Bounds on Localized Modes in the Crystal Impurity Problem

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Abstract

Using general properties of the crystal site representation normal mode matrix, we provide some very simple bounds on localized modes in simple, body-centered and face-centered cubic crystals with substitutional point defects. We derive a trace condition constraint on the net change in crystal eigenfrequencies caused by the introduction of a defect, with the condition being a completely general one which holds for any combination of central and non-central crystal force-constants and for all-neighbor interactions. Using this condition we show that the sufficient condition for producing localized modes in an arbitrary cubic crystal by a mass change at the defect site is that the defect mass be less than one half of that of the host atom mass which it replaces, and that the sufficient condition for producing localized modes in an arbitrary cubic crystal by force-constant changes alone is that the defect site self force-constant be greater than twice that of the pure crystal self force-constant of the host atom which it replaces.
I. INTRODUCTION

The substitutional insertion of a point defect impurity into an otherwise perfect host crystal will typically modify the spectrum of the $3N$ normal modes of the crystal$^1$, leading in certain circumstances (such as the insertion of impurities which are lighter in mass than the host atoms which they replace or which are more strongly coupled to the host crystal atoms than the ones they replace) to the generation of modes with frequencies which lie beyond the band maximum $\omega_{\text{max}}$ of the crystal. Such modes will not be plane waves which propagate throughout the crystal, but will instead fall off exponentially fast away from the defect site and thus be localized to it. Moreover, with the rest of the crystal atoms not participating appreciably in such localized modes, the intensity of the defect in such modes will be $N$ times larger than the intensity it would otherwise have had in a crystal plane wave mode, to thus give the localized mode enough intensity to render it observable. While such modes could be of relevance for phenomena such as the Mössbauer effect associated with the insertion of Mössbauer active defects into host crystals, historical recoil-free fraction Mössbauer studies only involved an averaging over all the lattice modes of the system, to thereby only allow one to infer the possible presence of localized modes indirectly. However, with the advent of dedicated synchrotron rings it became possible to monitor Mössbauer active systems mode by mode directly; and via nuclear resonant inelastic x-ray scattering studies, modes lying beyond the host crystal phonon band maximum have now explicitly been seen in the $^{57}$Fe/Cu and the $^{57}$Fe/NiAl systems.$^{2,3}$ Consequently, knowing whether the insertion of a defect into pure crystal hosts might generate localized modes can be of great value for such studies.

In this paper we use a very straightforward trace technique to enable us to identify some very general conditions under which such localized modes can be produced. We shall restrict our study to the most straightforward case of single point defects which are substitutionally inserted in the three primitive simple, body-centered and face-centered cubic crystals (these specific cases being amongst the most commonly experimentally studied ones), though with our approach being quite generic, it could in principle be adapted to encompass other crystal structures as well if desired. We shall provide results for various combinations of mass and force-constant changes, some which are specific to nearest-neighbor force-constants and some of which are general to all-neighbor force-constants. In Sec. II we derive the trace condition
on which all of our results are based, with the provided relation (Eq. (15) below) being an exact, all-neighbor relation which permits an arbitrary mass change ($M$ replaced by $M'$) at the defect site and arbitrary force-constant changes between the defect atom and any other atom in the entire crystal, despite which the resulting relation only involves the self-force constant $A_{xx}(0,0)$ at the defect site and the change $A'_{xx}(0,0)$ in it. In Sec. III we apply our trace condition to the case of an isotopic substitution where the only change is that in the mass at the defect site, to show that while having a lighter impurity ($M' < M$) is necessary for the generation of a localized mode, it is the condition $M' < M/2$ which is the sufficient one. In Secs. IV and V we apply our trace condition to some straightforward nearest-neighbor force-constant change cases for which there are extremely simple exact analytic solutions to the impurity problem (some typical examples of which being crystals with force-constants which are central or which are isotropic), to find that for all of them the sufficient condition for localized mode production by force-constant changes alone is given as the requirement that $A'_{xx}(0,0)/A_{xx}(0,0)$ be greater than $3/2$. Finally in Sec. V we examine more complicated force-constant change cases and go beyond nearest-neighbor force-constants, and while these situations do not admit of as straightforward a treatment as the cases considered in Sec. IV, nonetheless for them we are still able to extract a general sufficiency condition for the generation of localized modes in an arbitrary crystal by force-constant changes alone, namely that $A'_{xx}(0,0)/A_{xx}(0,0)$ be greater than two.

II. DERIVATION OF THE TRACE CONDITION

Since the very introduction of a defect breaks the translation invariance of the lattice, to derive a condition such as one involving a trace, we will need to work entirely in the coordinate space crystal site representation. To actually derive the trace condition we recall that in the harmonic approximation the equations of motion for the displacements from equilibrium $e^{-i\omega t}u_{\alpha}(\ell)$ of the atoms of a pure $3N$-dimensional cubic crystal lattice are given by

$$
\sum_{\beta,\ell'} \left[ A_{\alpha\beta}(\ell,\ell') - w^2 M(\ell') \delta_{\alpha\beta} \delta(\ell,\ell') \right] u_{\beta}(\ell') = 0 ,
$$

where $\ell$ ranges from 0 to $N - 1$, $\alpha = x, y, z$, $M(\ell)$ is the mass of the atom at site $\ell$, and $A_{\alpha\beta}(\ell,\ell')$ are the second order force-constants. Since Eq. (1) is an eigenvalue equation for the frequencies $\omega^2$, on defining a matrix $B_{\alpha\beta}(\ell,\ell') = M(\ell)\delta_{\alpha\beta} \delta(\ell,\ell')$, we immediately see
that the sum of the eigenfrequencies of the crystal is given by
\[ \sum_{i=1}^{3N} \omega_i^2 = \text{Tr}AB^{-1} \quad (2) \]

For a pure crystal in which all masses are equal to a common \( M(\ell) = M \) and all self force-constants are equal to a common \( A_{xx}(\ell, \ell) = A_{yy}(\ell, \ell) = A_{zz}(\ell, 0) \), Eq. (2) reduces to
\[ \frac{1}{3N} \sum_{i=1}^{3N} \omega_i^2 = \frac{A_{xx}(0, 0)}{M} \quad (3) \]

With the left-hand side of Eq. (3) being recognized as \( \mu_2 \), the second moment of the density of states, Eq. (3) thus recovers the well-known relation for pure crystals
\[ \mu_2 = \frac{A_{xx}(0, 0)}{M} \quad (4) \]

For the system with a substitutional point impurity of mass \( M' \) located at the origin of coordinates and changed force-constants \( A'_{\alpha\beta}(\ell, \ell') \), the displacements from equilibrium are now given as \( e^{-i\omega t}u_\alpha(\ell) \), with Eq. (1) then being replaced by
\[ \sum_{\beta,\ell'} \left[ A_{\alpha\beta}(\ell, \ell') - w^2M\delta_{\alpha\beta}\delta(\ell, \ell') \right] u_\beta(\ell') = \sum_{\beta,\ell'} V_{\alpha\beta}(\ell, \ell')u_\beta(\ell') \quad (5) \]

where the changes from the pure crystal case are described by the perturbation
\[ V_{\alpha\beta}(\ell, \ell') = -w^2(M - M')\delta_{\alpha\beta}\delta(\ell, 0)\delta(\ell', 0) + A_{\alpha\beta}(\ell, \ell') - A'_{\alpha\beta}(\ell, \ell') \quad (6) \]

On now defining a matrix \( B_{\alpha\beta}(\ell, \ell') = M\delta_{\alpha\beta}\delta(\ell, \ell') + (M' - M)\delta_{\alpha\beta}\delta(\ell, 0)\delta(\ell', 0) \), the sum of the eigenfrequencies of the perturbed crystal is then given by
\[ \sum_{i=1}^{3N} \omega_i'^2 = \text{Tr}A'[B']^{-1} \quad (7) \]

with the change in the sum of the eigenfrequencies thus being given by
\[ \sum_{i=1}^{3N} [\omega_i'^2 - \omega_i^2] = \text{Tr}A'[B']^{-1} - \text{Tr}AB^{-1} \quad (8) \]

