Description of resonant and localized defect vibrations

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The vibrational behavior of crystals with point defects is discussed with particular emphasis on defect-induced resonant and localized modes. A method due to Krumhansl and Matthew is applied to obtain a direct description of the local vibrational properties of the defect. For low-frequency resonances an analytic expression of the Green's function of the defect is derived which has the form of the Green's function of the one-dimensional oscillator with an effective force constant f^{eff}, an effective mass M^{eff}, and a velocity-proportional damping γ. An exact expression for γ in terms of f^{eff} and M^{eff} is given. Simple approximations for f^{eff} and M^{eff} are discussed, which are not based on the calculation of the perfect lattice Green's function. The method is also applied to resonances just below the maximum frequency, which are connected with the formation of localized modes. Furthermore, a simple derivation of upper and lower bounds for the frequencies of localized modes is presented.

I. INTRODUCTION

The dynamics of point defects has been extensively studied by the Green's-function method.[1-3] This method is based on a knowledge of the corresponding ideal lattice Green's functions. However, since in general only numerical results are available for these ideal Green's functions, analytical methods are very useful, especially for high-frequency localized modes[4] and low-frequency resonant modes.

Besides the standard Green's formalism a different treatment of the defect lattice dynamical problem has been proposed by Krumhansl and Matthew[5,6] and others.[7-10] This method is especially useful since it yields a direct description of the local vibrational properties of the defect. Although this description has the simple structure of the Einstein approximation, it is exact and has the further advantage of being applicable also to interstitials with additional degrees of freedom. Based on this method Krumhansl and Matthew[5] have derived qualitative results for localized and resonant modes of point defects with mass or force-constant changes.

The object of this paper is an analytic study of the characteristic defect vibrations introduced by impurities.[11] The application of the method of Krumhansl and Matthew allows us to give a very simple and physically evident description of the local vibrational behavior of the defect.

Resonances in the low-frequency limit are treated in Sec. III. The defect behaves as a simple damped Einstein oscillator, characterized by an effective force constant f^{eff} describing the static response, by an effective mass M^{eff}, a measure of the participation of the surrounding atoms in the vibration, and by a damping constant γ. An exact equation for the damping in terms of f^{eff} and M^{eff} is given in Sec. IV which to our knowledge has not been derived previously. The result is illustrated by a consideration of the average work done on the defect by harmonic forces. In Sec. V we give a method to derive approximate results for the characteristic quantities f^{eff} and M^{eff}.

The characterization of resonances by effective quantities is applied also to resonances just below the maximum frequency of the perfect crystal (Sec. VI). These resonances occur in such situations where, e.g., the force constants are just below a critical value needed for the existence of a localized mode. By a slight increase of the force constants or decrease of the defect mass, a localized mode appears above $\omega_{\max}$. Initially the intensity of this mode is very small. The remaining intensity forms a kind of resonance mode below $\omega_{\max}$ which slowly disappears when the localized frequency moves away from $\omega_{\max}$.

As a further application upper and lower bounds for the frequencies of localized modes can be derived very easily, including the previous lower bounds of Dettmann and Ludwig[12] and others[4] and upper bounds of Dean[13] and Fujita.[14]

The concept of an effective force constant and an effective mass has been discussed previously by Klein,[2] Agrawal and Ram,[15,16] and Stoneham.[17] However, the simplicity and the full advantage of this concept had not been used. Only recently Page[18,19] has given a description of low-frequency resonances in terms of such effective quantities. His method is based on the Green's-function technique and restricted to resonances caused by weakened force constants only. Our method is valid for all type of resonances and does not rely on numerical results for the ideal Green's function.

II. METHOD OF KRUMHANSL AND MATTHEW

In the follwing we will shortly derive the method of Krumhansl and Matthew,[5,6] which forms the basis for our paper. This method is similar to the one used earlier by Litzmann and Rosza[7] and Kunc[8] as well as by Mahanty[9] and Sachdew and Mahanty.[10]

The Green's function for the imperfect lattice is given by

$$(\phi - M\omega^2)G(\omega) = 1\,, \tag{1}$$

where $\phi_{ij}^{\vec{m}\vec{n}}$ denotes the matrix of the force constants and $M_{ij}^{\vec{m}\vec{n}} = M^{\vec{m}}\delta_{ij}^{\vec{m}\vec{n}}$ is the diagonal mass matrix. Since one is interested in a direct description of the vibrational behavior of the defect itself, the entire space of all atoms is divided into a central subspace C, which in most cases contains only the defect atom, and into a subspace R containing the remaining lattice atoms. Then the matrices ϕ, M, and G can be partitioned as

$$\phi = \begin{pmatrix} \phi_{CC} & \phi_{CR} \\ \phi_{RC} & \phi_{RR} \end{pmatrix}, \quad M = \begin{pmatrix} M_{CC} & 0 \\ 0 & M_{RR} \end{pmatrix},$$

$$G = \begin{pmatrix} G_{CC} & G_{CR} \\ G_{RC} & G_{RR} \end{pmatrix}, \tag{2}$$

and Eq. (1) yields

$$\begin{aligned} &(\phi_{CC} - M_{CC}\omega^2)G_{CC} + \phi_{CR}G_{RC} = 1\,, \\ &\phi_{RC}G_{CC} + (\phi_{RR} - M_{RR}\omega^2)G_{RC} = 0\,, \end{aligned} \tag{3}$$

and two additional equations for G_{CR} and G_{RR}, which are not given here since our main emphasis is on the Green's function G_{CC}, which alone describes the local vibrational properties of the defect. For G_{CC} we obtain from (3), by eliminating G_{RC},

$$\begin{aligned} G_{CC}(\omega) &= [\phi_{CC}^{\text{eff}}(\omega) - M_{CC}\omega^2]^{-1} \\ &= [\phi_{CC} - M_{CC}\omega^2 - \phi_{CR}\hat{G}_{RR}(\omega)\phi_{RC}]^{-1}\,, \end{aligned} \tag{4}$$

with

$$(\phi_{RR} - M_{RR}\omega^2)\hat{G}_{RR}(\omega) = 1\,.$$

This equation is similar to the Einstein approximation $G_{cc} \cong (\phi_{CC} - M_{CC}\omega^2)^{-1}$ describing the vibrations of the defect for a fixed rest crystal. However, it is an exact expression for the Green's function of the defect, since the motion of all other atoms is taken into account by the term $\phi_{CR}\hat{G}_{RR}(\omega)\phi_{RC}$.

