Notice that, in this model, for a very large anharmonic term, the localized mode (defined now by the intersection) is an eigenstate, since then the imaginary part of F vanishes. For a realistically small anharmonic force, however, the intersection will not be far removed from ϵ_k .

in general of the absolute values of the real and imaginary parts of $F(E)$ as E increases from 0 to $2\hbar\omega_L$. This latter follows from the rapid increase of the density of states of two phonons which is a factor in $\rho(k, \epsilon)$.

$D(E)$ and hence the denominator of the integrand of Eq. (21) can never have any roots but real ones, because of the Hermiticity of the Hamiltonian. We can therefore contract the contour around the cut and obtain

$(\Psi(0), \Psi(t))$

$$= -\frac{1}{\pi} \int_{-2\hbar\omega_L}^{2\hbar\omega_L} e^{-iEt} \frac{h(E)dE}{[E - \epsilon_k - g(E)]^2 + \hbar^2(E)}, \quad (23)$$

where we have set

$$F(E - i\delta) = g(E) + ih(E). \quad (24)$$

The form of Eq. (23) is such that if $h(E)$ is small and $g(E)$ is slowly varying in the neighborhood of E_0 where E_0 is chosen such that

$$E_0 - \epsilon_k - g(E_0) = 0, \quad (25)$$

then it becomes approximately

$$(\Psi(0), \Psi(t)) = e^{-iE_0 t} e^{-\Gamma t/2} \quad (26)$$

with

$$\Gamma/2 = \hbar(E_0) = \pi\rho(k, E_0). \quad (27)$$

This is the same result which would be obtained from first-order perturbation theory, except there E_0 would be replaced by ϵ_k . To obtain a numerical answer from Eq. (27) one needs first to find out what B_{klm} is implied by a reasonable form of C_{ij} in Eq. (2); this is not a trivial task because it involves finding the eigenvectors of the secular matrix of the imperfect harmonic crystal.

V. CALCULATION OF $F(E)$

We shall now take a simple model for the harmonic crystal with a single impurity, for which we already know the eigenvectors,¹⁰ and calculate $F(E)$ as expressed in Eq. (14).

A simple and perhaps fairly reasonable form for the anharmonic energy is

$$H' = b(x_{000} - x_{100})^3 - b(x_{000} - x_{-100})^3, \quad (28)$$

where x_{ijk} is the displacement in the x direction of the atom in the (ijk) simple cubic lattice site from its equilibrium position. In the model that we are using motions in the 3 Cartesian direction are independent and separable, so Eq. (28) represents a general central cubic anharmonic interaction between the impurity at (000) and its nearest neighbors. For positive b , H' gives rise to an extra repulsion for small interatomic distances, an extra attraction for large ones. It can be thought of as representing a physical situation where the impurity is a misfit in an otherwise perfect harmonic crystal.

If we now expand x_{ijk} in terms of the creation-annihilation operators a_s^\dagger, a_s according to

$$x_{ijk} = \sum_s (C_{s,ijk}^\dagger a_s^\dagger + C_{s,ijk} a_s) = \sum_s x_{ijk}^s, \quad (29)$$

(where the sum is over the normal modes of the imperfect harmonic crystal) and substitute into Eq. (28), we can pick out the terms having the form of those contained in \hbar [Eq. (1)].

$$\begin{aligned} \hbar = 3b \sum_{l,m} [(C_{l,000} - C_{l,100})(C_{m,000} - C_{m,100}) \\ - (C_{l,000} - C_{l,-100})(C_{m,000} - C_{m,-100})] \\ \times (C_{k,000}^\dagger - C_{k,100}^\dagger) a_l^\dagger a_m^\dagger a_k. \end{aligned} \quad (30)$$

Here, as before, l and m refer to normal modes in the quasicontinuum of the imperfect harmonic crystal (phonons), and k refers to the localized mode.

In arriving at Eq. (30) we have made use of the fact that the localized mode is always an even excitation of the lattice about the impurity position, i.e., $C_{k,100} = C_{k,-100}$. If we were to use boundary conditions such that the phonons, too, are either even or odd with respect to the impurity position, then the contributions to the sum in Eq. (30) will have (l even, m odd) or (l odd, m even). Thus

$$\begin{aligned} B_{klm} = 6b(C_{l,000} - C_{l,100})(C_{m,-100} - C_{m,100}) \\ \cdot (C_{k,000}^\dagger - C_{k,100}^\dagger) a_l^\dagger a_m^\dagger a_k \end{aligned} \quad (31)$$

for l corresponding to an even mode; B_{klm} vanishes otherwise.

Specializing now to the case of a mass impurity (no change in the harmonic forces connecting the impurity to its neighbors) we can calculate the C 's.