The utility of Eq. (8) is that its left-hand side measures whether modes are shifted to higher or lower frequency, while on its right-hand side it is only the sites which are explicitly involved in \( V_{\alpha\beta}(\ell, \ell') \) which do not drop out of the difference between the two 3N-dimensional traces. Our task is thus to first evaluate the right-hand side of Eq. (8) and then to seek constraints on its left-hand side.
In the simplest case where the only change is a mass change at the defect site, it is only the defect site contribution itself which is not cancelled in the trace difference, with the full change in frequency immediately being given by

$$\sum_{i=1}^{3N}[\omega_i'^2 - \omega_i^2] = \frac{3A_{xx}(0,0)}{M'} - \frac{3A_{xx}(0,0)}{M}. \quad (9)$$

When there is also a change in force-constant at the defect site, we recall that by Newton’s third law of motion there must also be changes in the force-constants at other sites too. Moreover, this same Newtonian law entails that the force-constants of a perturbed system with a defect have to obey

$$A'_{\alpha\beta}(\ell, \ell) = -\sum_{\ell' \neq \ell} A'_{\alpha\beta}(\ell', \ell) \quad (10)$$

for all $\ell$ in exactly the same way as the pure crystal force-constants have to obey

$$A_{\alpha\beta}(\ell, \ell) = -\sum_{\ell' \neq \ell} A_{\alpha\beta}(\ell', \ell) \quad (11)$$

With the $x$, $y$ and $z$ directions being equivalent in cubic crystals, in the general case which allows for arbitrary force-constant changes, Eq. (10) takes the form

$$\frac{1}{3} \sum_{i=1}^{3N}[\omega_i'^2 - \omega_i^2] = \frac{A_{xx}'(0,1)}{M} - \frac{A_{xx}(0,1)}{M} + \frac{A_{xx}'(1,1)}{M} - \frac{A_{xx}(1,1)}{M} + \frac{A_{xx}'(2,2)}{M} - \frac{A_{xx}(2,2)}{M} + \ldots. \quad (12)$$

As regards the pure and the perturbed force-constants, we recall that in terms of the two-body interatomic potential $\phi(r)$, the force-constants between an atom vibrating around site $R_\alpha(\ell)$ and one vibrating around the origin are defined as

$$A_{\alpha\beta}(\ell, 0) = -\left[ \frac{\partial^2 \phi(r)}{\partial u_\alpha(\ell) \partial u_\beta(\ell)} \right]_0 = -\left[ \frac{\phi''(r)}{r^2} - \frac{\phi'(r)}{r^3} \right] R_\alpha(\ell) R_\beta(\ell) - \frac{\phi'(r)}{r} \delta_{\alpha\beta}, \quad (13)$$

as calculated at the equilibrium separation $r$. Then, since the effect of the introduction of the defect is to alter the two-body potential between the defect and the host atoms while not affecting the potentials between any two host atoms themselves, the only non-self force-constants which will change will then be the $A'_{\alpha\beta}(\ell, 0)$ with $\ell \neq 0$, with Eq. (10) then obliging the self force-constants at the defect site and those at the $\ell \neq 0$ sites to respectively change as

$$A'_{\alpha\beta}(0,0) = -\sum_{\ell \neq 0} A'_{\alpha\beta}(\ell, 0),$$

$$A'_{\alpha\beta}(\ell, \ell) = -A'_{\alpha\beta}(\ell, 0) - \sum_{\ell' \neq \ell, 0} A_{\alpha\beta}(\ell, \ell') = -A'_{\alpha\beta}(\ell, 0) + A_{\alpha\beta}(\ell, \ell) + A_{\alpha\beta}(\ell, 0). \quad (14)$$
Given these relations and Eqs. (10) and (11), Eq. (12) can thus be simplified to
$$\frac{1}{3} \sum_{i=1}^{3N} [\omega_i^2 - \omega_i^2] = \frac{A'_{xx}(0, 0)}{M'} - \frac{A_{xx}(0, 0)}{M} - \frac{1}{M} \sum_{\ell \neq 0} [A'_{xx}(\ell, 0) - A_{xx}(\ell, 0)]$$
$$= \frac{A'_{xx}(0, 0)}{M'} + \frac{A'_{xx}(0, 0)}{M} - \frac{2A_{xx}(0, 0)}{M}.$$

Equation (15) is our main result, and is derived here with no restriction at all on the number of neighbors of the defect for which the force-constants might change. Nor does it presuppose any relation between $\phi''(r)$ and $\phi'(r)/r$. Despite the fact that Eq. (15) conveniently only involves the self force-constant at the defect site, nonetheless it is an all-neighbor result, one which additionally holds for any combination of central and non-central force-constants.

III. APPLICATION TO THE MASS DEFECT CASE

In the treatment of crystal impurity problem it is conventional to solve Eq. (5) by the lattice Green’s function technique, and since we will use some of its aspects to constrain the left-hand side of Eq. (15), we briefly recall the procedure. One first introduces the dynamical matrix of the pure crystal
$$D_{\alpha\beta}(\mathbf{k}) = \frac{1}{M} \sum_{\ell} A_{\alpha\beta}(0, \ell) e^{-i\mathbf{k} \cdot \mathbf{R}(\ell)}$$
(16)
as expressed in terms of the phonon modes $\mathbf{k}$ of the translational invariant pure crystal, and then defines its eigenvectors and eigenvalues according to
$$\sum_{\beta} D_{\alpha\beta}(\mathbf{k}) \sigma^j_\beta(\mathbf{k}) = \omega_j^2(\mathbf{k}) \sigma^j_\alpha(\mathbf{k}) ,$$
$$\sum_{\alpha} \sigma^{*j}_\alpha(\mathbf{k}) \sigma^j_\alpha(\mathbf{k}) = \delta_{jj} , \quad \sum_{j} \sigma^{*j}_\alpha(\mathbf{k}) \sigma^j_\beta(\mathbf{k}) = \delta_{\alpha\beta} ,$$
(17)
and then uses these eigenvectors and eigenvalues to construct the pure crystal lattice Green’s functions according to
$$g_{\alpha\beta}(\omega; \ell, \ell') = \frac{1}{NM} \sum_{k,j} \frac{\sigma^{*j}_\alpha(\mathbf{k}) \sigma^j_\beta(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{R}(\ell') - \mathbf{R}(\ell)}}{[\omega_j^2(\mathbf{k}) - \omega^2]}$$
(18)
as summed over the polarizations $j = (1, 2, 3)$ and momenta $\mathbf{k}$ of all the modes in the Brillouin zone. As constructed these Green’s functions obey
$$\sum_{\ell,\beta} A_{\alpha\beta}(0, \ell) g_{\alpha'\beta}(\omega; \ell, \ell') = M \omega^2 g_{\alpha'\alpha}(\omega; 0, \ell') + \frac{\delta_{\alpha,\alpha'}}{N} \sum_{\mathbf{k}} e^i\mathbf{k} \mathbf{R}(\ell'),$$
(19)
and thus immediately allow us to solve Eq. (15) in the form

\[ u_\alpha(\ell) = \sum_{\ell', \ell''} g_{\alpha \beta}(\omega'; \ell, \ell') V_{\beta \gamma}(\ell', \ell'') u_\gamma(\ell'') , \]  

(20)

with the eigenmodes being given as the solutions to the (3N-dimensional) determinantal condition \( |1 - G_0 V| = 0 \) as written in an obvious notation.