The remaining problem is the determination of $\hat{G}_{RR}$, i.e., the Einstein Green's function of the rest lattice for a fixed defect. This can be done by means of the ideal Green's function ${}^0G$ of the perfect crystal

$$({}^0\phi - {}^0M\omega^2)\,{}^0G(\omega) = 1\,. \tag{5}$$

For the case of an interstitial-type defect which introduces additional degrees of freedom into the lattice, the subspace R contains all the atoms of the ideal lattice. Then $\hat{G}$ can be calculated by the standard Green's-function method

$$\hat{G}_{RR} = {}^0G - {}^0GV\hat{G}_{RR} = [1/(1 + {}^0GV)]\,{}^0G\,, \tag{6}$$

with

$$V = \varphi - \Delta M\omega^2\,, \quad \varphi = \phi_{RR} - {}^0\phi\,, \quad \Delta M = M_{RR} - {}^0M\,.$$

For substitutional defects the space R contains fewer degrees of freedom than the perfect lattice. In this case we can also apply Eq. (6) if we replace ${}^0G$ by the Green's function ${}^0G_{RR}$, being the inverse of ${}^0\phi_{RR} - {}^0M_{RR}\omega^2$ in the subspace R alone. By applying the above partitioning technique to Eq. (5) ${}^0\hat{G}_{RR}$ can be given as

$${}^0G_{RR} = {}^0G_{RR} - {}^0G_{RC}(1/{}^0G_{CC})\,{}^0G_{CR}\,. \tag{7}$$

III. RESONANT MODES

Whereas the Green's function $G_{CC}(\omega)$ has poles at localized mode frequencies ω_l, it gives a finite response within the spectrum of the ideal crystal. However, this response can be especially large for resonant mode frequencies defined by

$$\det[\,\phi_{CC} - M_{CC}\omega_{\text{res}}^2 - \phi_{CR}\,\text{Re}\hat{G}_{RR}(\omega_{\text{res}})\phi_{RC}] = 0 \tag{8}$$

if for such frequencies the imaginary part of ${}^0G(\omega)$ is small, e.g., near the band edges $\omega \cong 0$ and $\omega \cong \omega_{\max}$.

In this section we shall discuss the low-frequency resonances, whereas resonances near $\omega_{\max}$ are considered in Sec. VI. Since $G_{CC}(\omega)$ has a quasipole at the resonance frequency, we expand $G_{CC}^{-1}(\omega)$ for small ω. According to Eq. (4) this means an expansion of $\phi_{CC}^{\text{eff}}(\omega)$ and $\hat{G}_{RR}(\omega)$ in powers of ω.

In analogy to Appendix C we obtain for the real part of $\hat{G}_{RR}$

$$\begin{aligned} \text{Re}\,\hat{G}_{RR}(\omega) &= \hat{G}_{RR}(0) + \omega^2[\partial_{\omega^2}\,\text{Re}\,\hat{G}_{RR}(\omega)]_{\omega^2 \to 0+} + \cdots \\ &= \phi_{RR}^{-1} + M_{RR}\omega^2[\tilde{P}(\phi_{RR} - M_{RR}\omega^2)^{-2}]_{\omega^2 \to 0+} \\ &\quad + \cdots \end{aligned} \tag{9}$$

with

$$\tilde{P}\,\frac{1}{x^2} = -\partial_x P\,\frac{1}{x} = -\left(\partial_x \frac{x}{x^2 + \eta^2}\right)_{\eta \to 0} = \left.\frac{x^2 - \eta^2}{(x^2 + \eta^2)^2}\right|_{\eta \to 0}.$$

The first term of this expansion results in an effective force constant for the defect,

$$f_{CC}^{\text{eff}} = \phi_{CC} - \phi_{CR}\phi_{RR}^{-1}\phi_{RC}\,, \tag{10a}$$

which determines the static response $G_{CC}(0) = 1/f^{\text{eff}}_{CC}$. The quadratic term determines an effective mass given by

$$M^{\text{eff}}_{CC} = -\left[\partial_{\omega^2} \operatorname{Re} 1/G_{CC}(\omega)\right]_{\omega^2 \to 0+} = M_{CC} + \phi_{CR} M_{RR} [\tilde{P}(\phi_{RR} - M_{RR}\omega^2)^{-2}]_{\omega^2 \to 0+} \phi_{RC} . \tag{10b}$$

Together with the expansion of the imaginary part, which is discussed in detail in Sec. IV,

$$\operatorname{Im} \phi_{CR} \hat{G}_{RR}(\omega) \phi_{RC} \cong \Gamma_{CC}\omega = M^{\text{eff}}_{CC} \gamma_{CC} \omega , \tag{10c}$$

the low-frequency behavior of the Green's function of the defect is given by

$$G_{CC}(\omega) = (f^{\text{eff}}_{CC} - M^{\text{eff}}_{CC}\omega^2 - i M^{\text{eff}}_{CC} \gamma_{CC} \omega)^{-1} . \tag{11}$$

For simplitiy we will assume in the following that the central subspace C consists of only one atom with cubic symmetry. Then the matrices in this subspace become diagonal 3×3 matrices, e.g., $f^{\text{eff}}_{CC} = f^{\text{eff}} \delta_{ij}$, and Eq. (11) agrees with the Green's function of an isotropic oscillator with velocity-dependent damping. This simple equation, where the embedding of the defect into the lattice is taken into account by an effective force constant, an effective mass, and a damping constant, determines the resonance frequency as

$$\omega^2_{\text{res}} = f^{\text{eff}}/M^{\text{eff}} . \tag{12}$$

Thus we can distinguish two kinds of resonances, "spring resonances," with small f^{eff} and "mass resonances," with large M^{eff}. Only the former give a large static response, $G_{CC}(0) = 1/f^{\text{eff}}$, which becomes infinite for $f^{\text{eff}} \to 0$, indicating that the considered defect configuration becomes instable.

The vibrational properties of an atom in an imperfect lattice are most conveniently described by its local frequency spectrum

$$Z^{\vec{m}}_i(\omega) = (2\omega M^{\vec{m}}/\pi) \operatorname{Im} G^{\vec{m}\vec{m}}_{ii}(\omega) , \tag{13}$$

with

$$\int_0^\infty d\omega \, z^{\vec{m}}_i(\omega) = 1 .$$

It gives a quantitative measure of what frequencies atom $\vec{m}$ is able to vibrate at (in direction i) and allows us to calculate all vibrational properties which depend only on atom $\vec{m}$, e.g., the thermal displacements squared,

$$\langle (s^{\vec{m}}_i)^2 \rangle_T = \int_0^\infty d\omega \, \frac{\epsilon(\omega, T)}{M^{\vec{m}}\omega^2} z^{\vec{m}}_i(\omega) , \tag{14}$$

with

$$\epsilon(\omega, T) = \tfrac{1}{2} \hbar\omega \coth(\hbar\omega/2kT) .$$

For the local spectrum of the defect d we obtain from Eq. (11), in the case of a threefold degenerate resonance,

$$z^d_i(\omega) = \frac{M^d}{M^{\text{eff}}} \frac{2}{\pi} \frac{\gamma\omega^2}{(\omega^2 - \omega^2_{\text{res}})^2 + \gamma^2\omega^2} \tag{15}$$

with

$$\int_0^\infty d\omega \, z^d_i(\omega) = \frac{M^d}{M^{\text{eff}}} ,$$

which represents an asymmetric Lorentzian (plotted in Fig. 1). Its normalization is given by M^d/M^{eff} and represents the fraction of the total spectrum contained in the resonance mode.

The damping γ of the resonance and thus the half-width $\Delta\omega$ of the local spectrum can be calculated exactly (see Sec. IV):

$$\Delta\omega \equiv \gamma = (3\pi/2\,{}^0M\omega^3_D)\,(f^{\text{eff}})^2/M^{\text{eff}} \tag{16a}$$

or

$$\Delta\omega/\omega_{\text{res}} = (3\pi/2\,{}^0M\omega^3_D)\,(f^{\text{eff}})^{3/2}(M^{\text{eff}})^{-1/2} , \tag{16b}$$

where ω_D is the Debye frequency of the ideal lattice. Owing to the $\frac{3}{2}$ power, spring resonances are much more weakly damped and give much shaper peaks in the spectrum than mass resonances. In both cases the half-width goes to zero for $\omega_{\text{res}} \to 0$ and the resonance degenerates into a δ function: $z^d_i(\omega) = (M^d/M^{\text{eff}})\delta(\omega)$.