Equation (5') of Ref. 10 may be written

$$x_{ijk}^s = g_{ijk,000}^s \delta\mu \omega_s^2 x_{000}^s, \quad (32)$$

where $g^s = g(\omega_s^2)$ is given there in Eq. (23'), and $\delta\mu$ is the difference between the impurity and host mass. Equation (32) implies that the frequencies of the normal modes for which the displacement of the impurity atom

¹⁰ W. M. Visscher, Phys. Rev. **129**, 28 (1963).

does not vanish are given by the roots of

$$g_{000,000} \delta \mu \omega_s^2 = 1, \quad (33)$$

and that the C 's of Eq. (31) satisfy

$$C_{s,\alpha} = (g_{\alpha 0}^s / g_{00}^s) C_{s,0} \quad (34)$$

for the even modes, and for the odd modes the C 's are the same as for the perfect crystal. In Eq. (34) we have denoted the triplet (ijk) by α . For the even modes, then, a complete specification of the C 's awaits only a normalization condition, which, upon requiring that

$$[p_{\alpha, \alpha'}] = -i \hbar \delta_{\alpha \alpha'} \quad (35)$$

and

$$[a_s, a_{s'}^\dagger] = \delta_{s' s}, \quad (36)$$

can be straightforwardly shown to be

$$|C_{s,0}|^2 = \frac{\hbar}{2\omega_s \mu} (g_{00}^s)^2 / \left[\sum_{\gamma} (g_{\gamma 0}^s)^2 + \frac{\delta \mu}{\mu} (g_{00}^s)^2 \right]. \quad (37)$$

Then, if we use the fact that

$$g_{00}^s - g_{10}^s = 2(\omega_s / \omega_L)^2 g_{00}^s + (2 / \mu \omega_L^2), \quad (38)$$

which can be verified from the forms of the g 's given in Eq. (25') of Ref. 10, Eq. (31) can be rewritten

$$|B_{klm}|^2 = (24b)^2 (\mu' / \mu)^4 k^4 l^4 |C_{k,0}|^2 |C_{l,0}|^2 \times |C_{m,1} - C_{m,-1}|^2, \quad (39)$$

where $\mu' = \mu + \delta \mu$ and $l = \omega_l / \omega_L$, $k = \omega_k / \omega_L$, and where m refers to an odd mode in which the impurity is located at a node. It then follows that $C_{m,\alpha}$ is not different from that for the perfect lattice, and therefore

$$|C_{m,1} - C_{m,-1}|^2 = (\hbar / 2\mu N \omega_m) 4 \sin^2 \varphi_x^m, \quad (40)$$

where N is the number of atoms in the crystal and φ_x^m is the x component of the wave vector of the m th phonon.

We are now in a position to write down an integral form for the sum in $F(E)$, Eq. (14). The sum over l can be replaced by an integral as follows:

$$\sum_l |C_{l,0}|^2 \rightarrow \frac{1}{2\pi i} \int_C \frac{\hbar}{2\omega_l} \frac{d\omega_l^2}{2\omega_l (g_{00}^l)^{-1} - \delta \mu \omega_l^2} \rightarrow \frac{\hbar}{2\pi \gamma} \int_0^{\omega_L} d\omega_l G(l), \quad (41)$$

where the contour encircles the zeroes of the denominator in the range $0 < \omega_l < \omega_L$, and the second step is achieved upon taking the limit $N \rightarrow \infty$ and contracting the contour about the cut which then appears from 0 to ω_L .

$$G(l) = 2\gamma \frac{\text{Im} g_{00}^l (\omega_l^2 - i\epsilon)}{(1 - \delta \mu \omega_l^2 \text{Re} g_{00}^l)^2 + (\delta \mu \omega_l^2 \text{Im} g_{00}^l)^2}, \quad (42)$$

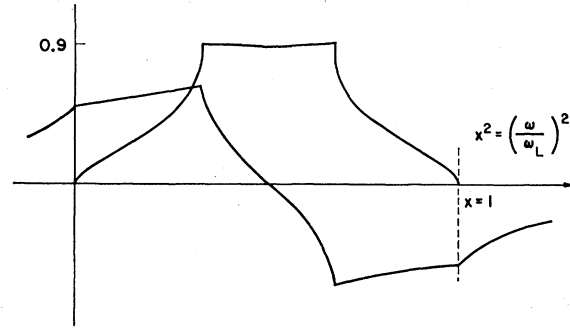


FIG. 4. Real and imaginary parts of $2\gamma g_{00}(\omega)$.

and γ is the harmonic force constant. The sum over m can be similarly expressed:

$$\sum_m \frac{\hbar}{2\mu N \omega_m} \rightarrow \frac{\hbar}{2\pi \gamma} \int_0^{\omega_L} d\omega_m G_0(m), \quad (43)$$

where

$$G_0(m) = 2\gamma \text{Im} g_{00}(\omega_m^2 - i\epsilon). \quad (44)$$

Now, if we take E to be removed from the real axis, we can write

$$F(E) = 2 \left(\frac{24b\hbar\omega_L}{\pi\gamma} \right)^2 \left(\frac{\mu'}{\mu} \right)^4 k^4 |C_{k,0}|^2 \int_0^1 \frac{dl dm l^4 G(l) G_0(m) \langle \sin^2 \varphi_x^m \rangle}{E - \epsilon_l - \epsilon_m}, \quad (45)$$

where the bracket denotes an average over all modes with energy ϵ_m . The dimensionless function $G(l)$ has been calculated numerically in Ref. 10; its shape for various impurity masses is exhibited in Fig. 9 of that paper and Fig. 4 of the present paper shows the real and imaginary parts of g_{00} . $|C_{k,0}|^2$ is, as can be seen from Eq. (29), just the contribution of the localized mode to the mean-square displacement of the impurity; this has also been calculated in Ref. 10. We can, semi-quantitatively, identify

$$bC_{k,0}/\gamma = r \quad (46)$$

as the ratio of the anharmonic potential energy of the impurity atom to its harmonic energy when the localized mode is excited.