For the simplest case of just a change in mass at the defect site, Eq. (20) requires the three components of the defect displacement vector to obey

\[
\begin{align*}
    u_x(0) &= -(M - M')\omega'^2 g_{xx}(\omega'; 0, 0) u_x(0) , \\
    u_y(0) &= -(M - M')\omega'^2 g_{yy}(\omega'; 0, 0) u_y(0) , \\
    u_z(0) &= -(M - M')\omega'^2 g_{zz}(\omega'; 0, 0) u_z(0) ,
\end{align*}
\]

(21)

where the cubic symmetry of the host lattice requires that \( g_{xx}(\omega'; 0, 0) \), \( g_{yy}(\omega'; 0, 0) \) and \( g_{zz}(\omega'; 0, 0) \) all be equal to each other, and thus that each one of them be given as

\[
g_{xx}(\omega'; 0, 0) = \frac{1}{NM} \sum_{k,j} \sigma_x^{ij}(k) \sigma_x^{ij}(k) = \frac{1}{3} \left[ g_{xx}(\omega'; 0, 0) + g_{yy}(\omega'; 0, 0) + g_{zz}(\omega'; 0, 0) \right]
\]

\[
= \frac{1}{3NM} \sum_{k,j} \frac{[\sigma_x^{ij}(k) \sigma_x^{ij}(k) + \sigma_y^{ij}(k) \sigma_y^{ij}(k) + \sigma_z^{ij}(k) \sigma_z^{ij}(k)]}{[\omega_x^{ij}(k) - \omega'^2]}
\]

\[
= \frac{1}{3NM} \sum_{k,j} \frac{1}{[\omega_x^{ij}(k) - \omega'^2]}
\]

\[
= \frac{1}{NM} \sum_{i=1}^{N} \frac{1}{(\omega_i^2 - \omega'^2)} = \frac{1}{M} \int_{\omega_{\text{max}}^2}^{\omega^2} d\omega^2 \frac{\nu(\omega^2)}{(\omega^2 - \omega'^2)}
\]

(22)

as now summed over \( N \) threefold degenerate pure crystal eigenmodes \( \omega_i^2 \). And with the determinantal condition then being given by \( |1 - G_0 V| = (M'/M)^3[1 - \rho(\omega'^2)S(\omega'^2)]^2(1)^{3N-3} = 0 \), in the mass defect case the perturbed simple, body-centered and face-centered cubic crystal modes are thus given as the solutions to the familiar

\[ 1 - \rho(\omega'^2)S(\omega'^2) = 0 , \]  

(23)

where \( \rho(\omega'^2) \) is given by

\[ \rho(\omega'^2) = \frac{M}{M'} - 1 \]  

(24)

and \( S(\omega'^2) \) is given by

\[
S(\omega'^2) = -1 - M\omega'^2 g_{xx}(\omega'; 0, 0) = \frac{1}{N} \sum_{i=1}^{N} \frac{\omega_i^2}{(\omega'^2 - \omega_i^2)} ,
\]

(25)
FIG. 1: Plot of $S(\omega^2)$ versus $\omega^2$. The line $AB$ corresponds to the value of $1/\rho(\omega^2)$ in a typical lighter defect case with $M' < M$, while the line $CD$ corresponds to the $1/\rho(\omega^2)$ associated with an infinitely heavy defect case.

as summed over the $N$ eigenfrequencies $\omega_i^2$ of the pure crystal.

For our purposes here we note that the function $S(\omega^2)$ is divergent at every pure crystal frequency, to thus contain the set of $N$ asymptotes indicated in Fig. (1). $S(\omega^2)$ starts out equal to minus one at $\omega^2 = 0$, and decreases to minus infinity at the first asymptote, with $S(\omega^2)$ thus having no zero below the lowest pure crystal band mode. Since the derivative of $S(\omega^2)$, viz.

$$
\frac{dS(\omega^2)}{d\omega^2} = -\frac{1}{N} \sum_{i=1}^{N} \frac{\omega_i^2}{(\omega^2 - \omega_i^2)^2} 
$$

is negative definite, the function $S(\omega^2)$ falls monotonically between asymptotes, to thus have a zero somewhere on the $OX$ axis between any two adjacent pure crystal modes, while
beyond the last pure crystal frequency eigenmode at $\omega_{\text{max}}^2$. The function $S(\omega^2)$ is positive, falling to zero at $\omega^2 = \infty$. As introduced, the function $S(\omega^2)$ thus has $N - 1$ zeroes inside the pure crystal phonon band and one zero outside.

In consequence of this structure for $S(\omega^2)$, we see that the curve $1/\rho(\omega^2) = M'/\{M - M'\}$ will intercept the $S(\omega^2)$ curve $N$ times no matter what the value of $M'/M\sqrt{2}$ with Eq. (21) thus always having the same number of mode solutions as the pure crystal (viz. $N$ solutions for each of the three $u_x(0)$, $u_y(0)$ and $u_z(0)$ sectors of Eq. (21)), with Eq. (23) and the threefold degeneracy of Eq. (21) thus accounting for the complete spectrum of eigenfrequencies of the perturbed crystal. When $M'$ is less than $M$ (typical intercept $AB$) the $N$ modes which satisfy Eq. (23) are all shifted to higher frequency compared to their pure crystal counterparts, with both sides of Eq. (9) thus consistently being positive. Similarly, when $M'$ is greater than $M$ (typical intercept $CD$) the $N$ modes which satisfy Eq. (23) are all shifted to lower frequency compared to their pure crystal counterparts, with both sides of Eq. (9) then consistently being negative. Finally, once the eigenfrequencies have been found, a return to Eq. (5) will then allow a determination of all of the $3N$ displacements $u_\alpha(\ell)$ in every mode, to then completely specify the crystal displacements of the perturbed crystal.

Since the zeroes of $S(\omega^2)$ other than the final one at $\omega^2 = \infty$ lie between adjacent asymptotes, an initial glance at Fig. (1) would suggest that when shifted upwards, each of $(N - 1)$ modes other than the mode at the band maximum itself could be shifted upward as far as the immediate next asymptote, to suggest that the quantity $\sum_{i=1}^{N-1}[\omega_i^2 - \omega_1^2]$ could be as large as $\omega_{\text{max}}^2 - \omega_1^2 \sim \omega_{\text{max}}^2$ (the net shift between the highest and lowest in-band frequency modes). However, we will now show that in fact the net shift must be much less than this, an outcome that will sharply constrain the implications of Eq. (15). To this end we need to obtain a bound on the sum of the in-band zeroes, $x_i^2$, of $S(\omega^2)$, and note that since the quantity $S(\omega^2)\Pi_i(\omega^2 - \omega_i^2)$ is an $N - 1$ dimensional polynomial in $\omega^2$, the sum of its zeroes can immediately be given as

$$\sum_{i=1}^{N-1} x_i^2 = \sum_{i=1}^{N} \omega_i^2 - \frac{\sum_{i=1}^{N} \omega_i^4}{\sum_{i=1}^{N} \omega_i^2} = \sum_{i=1}^{N} \omega_i^2 - \frac{\mu_4}{\mu_2} ,$$

where

$$\mu_n = \frac{1}{N} \sum_{i=1}^{N} \omega_i^n .$$

(27)

(28)
On defining the positive semi-definite quantity $\alpha$ via

$$\mu_4 - \mu_2^2 = \langle \omega^4 \rangle - \langle \omega^2 \rangle^2 = \langle [\omega^2 - \langle \omega^2 \rangle]^2 \rangle = \alpha \ ,$$

through use of Eq. (3) we then obtain

$$\sum_{i=1}^{N-1} [x_i^2 - \omega_i^2] = \omega_{\max}^2 - \mu_2 - \frac{\alpha}{\mu_2} = \omega_{\max}^2 - \frac{A_{xx}(0,0)}{M} - \frac{\alpha}{\mu_2} \ .$$

(30)

Now in general it can be shown that the quantity $A_{xx}(0,0)/M$ is related to $\omega_{\max}^2$ according to

$$\omega_{\max}^2 = \frac{2A_{xx}(0,0)(1+Z)}{M}$$

(31)

where the quantity $Z$ is given by

$$Z = \frac{\sum_{\ell} A_{xx}(0,\ell)}{A_{xx}(0,0)}$$

(32)

as summed over the even neighbors of the $\ell = 0$ site alone. With this sum only beginning with the second nearest neighbors, to good approximation we can neglect the contribution of $Z$, and can thus rewrite Eq. (30) as

$$\sum_{i=1}^{N-1} [x_i^2 - \omega_i^2] = \frac{\omega_{\max}^2}{2} - \frac{\alpha}{\mu_2} \ .$$

(33)

With $\alpha$ being positive, we thus see that the quantity $\sum_{i=1}^{N-1}[x_i^2 - \omega_i^2]$ cannot be larger than $\omega_{\max}^2/2$, with the zeroes of $S(\omega'^2)$ on average being no more than midway between adjacent asymptotes rather than close to the immediately adjacent higher ones.