To our knowledge the exact expression (16) for the damping has not been given previously. Only for special models[5,15] has the mass and force-constant dependence been discussed in the literature.

One remark about the validity of the above results has to be added. The low-frequency expression of $\hat{G}_{RR}(\omega)$ implies that $\hat{G}_{RR}$ is slowly varying and does not show any resonance behavior itself. As a consequence, for a defect with cubic sym-

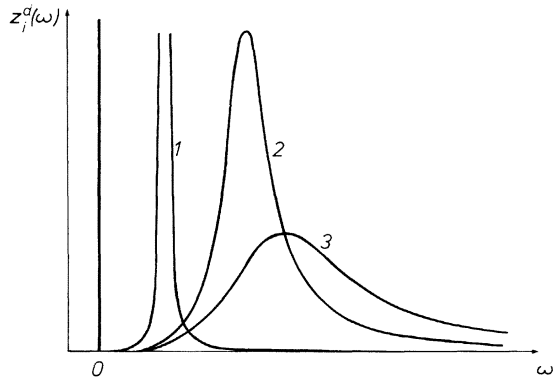

FIG. 1. Local vibrational spectrum in the case of low-frequency resonances for three different resonance frequencies $0 < \omega^{(1)}_{\text{res}} < \omega^{(2)}_{\text{res}} < \omega^{(3)}_{\text{res}}$. For $\omega_{\text{res}} = 0$ the spectrum degenerates into a δ function.

metry at most one resonance can occur. If $\hat{G}_{RR}(\omega)$ is not slowly varying, the central subspace must be enlarged, since sufficiently far from the defect the corresponding Green's function $\hat{G}_{RR}$ has the properties of the ideal Green s function ${}^0G$ and is slowly varying. Then more than one resonance can occur.

IV. DAMPING OF RESONANT MODES

In order to calculate the damping of the resonant modes, we have to consider the imaginary part of the Green's function for the imperfect crystal. We begin with the simpler case of substitutional defects, and we will then discuss the case of interstitials. Using Eq. (6), $\mathrm{Im}G$ is given by

$$\begin{aligned}\mathrm{Im}G &= \frac{1}{2i}(G-G^\dagger)\\ &= \frac{1}{2i}\left(\frac{1}{1+{}^0GV}\,{}^0G-{}^0G^\dagger\,\frac{1}{1+V^\dagger{}^0G^\dagger}\right)\\ &= \frac{1}{2i}\,\frac{1}{1+{}^0GV}\,({}^0G+{}^0GV^\dagger{}^0G^\dagger-{}^0G^\dagger\\ &\qquad -{}^0GV{}^0G^\dagger)\,\frac{1}{1+V^\dagger{}^0G^\dagger}\,,\end{aligned}\tag{17}$$

where $G^\dagger=G^*$ is the Hermitian adjunct of $G(\omega)$. Since $V=V^\dagger$ we obtain

$$\begin{aligned}\mathrm{Im}G &= [1/(1+{}^0GV)]\,\mathrm{Im}{}^0G[1/(1+V^\dagger{}^0G^\dagger)]\\ &= (1-GV)\,\mathrm{Im}{}^0G(1-VG^\dagger)\,.\end{aligned}\tag{18}$$

Expanding up to linear order in ω, we can replace $V(\omega)$ by $V(0)=\varphi$, $G(\omega)$ by $G(0)$, and $\mathrm{Im}{}^0G_{ii}^{\vec{m}\vec{n}}$ by $\frac{3}{2}(\pi\omega/{}^0M\omega_D^3)\delta_{ij}$ (see Appendix A). Because of the translational symmetry $(\sum_{\vec{n}}\varphi^{\vec{m}\vec{n}}=0)$, the result is

$$\mathrm{Im}G_{ij}^{\vec{m}\vec{n}}(\omega)\cong\mathrm{Im}{}^0G_{ij}^{\vec{m}\vec{n}}(\omega)\cong\tfrac{3}{2}(\pi\omega/{}^0M\omega_D^3)\delta_{ij}\,.\tag{19}$$

Thus for small ω the imaginary part of the Green's function of the defect is independent of the defect structure and depends only on the surrounding ideal lattice. As a consequence the local vibrational spectrum of the defect approaches for $\omega\to 0$ the ideal spectrum, besides a factor $M^d/{}^0M$:

$$z_i^d(\omega)\cong\frac{M^d}{{}^0M}\;{}^0z(\omega)=\frac{M^d}{{}^0M}\,\frac{3\omega^2}{\omega_D^3}\,.\tag{20}$$

By comparing this result with Eq. (15) for $\omega\to 0$, the formula (16) for the damping γ follows immediately.

The intuitive meaning of this result can be understood if we consider the average work done by external harmonic forces $F_i^{\vec{m}}(t)=f_i^{\vec{m}}\cos\omega_0 t$,

$$\langle W(t)\rangle=\frac{\omega_0}{2\pi}\int_0^{2\pi/\omega_0}W(t)\,dt\,,\tag{21}$$

with

$$W(t)=\sum_{\vec{m},i}F_i^{\vec{m}}(t)\dot{s}_i^{\vec{m}}(t)\,.$$

In terms of the frequency-dependent Green's function, $s_i^{\vec{m}}(t)$ can be written

$$\begin{aligned}s_i^{\vec{m}}(t) &= \frac{1}{2}\sum_{\vec{n},j}G_{ij}^{\vec{m}\vec{n}}(\omega_0)f_j^{\vec{n}}e^{i\omega_0 t}\\ &\quad+\frac{1}{2}\sum_{\vec{n},j}G_{ij}^{\vec{m}\vec{n}}(-\omega_0)f_j^{\vec{n}}e^{-i\omega_0 t}\,.\end{aligned}\tag{22}$$

From this $\langle W(t)\rangle$ follows as

$$\langle W(t)\rangle=\frac{\omega_0}{2}\sum_{\vec{m},\vec{n},i,j}f_i^{\vec{m}}\,\mathrm{Im}G_{ij}^{\vec{m}\vec{n}}(\omega_0)f_j^{\vec{n}}\,,\tag{23}$$

so that in the low-frequency limit we obtain

$$\langle W(t)\rangle=\frac{3\pi\omega_0^2}{2\,{}^0M\omega_D^3}\sum_i f_i^2\,,\tag{24}$$

with

$$f_i=\sum_{\vec{m}}f_i^{\vec{m}}\,,$$

which means that the averaged work does not depend on the properties of the defect and is determined only by the ideal lattice and the magnitude of the total force f_i.