The imaginary part of $F(E)$, according to Eq. (27), is equal to the half-width of the localized mode line.

$$\Gamma/2 = h(E) = \frac{2\hbar\omega_L}{\pi} (24r)^2 \left(\frac{\mu'}{\mu} \right)^4 k^4 \int_0^1 dl l^4 G(l) G_0 \left(\frac{E}{\hbar\omega_L} - l \right) \left\langle \sin^2 \varphi_x \left(\frac{E}{\hbar\omega_L} - l \right) \right\rangle. \quad (47)$$

An approximate numerical integration¹¹ for the case where $E=1.12\hbar\omega_L$, which is the harmonic localized mode energy for this model if $\mu'=0.5\mu$, yields the result that the integral in Eq. (47) is about 5×10^{-3} . For this case, then, we find

$$\Gamma/2 \approx 0.2\hbar\omega_L r^2. \quad (48)$$

Because of the fact that r is identified with the anharmonic interaction of an isolated impurity atom with its neighbors, it is difficult to make a numerical estimate for it. The usual parameter of anharmonicity, the Grüneisen constant,¹² is measured for interactions between atoms of the host crystal. But if we associate these quantities with each other, we find that a reasonable Grüneisen constant (of the order of unity) for a crystal implies that r for the force between each atom

¹¹ An analytic approximation can be made in the limit of small impurity mass.

¹² See, for example, P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 1.

and its nearest neighbors is of the order of 10^{-2} . Therefore, from Eq. (48) we see that the order of magnitude of the ratio of the half-width to energy of the anharmonic localized mode is 10^{-4} . Within the limitation of the calculations, this result is not in disagreement with the widths obtained in the references cited above.⁶ No careful quantitative work will be done here, because we do not believe the model we use to be realistic enough to warrant it. The significance of the present work lies more in the form than in the magnitude of the answers.

The real part of $F(E)$ is just Eq. (45) with the integral replaced by a principal value integral. It will be of the same order-of-magnitude as the imaginary part; hence the shift of the localized mode (downward in energy for frequencies close to the phonon cutoff) is comparable to its width.

VI. ACKNOWLEDGMENT

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Energy Bands for the Iron Transition Series*

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Preliminary energy-band calculations for elements of the iron transition series have been completed using the augmented plane-wave method. The results include plots of energy as a function of wave vector along a line of symmetry for elements crystallizing in the face-centered cubic (Ar, Co, Ni, Cu), body-centered cubic (V, Cr, Fe), and hexagonal close packed (Ti, Zn) structures. These results indicate the presence of systematic trends in the band structures for the various elements and provide some justification for the application of the rigid band model to transition metals and their alloys.

I. INTRODUCTION

ENERGY bands have been calculated for a majority of the elements in the iron transition series using the augmented plane-wave (APW) method.^{1,2} While the present results are preliminary in nature and not in any sense complete, they may be of some interest to experimentalists and theoreticians who are concerned with the electronic structure of the transition-series elements. The present results represent energy bands for three different crystal structures, with a variety of lattice constants. Despite the detailed differences that are imposed by symmetry requirements and variations in lattice constants, the results suggest some interesting and rather clear-cut trends in the band structure of these elements as one proceeds through the

transition series. These calculations lend some support to the rigid band model for the transition series. They support the hope that systematic studies of the band structure of the transition-series elements can provide useful qualitative, and perhaps quantitative, information concerning their electronic structure.

As in all calculations involving d electrons, the results are sensitive to the choice of potentials. The crystal potentials used in these calculations were all constructed in an analogous manner, and were approximated by a superposition of atomic potentials. The method involves the use of Hartree-Fock solutions to the corresponding atomic problem³ and the free-electron-exchange approximation.⁴ The details of this method for constructing approximate crystal potentials have been described earlier,⁵ though a brief resumé is presented in Sec. II of

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¹ J. C. Slater, *Phys. Rev.* **51**, 846 (1937).

² J. H. Wood, *Phys. Rev.* **126**, 517 (1962).

³ R. E. Watson, *Phys. Rev.* **119**, 1934 (1960); R. E. Watson and A. J. Freeman, *Phys. Rev.* **123**, 521 (1961).

⁴ J. C. Slater, *Phys. Rev.* **81**, 385 (1951).

⁵ L. F. Mattheiss, *Phys. Rev.* **133**, A1399 (1964).