Further support for this result can be obtained by considering Eq. (23) in the infinitely heavy defect limit in which $M' = \infty$, $\rho(\omega'^2) = -1$, corresponding to the line $CD$ in Fig. (1). In this case Eq. (9) reduces to

$$\sum_{i=1}^{N} [\omega_i'^2 - \omega_i^2] = -\frac{A_{xx}(0,0)}{M} = -\frac{\omega_{\max}^2}{2} \ ,$$

(34)

with the structure of Fig. (1) then yielding

$$-\frac{\omega_{\max}^2}{2} = 0 + (\omega_2'^2 - \omega_1^2) + (\omega_3'^2 - \omega_2^2) + ... - \omega_{\max}^2 > \sum_{i=1}^{N-1} [x_i^2 - \omega_i^2] - \omega_{\max}^2 \ ,$$

(35)

from which the bound

$$\sum_{i=1}^{N-1} [x_i^2 - \omega_i^2] < \frac{\omega_{\max}^2}{2}$$

(36)
then follows.

Having now established the bound on the zeroes of \( S(\omega'^2) \) which is given in Eqs. (33) and (36), we now note that for the pure mass defect case Eq. (9) requires that

\[
\sum_{i=1}^{N-1} [\omega_i^2 - \omega_i^2] + \omega_{\text{max}}^2 - \omega_{\text{max}}^2 = \frac{A_{xx}(0,0)}{M'} - \frac{A_{xx}(0,0)}{M},
\]

(37)

where \( \omega_{\text{max}}^2 \) is the largest shifted frequency. Since in the \( M' < M \) case the in-band modes have to lie to the left of the \( x_i^2 \) zeroes of \( S(\omega'^2) \), the in-band \( \sum_{i=1}^{N-1} [\omega_i^2 - \omega_i^2] \) can then never be any larger than \( \omega_{\text{max}}^2/2 \sim A_{xx}(0,0)/M \). Consequently, no matter what the value of \( \alpha \) of Eq. (29) (a quantity which varies from one crystal to the next), and no matter which particular crystal one might choose, if \( M' \) is less than \( M/2 \), the largest perturbed eigenfrequency \( \omega_{\text{max}}^2 \) would have to be larger than the pure crystal maximum \( \omega_{\text{max}}^2 \), and not only would it then lie beyond the pure crystal phonon band, once \( M' \) has been reduced enough to move the in-band modes as far to higher frequency as they are able to go (viz. to the zeroes of \( S(\omega'^2) \)), further reduction in \( M' \) would then cause \( \omega_{\text{max}}^2 \) to move further and further away from the band maximum. Hence while the condition \( M' < M \) is a necessary condition for producing a mode beyond the band maximum in simple, body-centered and face-centered cubic crystals, it is \( M' < M/2 \) which is the sufficient one, a result previously obtained by entirely different means.

IV. THE FORCE-CONSTANT CHANGE CASE

Because of Newton’s third law of motion, in the presence of force-constant changes the matrix \( V_{\alpha\beta}(\ell, \ell') \) of Eq. (5) will necessarily involve more atoms than just the one at the defect site and the problem is essentially intractable other than numerically if \( V_{\alpha\beta}(\ell, \ell') \) extends beyond the nearest neighbors of the defect. Moreover, even in the event that one restricts the force-constant changes to the defect and its nearest neighbors alone, for the simple cubic, body-centered cubic and face-centered cubic crystals the defect and its nearest neighbors respectively consist of a cluster of seven, nine and thirteen atoms, making \( V_{\alpha\beta}(\ell, \ell') \) 21-, 27- and 39-dimensional in those respective cases. Fortunately, because of the cubic crystal \( O_h \) symmetry at the defect site the \( V_{\alpha\beta}(\ell, \ell') \) matrix can be block diagonalized in the irreducible representations of the octahedral group, with typical decompositions

\[
\Gamma_{\text{sc}} = A_{1g} + E_g + F_{1g} + F_{2g} + 3F_{1u} + F_{2u}
\]
\[ \Gamma_{\text{bcc}} = A_{1g} + E_g + F_{1g} + 2F_{2g} + A_{2u} + E_u + 3F_{1u} + F_{2u} \]
\[ \Gamma_{\text{fcc}} = A_{1g} + A_{2g} + 2E_g + 2F_{1g} + 2F_{2g} + A_{2u} + E_u + 4F_{1u} + 2F_{2u} \]  

(38)

Since the displacement of the defect atom itself transforms as a 3-dimensional vector, the defect displacements must be located entirely in the \( F_{1u} \) modes, with all of the other relevant \( O_h \) irreducible representations being built solely out of appropriate linear combinations of the displacements of the nearest neighbors of the defect. As such the defect displacement appears in 3-dimensional, 3-dimensional and 4-dimensional representations in the three respective cubic crystal cases, with the defect sector thus leading to respective 3-dimensional, 3-dimensional and 4-dimensional blocks in Eq. (20) each one of which (just as in Eq. (21)) is threefold degenerate. While these blocks are still quite complicated in the case of central force-constants alone (as well as in some other specific cases such as isotropic force-constant crystals which we discuss in Sec. V) the determinantal condition \( |1 - G_0 V| = 0 \) associated with the \( F_{1u} \) block can be treated completely analytically, with both the body-centered cubic and face-centered cubic crystal eigenmodes being found to obey precisely the same Eq. (23) as before, viz.

\[ 1 - \rho(\omega^2) S(\omega^2) = 0 \]  

(39)

save only that this time \( \rho(\omega^2) \) is given by

\[ \rho(\omega^2) = \frac{M}{M'} - 1 + \frac{2\omega^2}{\omega_{\text{max}}^2} \left[ 1 - \frac{A_{xx}(0,0)}{A'_{xx}(0,0)} \right] \]  

(40)

For our purposes here we note that since the function \( S(\omega^2) \) is the same one as discussed previously, it still has the asymptote structure shown in Fig. (1). To determine the number of times the function \( 1/\rho(\omega^2) \) will intersect \( S(\omega^2) \) requires considering each possible combination of mass and force-constant changes in Eq. (40) separately. For \( M' \leq M \) and \( A'_{xx}(0,0) > A_{xx}(0,0) \) the quantity \( 1/\rho(\omega^2) \) is everywhere positive yielding the typical curve AX in Fig. (2) with its \( N \) intercepts (the point A is at \( +\infty \) when \( M' = M \)), with each crystal eigenmode having been shifted upwards to a higher frequency. For \( M' \geq M \) and \( A'_{xx}(0,0) < A_{xx}(0,0) \) the quantity \( 1/\rho(\omega^2) \) is everywhere less than or equal to \(-1\) yielding the typical curve EX in Fig. (2) with its \( N \) intercepts (the point E is at \(-\infty \) when \( M' = M \)), with each crystal eigenmode having been shifted downwards. For \( M' < M \) but \( A'_{xx}(0,0) < A_{xx}(0,0) \) the quantity \( 1/\rho(\omega^2) \) has to diverge somewhere, yielding the typical curve AGHX in Fig. (2) with its \( N \) intercepts if the divergence in \( 1/\rho(\omega^2) \) falls inside the
FIG. 2: Plot of $S(\omega^2)$ versus $\omega^2$. The line $AX$ corresponds to the value of $1/\rho(\omega^2)$ associated with a defect with $M' < M$ and $A'_{xx}(0,0) > A_{xx}(0,0)$, the line $EX$ corresponds to the $1/\rho(\omega^2)$ associated with $M' > M$ and $A'_{xx}(0,0) < A_{xx}(0,0)$, the curve $AGHX$ corresponds to the $1/\rho(\omega^2)$ associated with $M' < M$ and $A'_{xx}(0,0) < A_{xx}(0,0)$, and the curve $EJKX$ corresponds to the $1/\rho(\omega^2)$ associated with $M' > M$ and $A'_{xx}(0,0) > A_{xx}(0,0)$.