If f_i vanishes, e.g., for forces with even symmetry, $f_i^{\vec{m}}=-f_i^{-\vec{m}}$, higher terms of the expansion of $\mathrm{Im}{}^0G$ have to be taken into account. Then the result depends on the properties of the defect and is given by

$$\langle W(t)\rangle=\frac{\omega_0^4}{2}\sum_{ijkl}P_{ik}T_{ijkl}P_{jl}\,.\tag{25}$$

The tensor T_{ijkl} is defined in Appendix A and depends only on ideal lattice properties; $P_{ij}=\sum_{\vec{m}}R_i^{\vec{m}}K_j^{\vec{m}}$ is the dipole moment of the forces $\vec{K}=[1-\varphi G(0)]\vec{F}$, which are related to the forces $\vec{F}$ in the same way as in lattice statics the Kanzaki forces are to the original forces.[20] Whereas above the results for the damping γ (for $\mathrm{Im}G$) and for the averaged work $\langle W(t)\rangle$ have been derived under the assumption of a substitutional defect, we will now consider defects with additional degrees of freedom, i.e., interstitials, where $G(\omega)$ and ${}^0G(\omega)$ refer to spaces of different dimensions. Starting from definition (10c) for the damping and using Eq. (18) for $\mathrm{Im}\hat{G}_{RR}$ we obtain in the low-frequency limit

$$\begin{aligned}\Gamma_{CC}\omega &\cong \phi_{CR}[1-\hat{G}(0)\varphi]_{RR}\\ &\quad\times\mathrm{Im}\,{}^0G(\omega)[1-\varphi\hat{G}(0)]_{RR}\phi_{RC}\,,\end{aligned}\tag{26}$$

By inserting Eq. (19) this result can be further simplified by using the translational symmetry of ϕ. The calculations are straightforward (for de-

tails see Ref. 11) and yield the same formula (16) for the damping as for interstitial-type defects. Thus Eqs. (19), (20), and (24) are valid for interstitials, too. A more general proof of this statement for an arbitrarily disordered finite region embedded into an otherwise ideal crystal in given in Ref. 11.

V. EFFECTIVE FORCE CONSTANT AND EFFECTIVE MASS

According to Sec. IV the resonant mode is completely determined by the effective force constant f^{eff} and the effective mass M^{eff}, since the damping γ can be obtained from these quantities [Eq. (16)]. According to Eqs. (10a) and (10b) f^{eff} and M^{eff} can be calculated by means of the Green's function ${}^0G$ of the ideal lattice. But since in general only numerical results for ${}^0G$ are available, we will give other, equivalent expressions for these effective quantities which enable us to derive approximations without explicitly using the Green's function.

For simplicity we restrict the discussion, as above, to the case of a subspace C containing a defect with cubic symmetry. M^{eff} and f^{eff} can be calculated by means of a resonant mode $\vec{u}(\omega)$ determined by the following force-free equation of motion:

$$\sum_{\vec{n},j} \phi_{ij}^{\vec{m}\vec{n}} u_j^{\vec{n}}(\omega) - M^{\vec{m}}\omega^2 u_i^{\vec{m}}(\omega) = 0\,, \quad \text{for } \vec{m} \neq d\,, \tag{27}$$

if $u_i^d(\omega) = \delta_{ix}$ is given.

Applying Eq. (3), an expression for the displacement field $\vec{u}(\omega)$ in terms of the Green's function of the imperfect crystal is easily obtained:

$$u_i^{\vec{m}}(\omega) = G_{ix}^{\vec{m}d}(\omega)/G_{xx}^{dd}(\omega)\,. \tag{28}$$

Starting from the static equation

$$\sum_{\vec{n},j} \phi_{ij}^{\vec{m}\vec{n}} G_{jx}^{nd}(0) = \delta_{ix}^{\vec{m}d}\,, \tag{29}$$

multiplying from the left-hand side with $G_{xi}^{d\vec{m}}(0)$, summing over m and i, and dividing by $[G_{xx}^{dd}(0)]^2$, the result for f^{eff} is

$$f^{\text{eff}} = \frac{1}{G_{xx}^{dd}(0)} = \sum_{\vec{m},\vec{n},i,j} u_i^{\vec{m}}(0)\phi_{ij}^{\vec{m}\vec{n}} u_j^{\vec{n}}(0)\,. \tag{30}$$

By using the identity

$$\partial_{\omega^2} G(\omega) = G(\omega)\, M G(\omega)\,, \tag{31}$$

we can derive a similar expression for the effective mass by using Eq. (10b),

$$\begin{aligned} M^{\text{eff}} &= \text{Re}\left(\frac{1}{[G_{xx}^{dd}(\omega)]^2}\ \partial_{\omega^2} G_{xx}^{dd}(\omega)\right)_{\omega^2 \to 0+} \\ &= \text{Re}\left(\sum_{\vec{m},i} u_i^{\vec{m}}(\omega) M^{\vec{m}} u_i^{\vec{m}}(\omega)\right)_{\omega^2 \to 0+} \\ &= M^d + {}^0M\,\text{Re}\left(\sum_{\substack{\vec{m},i \\ \vec{m}\neq d}} [u_i^{\vec{m}}(\omega)]^2\right)_{\omega^2 \to 0+}. \end{aligned} \tag{32}$$

Thus M^{eff} consists of the defect mass M^d plus additional contributions from the masses of the other vibrating atoms near the defect weighed by the square of the amplitudes $\vec{u}^{\vec{m}}$. As will be shown below the additional contribution can be positive or negative. Whereas f^{eff} is determined by the static displacement field $\vec{u}(0)$, in this equation we cannot exchange the limit $\omega^2 \to 0+$ with the summation over $\vec{m}$. The sum $\sum_{\vec{m}} [u_i^{\vec{m}}(0)]^2$ diverges, since for large distances $G_{ix}^{\vec{m}d}(0)$ and $u_i^{\vec{m}}(0)$ merely decrease as $1/|\vec{R}^{\vec{m}} - \vec{R}^d|$.

For the resonance frequency we obtain

$$\omega_{\text{res}}^2 = (\vec{u}(0), \phi\vec{u}(0))/\text{Re}[(\vec{u}(\omega), M\vec{u}(\omega))]_{\omega^2 \to 0+}\,, \tag{33}$$

which is similar to the Rayleigh quotient for localized modes.[12]

The results for f^{eff} and M^{eff} in terms of the mode $\vec{u}(\omega)$ enable us to derive approximate expressions for the effective quantities if approximations for $\vec{u}(\omega)$ are given. In order to avoid the use of Green's functions, we solve Eq. (27) for the static case under the additional assumption that all atoms outside a finite region N surrounding the defect are fixed. The calculation of the displacements of these atoms requires only the inversion of the matrix ϕ_{NN} in this finite subspace.

The expression for f^{eff} obtained in this way represents always upper bounds for the exact value,

$$f^{\text{eff}} \leq \phi_{CC} - \phi_{CN}(1/\phi_{NN})\phi_{NC}\,. \tag{34}$$

The simplest approximation of this kind is the Einstein approximation $f_E^{\text{eff}} = \phi_{CC}$, where all atoms besides the defect are fixed. Here $f^{\text{eff}} \leq \phi_{CC}$ is obvious from Eq. (10a), since ϕ_{RR} is positive definite. For an arbitrary region N we write Eq. (32)

$$\begin{aligned} \frac{1}{f^{\text{eff}}} &= G_{CC}(0) = \left(\frac{1}{\phi}\right)_{CC} \\ &= \frac{1}{\phi_{CC} - \phi_{CR}(1/\phi_{RR})\phi_{RC}}\,, \end{aligned} \tag{35}$$

and obtain in analogy

$$\left(\frac{1}{\phi_{RR}}\right)_{NN} = \frac{1}{\phi_{NN} - \phi_{NR'}(1/\phi_{R'R'})\phi_{R'N}}\,, \tag{36}$$

where the subspace R' contains the atoms of $R = N + R'$ not belonging to N. Since ϕ is positive definite we have

$$\phi_{CR}(1/\phi_{RR})\phi_{RC} = \phi_{CN}(1/\phi_{RR})_{NN}\phi_{NC}\,,$$

and

$$(1/\phi_{RR})_{NN} \geq 1/\phi_{NN}\,, \tag{37}$$

which yields the inequality (34).

To obtain similar approximations for $M^{\rm eff}$ we have to avoid the divergence problem of $\sum_{\vec{m}}[u_i^{\vec{m}}(0)]^2$. From Appendix D the Green's function $G_{ix}^{\vec{m}d}(\omega)$ approaches ${}^0G_{ix}^{\vec{m}d}(\omega)$ for large distances $|R^{\vec{m}} - R^d|$ and small frequencies ω, so that we obtain for $u_i^{\vec{m}}(\omega)$ the asymptotic value

$$u_i^{\vec{m}}(\omega) = (f^{\rm eff}/{}^0f^{\rm eff})\,{}^0u_i^{\vec{m}}(\omega)\,, \tag{38}$$

with

$${}^0f^{\rm eff} = 1/{}^0G_{xx}^{dd}(0)\,,$$

where in analogy to Eq. (28) the displacements ${}^0u_i^{\vec{m}}(\omega)$ of the ideal lattice are defined

$${}^0u_i^{\vec{m}}(\omega) = {}^0G_{ix}^{\vec{m}d}(\omega)/{}^0G_{xx}^{dd}(\omega) \cong {}^0f^{\rm eff}\,{}^0G_{ix}^{\vec{m}d}(\omega)\,. \tag{39}$$

If ${}^0M^{\rm eff}$ denotes the effective mass for the ideal crystal, defined in analogy to Eq. (32), we obtain the identity

$$M^{\rm eff} = \left(\frac{f^{\rm eff}}{{}^0f^{\rm eff}}\right)^2 {}^0M^{\rm eff} + \sum_{\vec{m},\,i}\left[M^{\vec{m}}[u_i^{\vec{m}}(0)]^2 - {}^0M\left(\frac{f^{\rm eff}}{{}^0f^{\rm eff}}\right)^2[{}^0u_i^{\vec{m}}(0)]^2\right]. \tag{40}$$

In this form no difficulty arises from the limit $\omega^2 \to 0$ due to the subtraction of the diverging parts. For a strong spring resonance ($f^{\rm eff} \ll {}^0f^{\rm eff}$) we may neglect the terms with $(f^{\rm eff}/{}^0f^{\rm eff})^2$ and obtain in a rough approximation

$$M^{\rm eff} \cong M^d + {}^0M \sum_{\vec{m}\neq d,\,i}[u_i^{\vec{m}}(0)]^2 > M^d\,, \tag{41}$$

provided that the sum is restricted to a finite and not too large number of atoms, since the sum diverges for an infinite crystal.

On the other hand, Eq. (41) is rather useless for mass resonances. For an isotopic defect we obtain $f^{\rm eff} = {}^0f^{\rm eff}$ and $u_i^{\vec{m}}(0) = {}^0u_i^{\vec{m}}(0)$, so that the effective mass is given by

$$M^{\rm eff} = M^d + {}^0M^{\rm eff} - {}^0M\,. \tag{42}$$

Numerical solutions for a fcc lattice with nearest-neighbor interaction yield ${}^0M^{\rm eff} = 0.63\,{}^0M$ and thus $M^{\rm eff} < M^d$, whereas Eq. (41) implies $M^{\rm eff} > M^d$. As a consequence $M^{\rm eff}$ cannot be calculated by an evaluation of the equation of motion for a finite number of atoms.

Only in special cases, e.g., for resonant modes with even symmetry, $u_i^{\vec{m}} = -u_i^{-\vec{m}}$, where $u_i^{\vec{m}}(0)$ decreases as $(1/R^{\vec{m}})^2$, the sum in Eq. (41) converges, and obviously we obtain lower bounds for $M^{\rm eff}$ for an arbitrary finite region N. Such modes are of less interest for the above-considered case of a single-atom defect, since the defect remains at rest. However, they are important in, e.g. the case of split interstitials.[11,21]

The concept of an effective mass and its calculation by static Green's functions have been used recently also by Page[18,19] in a somewhat different way. Since expression (33) for the resonance frequency is insensitive to small changes of $\tilde{u}(\omega)$, Page has replaced the resonant mode $\tilde{u}(\omega)$ by a slightly different mode, $\tilde{u}(0)$. Owing to small additional negative force constants this "decay mode" is determined by the condition that the corresponding $\tilde{f}^{\rm eff}$ vanishes, and it describes the amplitude distribution with which the defect configuration decays, since $\tilde{f}^{\rm eff} = 0$ determines the stability limit of this configuration. By the procedure of Page the effective mass is calculated by Eq. (41), where the $\tilde{u}(0)$ is replaced by $\tilde{u}(0)$. In this case no convergence problem arises, since according to Eq. (38) the leading $1/R$ term vanishes, so that $\tilde{u}(0)$ decreases as $1/R^3$ for large distances.[18] However, this is true only for the exact decay mode $\tilde{u}(0)$ with $\tilde{f}^{\rm eff} = 0$, which therefore has to be calculated by the Green's-function technique. Moreover, this method is restricted to resonances stemming from weakened force constants and always yields $M^{\rm eff} > M^d$ [Eq. (41)]. This is, however, not true in general, as we have seen before.

VI. RESONANT AND LOCALIZED MODES NEAR THE BAND EDGE $\omega_{\rm max}$

Resonant modes can occur not only at low frequencies but also at the upper band edge, where $\mathrm{Im}\,{}^0G(\omega)$ vanishes as $(\omega_{\rm max}^2 - \omega^2)^{1/2}$. They are connected with the formation of localized modes, since a slight increase of the force constants or a slight decrease of the defect mass leads to the appearance of a localized mode just above $\omega_{\rm max}$.

According to Appendixes B and C we can write $G_{xx}^{dd}(\omega)$ near the upper band edge as

$$G_{xx}^{dd}(\omega) = [f^{\rm eff} - M^{\rm eff}(\omega^2 - \omega_{\rm max}^2) - iM^{\rm eff}\gamma(\omega_{\rm max}^2 - \omega^2)^{1/2}]^{-1}\,. \tag{43}$$

The effective quantities $f^{\rm eff} = f^{\rm eff}(\omega_{\rm max})$, $M^{\rm eff}$, and γ are contrary to the effective quantities of Sec. III determined by the behavior of $G_{xx}^{dd}(\omega)$ at $\omega_{\rm max}$,

$$f^{\rm eff} = 1/G_{xx}^{dd}(\omega_{\rm max})\,, \tag{44a}$$

$$M^{\rm eff} = -\{\partial_{\omega^2}\,\mathrm{Re}[1/G_{xx}^{dd}(\omega)]\}_{\omega^2\to\omega_{\rm max}^2-0}\,, \tag{44b}$$

$$\gamma = -\frac{1}{M^{\rm eff}}\left((\omega_{\rm max}^2 - \omega^2)^{-1/2}\,\mathrm{Im}\,\frac{1}{G_{xx}^{dd}(\omega)}\right)_{\omega^2\to\omega_{\rm max}^2-0}. \tag{44c}$$

We should emphasize an important difference between the low-frequency resonances and the reso-

nances near ω_{max}. Whereas the damping γ approaches zero for $\omega_{res} \to 0$, this is not the case for $\omega_{res} \to \omega_{max}$. From Appendix B, $\mathrm{Im}\,{}^0G^{\vec{m}\vec{n}}_{ij}(\omega)$ explicitly depends on $\vec{m}$ and $\vec{n}$ near ω_{max}, so that according to Eq. (18) γ remains finite for $\omega_{res} \to \omega_{max}$ and the spectrum of the mode does not degenerate into a δ function.