band,\textsuperscript{12} and analogously also yielding $N$ intercepts if the divergence is outside the band (not shown).\textsuperscript{13} Finally, for $M' > M$ and $A'_{xx}(0,0) > A_{xx}(0,0)$ there will again be $N$ intercepts (typical curve $EJKX$).\textsuperscript{14}

As we thus see, no matter what particular values $M'/M$ and $A'_{xx}(0,0)/A_{xx}(0,0)$ might actually take, in all cases there are precisely $N$ intercepts, and thus precisely $3N$ eigenmodes in the $F_{1u}$ sector. However, since this exhausts the number of degrees of freedom for the problem, Eq. [20] cannot generate any further eigenmode solutions. Consequently, none
of the determinantal conditions associated with any of the other irreducible octahedral representations in the cluster can yield eigenmode solutions, though just as with all the rest of the atoms in the crystal, the \( u_\alpha(\ell) \) displacements associated with these other irreducible representations will, via Eq. (15), still participate in the \( F_{1u} \) mode oscillations.

With the eigenmodes associated with the \( F_{1u} \) sector thus exhausting the eigenspectrum, it will be these modes alone which will contribute to the trace condition of Eq. (15). And with the zeroes of \( S(\omega^2) \) still obeying Eq. (33), for a defect with \( M' = M \) in a crystal with central force-constants alone and eigenmodes which then obey

\[
\sum_{i=1}^{N} [\omega_i'^2 - \omega_i^2] = \sum_{i=1}^{N-1} [\omega_i'^2 - \omega_i^2] + \omega_{\text{max}}^2 - \omega_{\text{max}}^2 = \frac{2A'_{xx}(0,0)}{M} - \frac{2A_{xx}(0,0)}{M},
\]

and in-band modes which can never be shifted up beyond the immediate next zeroes of \( S(\omega^2) \) (typical curve AX in Fig. (2)), we can conclude that no matter which central force-constant crystal we may choose, there will definitely be a localized mode if \( A'_{xx}(0,0)/A_{xx}(0,0) \) is greater than \( 3/2 \), with this condition thus being sufficient to guarantee localized modes in nearest-neighbor central force-constant cubic crystals when there is no change in mass.\(^\text{15}\)

\section*{V. EXTENSION TO MORE GENERAL SITUATIONS}

To extend these results to other cases, we need to consider both non-central force-constants and go beyond nearest neighbors. As regards the issue of non-central force-constants, we note that within the nearest-neighbor approximation a complete and exact general relation for locating the perturbed crystal \( F_{1u} \) modes has recently actually been obtained.\(^\text{16}\) Specifically, it was found for the body-centered cubic crystal (and thus by extension for the face-centered cubic crystal as well since it is the reciprocal lattice of the body-centered cubic and we work in the harmonic approximation where momentum and position are treated equivalently)\(^\text{17}\) that the general determinantal condition \( |1 - G_0 V| = 0 \) in the perturbed \( F_{1u} \) mode sector can be written as \( |1 - G_0 V| = \Delta^3 = 0 \) where the nearest-neighbor, arbitrary force-constant \( \Delta \) is given as

\[
\Delta = \frac{M'}{M} \left\{ \frac{A'_{xx}(0,0)}{A_{xx}(0,0)} \left[ 1 - \rho(\omega^2) S(\omega^2) \right] \left[ 1 - \hat{R} \right] - \mu \hat{R} \left[ S(\omega^2) \left( 1 - \frac{M}{M'} \right) + 1 \right] \right\},
\]

expressed here in terms of the two quantities \( \rho(\omega^2) \) and \( S(\omega^2) \) which were given previously and two additional quantities \( \mu \) and \( \hat{R} \) which are needed now. To define these two additional
quantities one needs to introduce the pure crystal lattice Green’s function combination

\[ R = g_{xy}(\omega'; \ell = 0, \ell' = 222) + g_{xy}(\omega'; \ell = 0, \ell' = 220) \]

\[ = \frac{1}{NM} \sum_{\mathbf{k},j} \sigma^x_j(\mathbf{k}) \sigma^y_j(\mathbf{k}) \left[ e^{i\mathbf{k} \cdot \mathbf{R}(222)} + e^{i\mathbf{k} \cdot \mathbf{R}(220)} \right], \tag{43} \]

and in terms of the interatomic potential \( \phi(r) \) between two pure crystal nearest neighbors and the interatomic potential \( \hat{\phi}(r) \) between the defect and a host crystal nearest neighbor, define pure and impure lattice force-constants via

\[
A_{\alpha\beta}(0, 111) = \begin{pmatrix} \alpha + \beta & \alpha & \alpha \\ \alpha & \alpha + \beta & \alpha \\ \alpha & \alpha & \alpha + \beta \end{pmatrix}, \quad A'_{\alpha\beta}(0, 111) = \begin{pmatrix} \hat{\alpha} + \hat{\beta} & \hat{\alpha} & \hat{\alpha} \\ \hat{\alpha} & \hat{\alpha} + \hat{\beta} & \hat{\alpha} \\ \hat{\alpha} & \hat{\alpha} & \hat{\alpha} + \hat{\beta} \end{pmatrix},
\]

\[ A_{xx}(0, 0) = -8(\alpha + \beta), \quad A'_{xx}(0, 0) = -8(\hat{\alpha} + \hat{\beta}), \tag{44} \]

where

\[
\alpha = -\frac{1}{3} \left( \phi''(r) - \frac{\phi'(r)}{r} \right), \quad \beta = -\frac{\phi'(r)}{r},
\]

\[
\hat{\alpha} = -\frac{1}{3} \left( \hat{\phi}''(r) - \frac{\hat{\phi}'(r)}{r} \right), \quad \hat{\beta} = -\frac{\hat{\phi}'(r)}{r} \tag{45} \]

(as evaluated at the pure crystal nearest-neighbor equilibrium separation \( r \)), with \( \hat{R}, \mu \) and \( \mu\hat{R} \) then being given by

\[
\hat{R} = \frac{(\alpha + \beta)(\beta - \hat{\beta})(3\alpha - 3\hat{\alpha} + \beta - \hat{\beta})R}{\alpha(\alpha - \hat{\alpha} + \beta - \hat{\beta})},
\]

\[
\mu = \frac{2(\alpha\hat{\beta} - \beta\hat{\alpha})^2}{(\alpha + \beta)^2(\beta - \hat{\beta})(3\alpha - 3\hat{\alpha} + \beta - \hat{\beta})},
\]

\[
\mu\hat{R} = \frac{2(\alpha\hat{\beta} - \beta\hat{\alpha})^2R}{\alpha(\alpha + \beta)(\alpha - \hat{\alpha} + \beta - \hat{\beta})}. \tag{46} \]

Equation (42) is not only a very compact relation (it only requires knowledge of two pure crystal Green’s functions combinations, viz. \( g_{xx}(\omega'; 0, 0) \) and \( R \)), but it additionally reduces to the previous condition given in Eq. (39) whenever \( \mu\hat{R} \) is zero. Now while the quantity \( \mu\hat{R} \) would vanish when \( \beta = \hat{\beta} = 0 \), viz. the previously discussed central force-constant case, it would also vanish when \( \alpha = \hat{\alpha} = 0 \), viz. the isotropic force-constant case, and also whenever \( \hat{\alpha}/\alpha \) and \( \hat{\beta}/\beta \) are equal, viz. in the mixed case in which the fractional changes in the central and isotropic components of the force-constants are equal to each other, with
\( A'_{xx}(0,0)/A_{xx}(0,0) = (\hat{\alpha} + \hat{\beta})/(\alpha + \beta) \) being equal to \( \hat{\alpha}/\alpha = \hat{\beta}/\beta \) in all such cases. For all of these cases then, the condition \( A'_{xx}(0,0)/A_{xx}(0,0) > 3/2 \) is sufficient to guarantee localized modes in nearest-neighbor crystals when there is no change in mass.