Noting that $i(\omega_{max}^2 - \omega^2)^{1/2}$ becomes real for $\omega^2 > \omega_{max}^2$, we obtain the local vibrational spectrum as a function of ω^2 as

$$z_x^d(\omega^2) = \frac{M^d}{\pi}\,\mathrm{Im}\,G_{xx}^{dd}(\omega^2) = \frac{M^d}{M^{\mathrm{eff}}} \times \begin{cases} \dfrac{1}{\pi}\dfrac{\gamma(\omega_{max}^2-\omega^2)^{1/2}}{(f^{\mathrm{eff}}/M^{\mathrm{eff}}+\omega_{max}^2-\omega^2)^2+\gamma^2(\omega_{max}^2-\omega^2)}, & \text{for } \omega^2<\omega_{max}^2 \\ \delta(f^{\mathrm{eff}}/M^{\mathrm{eff}}-(\omega^2-\omega_{max}^2)-\gamma(\omega^2-\omega_{max}^2)^{1/2}), & \text{for } \omega^2>\omega_{max}^2 \end{cases} . \tag{45}$$

For negative f^{eff} the δ function gives no contribution and the spectrum contains only a resonant mode at $\omega_{res}^2 \cong \omega_{max}^2 - |f^{\mathrm{eff}}|/M^{\mathrm{eff}}$ [for $|f^{\mathrm{eff}}|/M^{\mathrm{eff}} \gg \frac{1}{4}\gamma^2$]. For $f^{\mathrm{eff}} \to 0$ this mode degenerates and shows a square-root singular behavior as $(\omega_{max}^2-\omega^2)^{-1/2}$ at the band edge. For positive f^{eff} the δ function describes a localized mode,

$$z_x^d(\omega^2) = (M^d/M_{\mathrm{loc}}^{\mathrm{eff}})\delta(\omega^2-\omega_l^2)\,, \tag{46}$$

with

$$M_{\mathrm{loc}}^{\mathrm{eff}} = M^{\mathrm{eff}}[1+\tfrac{1}{2}\gamma(\omega_l^2-\omega_{max}^2)^{-1/2}]\,,$$

where the localized frequency ω_l is given

$$\omega_l^2 = \omega_{max}^2 + [(f^{\mathrm{eff}}/M^{\mathrm{eff}}+\tfrac{1}{4}\gamma^2)^{1/2} - \tfrac{1}{2}\gamma]^2 \cong \begin{cases} \omega_m^2 + \left(\dfrac{f^{\mathrm{eff}}}{\gamma M^{\mathrm{eff}}}\right)^2, & \text{for } \dfrac{f^{\mathrm{eff}}}{M^{\mathrm{eff}}} \ll \dfrac{\gamma^2}{4} \\ \omega_m^2 + \dfrac{f^{\mathrm{eff}}}{M^{\mathrm{eff}}}, & \text{for } \dfrac{f^{\mathrm{eff}}}{M^{\mathrm{eff}}} \gg \dfrac{\gamma^2}{4} \end{cases} . \tag{47}$$

For high frequencies, $\omega_l^2 \gg \omega_{max}^2$, the effective mass $M_{\mathrm{loc}}^{\mathrm{eff}}$ is given by the "normal contribution" M^{eff}. However, for $\omega_l \to \omega_{max}$ it becomes infinite, indicating that more and more atoms take part in the vibration. Thus this mode becomes more and more delocalized, so that its contribution $M^d/M_{\mathrm{loc}}^{\mathrm{eff}}$ to the spectrum of the defect approaches zero.

For $f^{\mathrm{eff}} > 0$, in addition to the localized mode there is a kind of a resonant mode below the band edge with resonance frequency

$$\omega_{res}^2 \cong \omega_{max}^2 - \tfrac{1}{3} f^{\mathrm{eff}}/M^{\mathrm{eff}}\,. \tag{48}$$

The intensity within the band can be calculated by residuum calculus,

$$\int_{-\infty}^{\omega_{max}^2} d\omega^2\, z_x^d(\omega^2) = \begin{cases} M^d/M^{\mathrm{eff}} - M^d/M_{\mathrm{loc}}^{\mathrm{eff}}, & \text{for } f^{\mathrm{eff}} > 0 \\ M^d/M^{\mathrm{eff}}, & \text{for } f^{\mathrm{eff}} < 0\,. \end{cases} \tag{49}$$

Equation (49) indicates that the total intensity of the vibrational spectrum is always given by M^d/M^{eff}. For negative f^{eff} it is contained in the resonant mode alone, whereas for increasing positive f^{eff} more and more intensity is transferred to the localized mode.

This behavior of the spectrum is shown in Fig. 2, where it is plotted for three different values of f^{eff} ($f^{\mathrm{eff}} < 0$, $f^{\mathrm{eff}} = 0$, $f^{\mathrm{eff}} > 0$). The dashed line indicates as a measure for the intensity of the localized mode the height of the δ function as a function of its frequency.

VII. LOCALIZED MODES

Since Eq. (4) conveniently describes the vibrational behavior of the defect, it is also applicable for a calculation of localized modes. The frequency ω_l of a localized mode is determined by

$$M_{CC}\,\omega_l^2 = \phi_{CC}^{\mathrm{eff}}(\omega_l) = \phi_{CC} - \phi_{CR}\hat{G}_{RR}(\omega_l)\phi_{RC} = \phi_{CC} - \phi_{CR}[1/(\phi_{RR} - M_{RR}\omega_l^2)]\phi_{RC}\,. \tag{50}$$

If the retardation of the Green's function is taken into account by an infinitesimal damping $i\eta\omega$ ($\eta \to 0+$), an expansion of Eq. (4) yields

$$G_{CC}(\omega) = 1/M_{\mathrm{loc}}^{\mathrm{eff}}(\omega_l^2 - \omega^2 - i\eta\omega)\,, \qquad z_x^d(\omega) = (M^d/M_{\mathrm{loc}}^{\mathrm{eff}})\delta(\omega-\omega_l)\,, \tag{51}$$

where the effective mass is given by

$$M_{\mathrm{loc}}^{\mathrm{eff}} = M_{CC} + [\partial_{\omega^2}\phi_{CR}\,\hat{G}_{RR}(\omega)\phi_{RC}]_{\omega=\omega_l} = M^d + {}^0M\sum_{m\neq d,i}[u_i^{\vec{m}}(\omega_l)]^2\,. \tag{52}$$

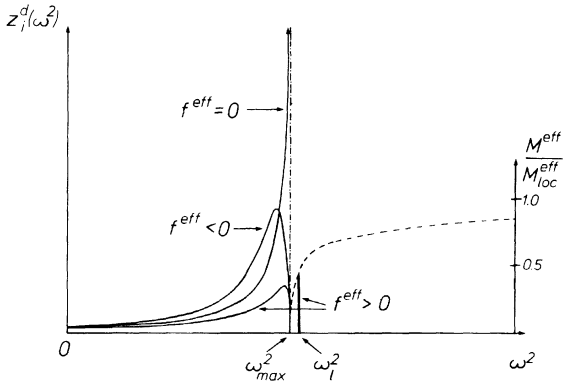

FIG. 2. Local frequency spectrum for resonances near ω_{max}. The intensity $M^{\mathrm{eff}}/M_{\mathrm{loc}}^{\mathrm{eff}}$, contained in the localized mode, is indicated by the height of the δ function.