To treat cases where the quantity \( \mu \) is not zero is not as straightforward, since unlike the \( g_{xx}(\omega';0,0) \) Green’s function, the \( R \) combination cannot be reduced to a sum solely over pure crystal eigenfrequencies as the polarization vectors cannot readily be eliminated from Eq. (43), with Eq. (42) not obviously being reducible to an expression which only involves the pure crystal density of states \( \nu(\omega^2) \). However, despite this, it is still possible to extract a sufficiency condition for localized modes. Specifically, even though \( R \) does involve the pure crystal polarization vectors, as can be seen from Eq. (43), its poles, and thus its asymptotes, are nonetheless precisely the same as those possessed by \( g_{xx}(\omega';0,0) \), with the asymptotes of \( \Delta \) then being none other than the asymptotes of \( S(\omega'^2) \), i.e. none other than the ones exhibited in Fig. (2). To determine what happens when we take \( \mu \) to be non-zero then, we need to monitor how the intercept structure displayed in Fig. (2) gets modified as we slowly switch \( \mu \) on.

To explicitly see what happens when we switch \( \mu \) on, it is instructive to first return to the central force-constant case, and consider the situation in which we start with some arbitrary \( A'_{xx}(0,0) \) which is bigger than \( A_{xx}(0,0) \) and some initial \( M' \) which is equal to \( M \), and them slowly start to increase \( M' \). We thus start with a \( \rho(\omega'^2) \) which is equal to \( (2\omega'^2/\omega^2_{\text{max}})[1 - A_{xx}(0,0)/A'_{xx}(0,0)] \), and thus with a \( 1/\rho(\omega'^2) \) which is everywhere positive and infinite at \( \omega'^2 = 0 \) (viz. curve AX of Fig. (3)). When we now allow \( M' \) to be just a little bit bigger than \( M \), \( \rho(\omega'^2) \) will now take small negative values at the smallest \( \omega'^2 \), and then quickly revert back to being positive again as \( \omega'^2 \) is increased. Consequently, \( 1/\rho(\omega'^2) \) will now take large negative values at the smallest \( \omega'^2 \), while also quickly reverting back to being positive again as \( \omega'^2 \) is increased (viz. curve EJKX of Fig. (3)). As can therefore be seen from Fig. (3), the net effect of letting \( M' \) be just a little bit bigger than \( M \) is that rather than increasing, the frequency of the lowest mode is instead decreased. Now since the trace condition of Eq. (15) holds for both of these two cases, we can write a trace condition for the difference between the two cases, viz.

\[
\sum_{i=1}^{N} [\omega'^2_i(M' > M) - \omega'^2_i(M' = M)] = \frac{A'_{xx}(0,0)}{M'} - \frac{A'_{xx}(0,0)}{M} \tag{47}
\]

with the net effect of a small difference between \( M' \) and \( M \) on the right-hand side of Eq.
FIG. 3: Plot of $S(\omega'^2)$ versus $\omega'^2$. The line AX corresponds to the value of $1/\rho(\omega'^2)$ associated with a defect with $M' = M$ and $A'_xx(0,0) > A_{xx}(0,0)$, and the curve EJKX corresponds to the $1/\rho(\omega'^2)$ associated with the same $A'_xx(0,0) > A_{xx}(0,0)$ but with $M'$ slightly larger than $M$.

(47) entailing a small net total shift on the left-hand side, and thus a net shift in each individual eigenmode of order $1/N$ of the shift on the right-hand side. Moreover, with the change in the right-hand side of Eq. (47) being continuous, the change on the left-hand side must be continuous as well. Consequently, with the transition from curve AX to curve EJKX needing to also be continuous, the lowest impure crystal eigenfrequency must then have continuously traversed the lowest lying of the pure crystal asymptotes on its way, with the lowest lying pure crystal eigenfrequency then being an impure crystal eigenfrequency at the point at which the asymptote is reached. Since $S(\omega'^2)$ is infinite at any pure crystal eigenfrequency, for such a pure crystal eigenfrequency to also be a mode of the impure
crystal, \(1/\rho(\omega^2)\) must equally be infinite at the pure crystal eigenfrequency, and it indeed is in this particular case since an increase in mass and an increase in force-constant act oppositely in \(\rho(\omega^2)\), to thereby allow \(\rho(\omega^2)\) to indeed vanish at the lowest pure crystal eigenfrequency.

An alternate way to modify the curve \(AX\) is not to change the mass at the defect site at all, but to keep \(M'\) fixed at \(M\) and to instead start to allow an \(A'_{xx}(0,0)\) which is already bigger than \(A_{xx}(0,0)\) to get even bigger. Such an increase will cause all of the impure crystal eigenfrequencies of Fig. (3) to increase, but will never permit any of them to ever reach or traverse the next immediate pure crystal asymptote since a \(\rho(\omega^2) = (2\omega^2/\omega_{\text{max}}^2)[1 - A_{xx}(0,0)/A'_{xx}(0,0)\] which only involves force-constant changes can never vanish at any non-zero \(\omega^2\). We thus recognize two possible options as we start to vary parameters, namely that an impure crystal eigenmode can cross a pure crystal asymptote if \(\rho(\omega^2)\) has a zero there, or cannot do so if \(\rho(\omega^2)\) has no zero. If we thus picture the \(N\) asymptotes in Fig. (3) as dividing the \(\omega^2 > 0\) region into \(N+1\) compartments (\(N-1\) of which lie between pure crystal eigenfrequencies, with the other two lying below the lowest pure crystal eigenfrequency and above the largest one), we see that small changes in parameters can cause the locations of eigenmodes to either move slightly within any given compartment or to cross into an adjacent one, doing so in either case without radically altering the value of the total in-band difference \(\sum_{i=1}^{N-1}[^{\omega_i^2} - \omega_i^2]\) contained on the left-hand side of Eq. (15).

To see how this analysis pertains to non-central force-constant crystals with non-zero \(\mu\), we need to determine whether or not switching on \(\mu\) can cause modes to change compartments. To make such a determination, we note that according to Eq. (42), in the event of no mass change at the defect site, the eigenfrequencies associated with a general force-constant change in a nearest-neighbor crystal are given as the solutions to

\[
S(\omega^2) = \frac{1}{\rho(\omega^2)} \left[ 1 - \frac{A_{xx}(0,0)\mu\hat{R}}{A'_{xx}(0,0)[1 - \hat{R}]} \right] = \frac{\omega_{\text{max}}^2A_{xx}(0,0)}{2\omega^2[A'_{xx}(0,0) - A_{xx}(0,0)]} \left[ \frac{A'_{xx}(0,0)}{A_{xx}(0,0)} - \frac{\mu\hat{R}}{[1 - \hat{R}]} \right].
\]

Since the pure crystal Green’s function \(\hat{R}\) has the same set of asymptotes as \(S(\omega^2)\), whenever \(S(\omega^2)\) diverges, \(\hat{R}\) will do so also. However since \(\hat{R}/(1 - \hat{R})\) is finite at frequencies at which \(\hat{R}\) is infinite, we see from Eq. (48) that in the force-constant change case no matter what value we allow for \(\mu\), the perturbed eigenmodes are unable to ever leave their respective

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frequency compartments.