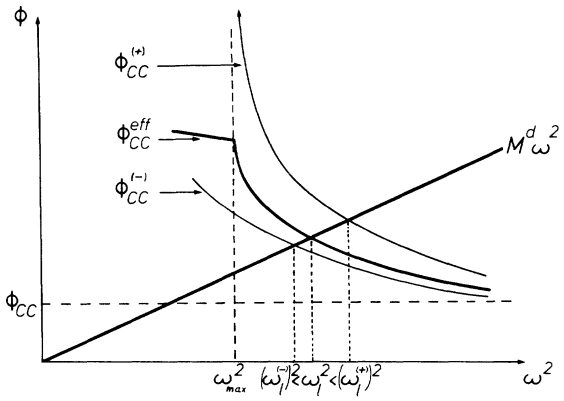

FIG. 3. Graphical construction to obtain lower and upper bounds for the localized mode frequency ω_l.

In contrast to the low-frequency resonances the sum converges because of the exponential decrease of the localized mode $\vec{u}^m(\omega_l)$, with R^m, so that $M^{\text{eff}}_{\text{loc}} > M^d$ always.

Without needing any explicit results for the lattice Green's function we can apply Eq. (50) for a calculation of upper and lower bounds for the localized frequency ω_l. As shown in Fig. 3 this frequency is determined by the intersection of $M^d\omega^2$ with $\phi^{\text{eff}}_{CC}(\omega^2)$.

Assuming that the crystal has no localized modes if the defect remains at rest, the quantity ${}^0M\omega^2 - \phi_{RR}$ is for $\omega^2 > \omega^2_{\max}$ positive definite. Further, $\phi^{\text{eff}}_{CC}(\omega^2)$ decreases monotonically for $\omega^2 > \omega^2_{\max}$ and approaches the limiting value ϕ_{CC} as $1/\omega^2$. In this case we obtain at most one intersection of $\phi^{\text{eff}}_{CC}(\omega^2)$ with $M^d\omega^2$, i.e., only one localized mode can exist. The extension to cases with several localized modes can be done by group-theory arguments.

From Fig. 2 it is obvious that whenever we have an approximation $\phi^{(+)}_{CC}(\omega^2)$ or $\phi^{(-)}_{CC}(\omega^2)$, with

$$\phi^{\text{eff}}_{CC}(\omega^2) < \phi^{(+)}_{CC}(\omega^2) \quad \text{or} \quad \phi^{\text{eff}}_{CC}(\omega^2) > \phi^{(-)}_{CC}(\omega^2), \tag{53}$$

for $\omega^2 > \omega^2_{\max}$, the intersection with $M^d\omega^2$ gives an upper bound $\omega_l^{(+)}$ or a lower bound $\omega_l^{(-)}$ for the exact frequency ω_l, so that

$$\omega_l^{(-)} < \omega_l < \omega_l^{(+)}. \tag{54}$$

We will now give some examples for such bounds. An expansion of $({}^0M\omega^2 - \phi_{RR})^{-1}$ in powers of $1/\omega^2$ yields

$$\phi^{\text{eff}}_{CC}(\omega^2) = \phi_{CC} + (1/{}^0M\omega^2)\phi_{CR}\phi_{RC} + [1/({}^0M\omega^2)^2]\phi_{CR}\phi_{RR}\phi_{RC} + \cdots, \tag{55}$$

where all terms are positive. The simplest approximation, $\phi^{(-)}_{CC} = \phi_{CC}$, gives the Einstein frequency

$$\omega_E^2 = \phi_{CC}/M^d < \omega_l^2, \tag{56}$$

and moreover we obtain an infinite number of lower bounds, approaching ω_l^2 from below if higher orders of $1/\omega^2$ are taken into account.

Somewhat better lower bounds can be derived in analogy to the bounds for f^{eff} in Sec. V. Since ${}^0M\omega^2 - \phi_{RR}$ is positive definite for $\omega^2 > \omega^2_{\max}$, the arguments which lead to Eq. (36) give the following approximation:

$$\phi^{\text{eff}}_{CC}(\omega^2) > \phi^{(-)}_{CC}(\omega^2) = \phi_{CC} - \phi_{CN}[1/(\phi_{NN} - {}^0M\omega^2)]\phi_{NC}. \tag{57}$$

Therefore the Einstein approximation for the combined spaces C and N (all other atoms fixed) gives a lower bound for ω_l. This result has also been shown earlier by a variational principle[12] for the Rayleigh-quotient.

To obtain upper bounds for the localized frequency ω_l we apply the following inequality:

$$\phi_{RR} - {}^0M\omega^2 < {}^0M(\omega^2_{\max} - \omega^2), \tag{58}$$

which is due to the positive definiteness of ${}^0M\omega^2 - \phi_{RR}$, for $\omega^2 > \omega^2_{\max}$. This yields

$$\phi^{\text{eff}}_{CC}(\omega^2) < \phi^{(+)}_{CC}(\omega^2) = \phi_{CC} + \phi_{CR}\phi_{RC}/{}^0M(\omega^2 - \omega^2_{\max}). \tag{59}$$

Bounds of this type have been discussed by Fujita,[14] in particular for simple cubic lattices in several dimensions. The earlier results of Dean[13] follow if we estimate expression (58) further by replacing ω by a lower bound $\omega_l^{(-)}$, e.g., the Einstein approximation. These upper bounds can be improved either by enlarging the defect region C (Ref. 14) or by expanding the expression $(\phi_{RR} - {}^0M\omega^2)^{-1}$ according to Taylor. By taking into account the first, third, and fifth terms of this expansion we always get upper bounds, e.g.,

$$\phi^{(+)}_{CC}(\omega^2) = \phi_{CC} + [1/{}^0M(\omega^2 - \omega^2_{\max})]\phi_{CR} \times \left[1 - \frac{{}^0M\omega^2_{\max} - \phi_{RR}}{{}^0M(\omega^2 - \omega^2_{\max})} + \left(\frac{{}^0M\omega^2_{\max} - \phi_{RR}}{{}^0M(\omega^2 - \omega^2_{\max})}\right)^2\right]\phi_{RC}, \tag{60}$$

since $1/(1+x) < 1 - x + x^2$ for $x > 0$.

If the localized frequency ω_l is too near to $\omega_{\max}$, all of the above upper bounds yield less useful approximations, since $\phi^{(+)}_{CC}(\omega^2)$ diverges to infinity at $\omega_{\max}$.

ACKNOWLEDGMENT

It is a pleasure to thank Professor G. Leibfried for his continued interest and for many discussions.