Despite this though, since \( \hat{R} \) does have asymptotes, it can be expected that \( \hat{R} \) would change sign on its way between adjacent asymptotes (though it could drop to some minimum and then go back to the next asymptote without ever changing sign), and thus we can anticpate that there will be some frequencies at which \( \hat{R} \) can take an assigned value equal to one. At such frequencies the right-hand side of Eq. (48) would then diverge, and since \( \hat{R} \) (and thus \( S(\omega^2) \)) is not itself diverging at those points, such points would not be solutions to Eq. (48), but would instead be points between pure crystal eigenfrequencies at which the right-hand side of Eq. (48) would undergo a discontinuity. Now while such a discontinuity cannot take the eigenmode out of its frequency compartment, if the discontinuity is to have any effect at all, its only possible one would be to move the eigenmode out of the \( F_{1u} \) mode sector determinant altogether. Specifically, unlike the case of a perturbation of a central force-constant crystal where the \( F_{1u} \) sector determinant accounts for all of the perturbed crystal eigenmodes, once we introduce non-central force-constants we have to consider the possibility that eigenmodes could move into the determinantal blocks of \( |1 - G_0 V| \) which are associated with the other irreducible octahedral representations of the cluster as given in Eq. (38). However, recalling that all such eigenmodes are also controlled by Eq. (20), and recalling that all the pure lattice Green’s functions which appear in Eq. (20) have the common asymptote structure associated with Eq. (18) and thus a compartment structure identical to that of \( S(\omega^2) \) itself, we see that even if the eigenmodes do migrate into different irreducible \( O_h \) sectors, since the left-hand side of the trace condition of Eq. (15) is a sum over all of the modes of the crystal and not just over those associated with the \( F_{1u} \) sector alone (a sum that thus includes the entire cluster of Eq. (38) anyway), and since we are only making a small change on the right-hand side of Eq. (15), when the eigenmodes do move to other irreducible representations, they can still only move to equivalent compartments with the same frequency ranges as the ones they started in. As such then, independent of which specific sector the modes actually find themselves in after crossing any \( \hat{R} = 1 \) discontinuity, they could only cross into the same frequency compartments they were already in.

However, once the eigenmodes have moved out of the \( F_{1u} \) sector, they would then be in some other irreducible \( O_h \) representation where the \( F_{1u} \) mode Eq. (48) would not apply. Hence in these other representations additional changes in \( \mu \) (beyond the ones needed to first bring the force-constant dependent \( \hat{R} \) of Eq. (46) to one) could perhaps then move
the eigenmodes into adjacent compartments. However, for that to happen the eigenmodes would have to cross the pure crystal asymptotes, with those particular eigenmodes then needing to be common eigenmodes of both the pure and impure crystals at the requisite value of $\mu$. However, in order for an eigenmode to be an eigenmode at all, the eigenmode would need to be at a zero of the full $|1 - G_0V|$, i.e. it would not only need to be at a zero of the determinantal block of some particular irreducible sector, but also to not give an infinite value to any of the other blocks which multiply the given determinantal block of interest in the full $|1 - G_0V|$ of the full crystal. However, inspection of the $F_{1u}$ mode $\Delta$ of Eq. (42) shows that it is actually divergent at a pure crystal eigenmode (where it diverges as $S(\omega^2)\hat{R}$), and thus once there is no asymptote crossing in the $F_{1u}$ mode sector, there cannot be any in any other irreducible representation either. Thus regardless of whether or not the $\hat{R} = 1$ discontinuities take the impure crystal eigenmodes out of the $F_{1u}$ sector, the modes cannot leave the frequency compartments they were already in when $\mu$ was zero. Hence if a mode already was in the compartment which lies beyond the pure crystal maximum eigenfrequency when the parameter $\mu$ was equal to zero, the mode will remain beyond the band no matter how $\mu$ might then vary. Moreover the in-band modes will remain in which ever compartments they had been in when $\mu$ was zero.

We thus recognize two specific consequences of switching $\mu$ on, namely that modes have to stay within their respective $\mu = 0$ compartments, but that they are no longer prevented from traversing the zeroes of $S(\omega^2)$. Thus suppose we start off with a central force-constant crystal with $\mu = 0$ and $M' = M$, and with $A'_{xx}(0,0)/A_{xx}(0,0) = (\hat{\alpha} + \hat{\beta})/(\alpha + \beta) = \hat{\alpha}/\alpha = \hat{\beta}/\beta$ conveniently set right at the threshold value of $3/2$, and then slowly switch $\mu$ on. The in-band modes could now move up or down, moving to no lower than the immediately previous pure crystal eigenmodes (net shift of the in-band mode $\sum_{i=1}^{N-1} [\omega_i^2 - \omega_t^2]$ of down to $-\omega_{\text{max}}^2$), or moving upwards possibly as far as the next immediate pure crystal asymptotes (net shift of up to $\omega_{\text{max}}^2$). Then regardless of what value $\mu$ may actually take and regardless of which particular irreducible representation any specific eigenmode may actually lie in, Eq. (41) will nonetheless still hold when there is no mass change since the trace is taken over the entire set of irreducible $O_h$ representations and not just over the $F_{1u}$ mode. On recalling that $\omega_{\text{max}}^2 = 2A_{xx}(0,0)/M$ for a nearest-neighbor crystal, we see that the necessary condition that $\omega_{\text{max}}^2 - \omega_t^2$ be positive is given by having the in-band modes move down as far as they possibly can, to thereby require $A'_{xx}(0,0)$ to be positive, while the sufficient condition is
given by having the in-band modes move up by as far as they possibly can, viz.

$$\omega'^2_{\text{max}} - \omega^2_{\text{max}} \geq \frac{2A'_{xx}(0,0)}{M} - \frac{4A_{xx}(0,0)}{M},$$

with the condition that $A'_{xx}(0,0)/A_{xx}(0,0)$ be greater than two thus being sufficient to guarantee the generation of localized modes by force-constant changes alone in an arbitrary nearest-neighbor cubic crystal.

To proceed beyond nearest neighbors is also not straightforward as no exact analog of Eqs. (39) and (42) is currently known. (For the case of second-nearest neighbors, the second-neighbor generalization of the irreducible decomposition of Eq. (38) has been used to bring the problem to a reasonably manageable form.) However, in the event of non-nearest neighbor force-constants, even though the cluster required for the matrix $V_{\alpha\beta}(\ell', \ell'')$ in Eq. would be much larger, and even though more pure lattice Green’s functions would be required, nonetheless every single one of these Green’s functions would still have exactly the same asymptote and compartment structure as $S(\omega'^2)$. Thus if we start at the eigenmodes of a general nearest-neighbor crystal with non-zero $\mu$ and $M' = M$ and slowly start to increase the strength of the non-nearest neighbor force-constants (central or otherwise), we would again be constrained by the same set of pure crystal compartments in exactly the same way as before (save that there would be yet more irreducible representations of $O_h$ to migrate to — with all of them also contributing to the left-hand side of the trace condition), to again allow us to infer that even in the most general possible case imaginable (arbitrary central and non-central force-constants and arbitrary number of participating neighbors), in the absence of any change in mass, the condition $A'_{xx}(0,0)/A_{xx}(0,0) > 2$ would still be sufficient to guarantee localized modes.

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5. The force-constants yielded by potentials for which \( \phi'(r) \) is zero when the atoms are in their equilibrium positions are referred to as being central, while those associated with potentials which obey \( \phi'(r)/r = \phi''(r) \) at equilibrium are referred to as being isotropic.

6. Even though \( g_{xx}(\omega';0,0) \) involves a \( 3N \)-dimensional sum on both \( \vec{k} \) and \( j \), the \( \sigma_x^j(\vec{k})\sigma_x^j(\vec{k}) \) term in the expression for \( g_{xx}(\omega';0,0) \) only permits the \( j \) sum to contribute once, since in the basis in which \( D_{\alpha\beta}(\vec{k}) \) is diagonalized we can choose the polarization vectors \( \sigma_x^j(\vec{k}) \) so that only one polarization eigenvector has a non-zero \( x \) component. The function \( g_{xx}(\omega';0,0) \) thus only possesses \( N \) poles, poles then also possessed by \( g_{yy}(\omega';0,0) \) and \( g_{zz}(\omega';0,0) \) as well, with the full \( 3N \) dimensionality of the eigenfrequencies then being recovered via the existence of eigenmode equations for all three of \( u_x(0,0,0) \), \( u_y(0,0,0) \) and \( u_z(0,0,0) \) in Eq. (21). To reflect this our notation here is that any eigenfrequency which appears once in an eigenmode summation from \( i = 1 \) to \( i = N \) will appear three times in an eigenmode summation from \( i = 1 \) to \( i = 3N \).

7. For any choice of the \( M'/M \) ratio, the curve \( 1/\rho(\omega^2) = M'/(M - M') \) is parallel to the \( OX \) axis in Fig. (1), lying above the line \( OX \) when \( M > M' \) and below the line \( CD \) when \( M' > M \), being at \( \pm\infty \) when \( (M - M') = 0 \pm \).

8. An initial glance at Fig. (1) would appear to imply that no matter how close \( M' \) is to \( M \), as long as \( M' \) is less than \( M \) there would be a solution to Eq. (23) beyond the band maximum, with the \( M' \leq M \) condition then being both necessary and sufficient. However if this solution is as close to \( \omega_{\text{max}} \) as \( \omega_{\text{max}} \) itself is to the in-band mode just below it (viz. within \( \omega_{\text{max}}/N \)), the effect of \( M' \) would then be to just slightly displace the band maximum, with the wave function of the mode then being a plane wave which is slightly distorted at the defect site but not at all localized to it; with it only being the condition that \( M' \) be less than \( M/2 \) which guarantees that the mode outside the band necessarily move away from the band edge (i.e. all of the decrease in \( M'/M \) in going from one to 1/2 could be used up entirely in moving the in-band modes to their allowed highest frequency maxima at the zeroes of \( S(\omega^2) \)). In passing we note that in order to
determine whether there is a bona fide mode outside the band which is localized to the defect site, instead of using the trace condition we can also simply solve Eq. 23 directly. However, in doing so we need to allow for the fact that beyond the band edge $S(\omega^2)$ falls precipitously from its asymptote at $\omega^2 = \omega_{\text{max}}^2$. Specifically, since $S(\omega^2)$ is completely well-behaved outside the band and nowhere near infinite in value there, we can define its value at the band maximum as a continuation of its values outside the band. This is equivalent to replacing $S(\omega^2)$ by its principal value $S_P(\omega^2)$ (essentially one half of the sum of the values of $S(\omega^2)$ on the two sides of the asymptote), to then yield an $S_P(\omega_{\text{max}}^2) = S_m$ which is completely finite. With $S(\omega^2)$ decreasing monotonically beyond the band maximum, localized modes will then appear outside the band when $M/M' \geq 1 + 1/S_m$. Since it can be shown on general grounds that for any cubic crystal the quantity $S_m$ defined this way has to lie in the range $1 < S_m < \infty$ (with the particular value that $S_m$ takes in any given crystal being dependent on that crystal), the quantity $1 + 1/S_m$ must lie in the range $1 \leq 1 + 1/S_m \leq 2$, with $M/M' \geq 2$ thus being a sufficient condition for producing a localized mode via a mass defect in any cubic crystal.

9 For the face-centered cubic crystal for instance the normalized four-dimensional basis of displacements for the $4F_{1u}$ mode ($\alpha_0, \alpha_1, \alpha_2, \alpha_3$) is given (in face-centered cubic crystal site notation) by $\alpha_0 = u_x(0, 0, 0), \alpha_1 = (1/2\sqrt{2})[u_x(1, 1, 0) + u_x(1, 1, 1) + u_x(1, 0, 1) + u_x(1, 0, 0) + u_x(1, 0, 0)] = (1/2\sqrt{2})[u_y(0, 1, 0) + u_y(0, 1, 1) + u_y(0, 1, 1) + u_y(0, 1, 0)] = (1/2\sqrt{2})[u_z(1, 0, 0) + u_z(1, 0, 0) + u_z(1, 0, 0) + u_z(1, 0, 0)].$ Degenerate with this basis are two others, one based on $u_y(0, 0, 0)$ and the other on $u_z(0, 0, 0)$.

10 P. D. Mannheim, Phys. Rev. 165, 1011 (1968).

11 P. D. Mannheim and S. S. Cohen, Phys. Rev. B 4, 3748 (1971).

12 On the $AGHX$ curve the loss of an intercept outside the band is compensated for by having an additional intercept in the region where the $1/\rho(\omega^2)$ divergence is located, with all modes below the line $GH$ being shifted upwards, and all modes above the line $GH$ being shifted downwards.

13 After first intercepting the $S(\omega^2)$ curve $N$ times in the positive region before reaching the point where it diverges, on reaching this point the function $1/\rho(\omega^2)$ then crosses into the negative region with no further intercepts then being encountered.

14 On the $EJKX$ curve the absence of any intercept at all in the region where the $1/\rho(\omega^2)$ divergence is located is compensated for by having an additional intercept outside the band,
with all modes below the line $JK$ being shifted downwards, and all modes above the line $JK$ being shifted upwards.

While the curve $AX$ in Fig. (2) shows that it is necessary to have $A'_{xx}(0,0)/A_{xx}(0,0)$ be greater than one in order to shift frequencies upwards, this requirement is only necessary for the production of localized modes by central force-constant changes alone, with it being the requirement that $A'_{xx}(0,0)/A_{xx}(0,0)$ be greater than $3/2$ which is then the sufficient one. (All of the increase in $A'_{xx}(0,0)/A_{xx}(0,0)$ in going from one to $3/2$ could be used up in moving the in-band modes to their allowed highest frequency maxima at the zeroes of $S(\omega')$.) In passing we note that as such, this sufficiency condition initially appears to be at variance with Eq. (39), since Eq. (39) would produce a mode right at the band maximum if $2(1-A_{xx}(0,0)/A'_{xx}(0,0)) = 1/S_m$ and would thus suggest that $A'_{xx}(0,0)/A_{xx}(0,0) > 2$ is needed to produce a mode outside the band since $S_m$ can be small as one. However, while we had indicated earlier that in general $S_m$ could be as small as one, for pure central force-constant cubic crystals it turns out that $S_m$ is actually altogether larger making the $A'_{xx}(0,0)/A_{xx}(0,0) > 3/2$ condition the more powerful. For pure central force-constant crystals $S_m$ is formally found to take the value $S_m = \infty$, a value which however very quickly comes down to order one when there is a small non-central force-constant admixture – for rare gas solids for instance $S_m$ is given by $S_m = 3$ even though there is only a two percent non-central component.

P. D. Mannheim, Arbitrary Force-Constant Changes in the Crystal Impurity Problem, cond-mat/0512188 (submitted to Phys. Rev. B).

While not sought here, one can anticipate a qualitatively similar form for the determinant $\Delta$ in the simple cubic case.

The utility of Eq. (42) is that while the sum over all of the $F_{1u}$ mode basis neighbor sites would initially generate a rather large number of pure lattice Green’s functions in Eq. (20), through repeated use of the Green’s function relations of Eq. (19) one is, in the nearest-neighbor approximation, able to reduce the number of needed Green’s functions to a primitive set of just $g_{xx}(\omega'; 0,0)$ and $R$.

The presence of any analogs of the zeroes of $S(\omega'^2)$ in the other irreducible $O_h$ sectors could prevent the eigenmodes from actually being able to go all the way to the next adjacent asymptotes.

K. Lakatos and J. A. Krumhansl, Phys. Rev. 175, 841 (1968).
To be slightly more precise, in relating $\omega^2_{\text{max}}$ to $2A_{xx}(0,0)/M$ in the non-nearest neighbor case, one should also take into account the factor $Z$ as given in Eq. (31), though we neglect this effect here.