APPENDIX A: LOW-FREQUENCY BEHAVIOR OF $\mathrm{Im}^0G(\omega)$

The ideal Green's function of an infinite lattice can be represented in terms of plane waves as an integral over the first Brillouin zone,

$$ {}^0G_{ij}^{\vec{m}\vec{n}}(\omega) = {}^0G_{ij}^{(\vec{m}-\vec{n})}(\omega) = \sum_\sigma \int_{V_B} \frac{d\vec{k}}{V_B}\, e_i^\sigma(\vec{k}) e_j^\sigma(\vec{k}) \frac{\exp[i\vec{k}\cdot(\vec{R}^{\vec{m}} - \vec{R}^{\vec{n}})]}{{}^0M[\omega_\sigma^2(k) - (\omega + i\eta)^2]}\,, \quad \eta \to 0+, \tag{A1}$$

where the polarization vectors $\vec{e}^\sigma(\vec{k})$ and the eigenfrequencies $\omega_\sigma(\vec{k})$ of ${}^0\phi$ are labeled by the wave vector $\vec{k}$ and the polarization index σ. Because of the symmetry ${}^0\phi_{ij}^{\vec{m}\vec{n}} = {}^0\phi_{ji}^{\vec{n}\vec{m}}$ the polarization vectors are chosen as real and $\exp(i\vec{k}\cdot\vec{R}^{\vec{m}-\vec{n}})$ can be replaced by $\cos(\vec{k}\cdot\vec{R}^{\vec{m}-\vec{n}})$. Thus $\mathrm{Im}^0G(\omega)$ is given by (with $\vec{h} = \vec{m} - \vec{n}$)

$$ \mathrm{Im}^0G_{ij}^{(\vec{h})}(\omega) = \frac{\pi\,\mathrm{sgn}\omega}{{}^0MV_B} \sum_\sigma \int_{V_B} dk\, e_i^\sigma(\vec{k}) e_j^\sigma(\vec{k}) \cos(\vec{k}\cdot\vec{R}^{\vec{h}}) \delta(\omega^2 - \omega_\sigma^2(\vec{k}))\,. \tag{A2}$$

For small frequencies the only contribution results from wave vectors $\vec{k}$ near the origin, $\vec{k} = 0$. Here the polarization vectors depend only on the direction $\vec{\kappa}$ of $\vec{k}$, and

$$ \omega_\sigma(\vec{k}) = c_\sigma(\vec{\kappa})k, \quad \text{with } \vec{k} = k\vec{\kappa}\,, \tag{A3}$$

where $c_\sigma(\vec{\kappa})$ is the velocity of sound in direction $\vec{\kappa}$. Expanding the cosine for $R^{\vec{n}} \ll c_\sigma(\vec{\kappa})/\omega$ and integrating over k, we obtain

$$ \mathrm{Im}^0G_{ij}^{(\vec{h})}(\omega) = \frac{\pi}{2\,{}^0MV_B} \sum_\sigma \int d\Omega_{\vec{\kappa}}\, e_i^\sigma(\vec{\kappa}) e_j^\sigma(\vec{\kappa}) \left(\frac{\omega}{c_\sigma^3(\vec{\kappa})} - \frac{1}{2}\, \frac{\omega^3}{c_\sigma^5(\vec{\kappa})}\, (\vec{\kappa}\cdot\vec{R}^{\vec{h}})^2 + \cdots \right). \tag{A4}$$

The term proportional to ω and an additional term proportional to ω^3, which arises due to the deviation of $\omega_\sigma(\vec{k})$ from $c_\sigma(\vec{\kappa})k$ for larger $\vec{k}$ values, are independent of $\vec{h}$. For cubic crystals they are proportional to δ_{ij} and the ideal Green's function can be represented

$$ \mathrm{Im}^0G_{ij}^{(\vec{h})}(\omega) = \alpha\omega(1 + \alpha'\omega^2)\delta_{ij} - \omega^3 \sum_{kl} R_k^{\vec{h}} T_{ijkl} R_l^{\vec{h}} + \cdots\,. \tag{A5}$$

For isotopic crystals α and T_{ijkl} are determined by the longitudinal and transverse velocity of sound (c_l, c_t),

$$ \alpha = \frac{2}{3\,{}^0MV_B} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right), $$

$$ T_{ijkl} = \frac{2}{30\,{}^0MV_B} \left[\left(\frac{4}{c_t^5} + \frac{1}{c_l^5} \right) \delta_{ij}\delta_{kl} + \left(\frac{1}{c_l^5} - \frac{1}{c_t^5} \right) (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \right]. \tag{A6}$$

According to (A5) the spectrum ${}^0z(\omega)$ agrees for small frequencies with a Debye spectrum

$$ {}^0z(\omega) = 3\omega^2/\omega_D^3, \quad \omega_D^3 = \tfrac{3}{2}\,{}^0M/\pi\alpha\,. \tag{A7}$$

APPENDIX B: BEHAVIOR OF $\mathrm{Im}^0G(\omega)$ NEAR ω_{max}

Similar to the spectrum[1] ${}^0z(\omega)$ the imaginary part of ${}^0G(\omega)$ also shows singularities at critical points $\vec{k}^c$, where $\mathrm{grad}\,\omega_\sigma(\vec{k})$ vanishes. The behavior of Im^0G at the upper band edge is given by the critical points $\vec{k}^\nu$, for which $\omega_\sigma^2(\vec{k}^\nu) = \omega_{max}^2$ (ν denotes the various equivalent $\vec{k}^c$ values in the first Brillouin zone). An expansion of $\omega_\sigma^2(\vec{k})$ near $\vec{k}^\nu$ yields

$$ \omega_\sigma^2(\vec{k}) = \omega_{max}^2 - \sum_{\alpha=1}^{3} \lambda_\alpha (k_\alpha - k_\alpha^\nu)^2 + \cdots\,, \tag{B1}$$

with $\lambda_\alpha > 0$, if the coordinate system is chosen to coincide with the main axes of $\partial^2\omega_\sigma^2(\vec{k})/\partial k_i\,\partial k_j$ at $\vec{k}^\nu$. Inserting this expansion into the representation (A2) for $\mathrm{Im}^0G(\omega)$, the integration can be extended over the whole space, since only $\vec{k}$ vectors near $\vec{k}^\nu$ give contributions. By setting $K_\alpha = \sqrt{\lambda_\alpha}\,(k_\alpha - k_\alpha^\nu)$ we obtain

$$ \mathrm{Im}^0G_{ij}^{(\vec{h})}(\omega) \cong \frac{\pi\,\mathrm{sgn}\omega}{2\,{}^0MV_B} \left(\frac{\omega_{max}^2 - \omega^2}{\lambda_1\lambda_2\lambda_2} \right)^{1/2} \Theta(\omega_{max}^2 - \omega^2) \int_0^\infty dK \int d\Omega_{\vec{K}} e_i^\sigma(\vec{k}) e_j^\sigma(\vec{k}) \cos(\vec{k}\cdot\vec{R}^{\vec{h}}) \delta(K - (\omega_{max}^2 - \omega^2)^{1/2}), \tag{B2}$$

with

$$\Theta(x)=\begin{cases}0, & \text{for } x<0\\ 1, & \text{for } x>0\,.\end{cases}$$

Integration over K and expansion in powers of $(\omega_{\max}^2-\omega^2)^{1/2}$ yields in first order

$$\mathrm{Im}^0G_{ij}^{(\vec{h})}(\omega)\cong\frac{\pi\,\mathrm{sgn}\,\omega}{2\,{}^0MV_B}\left(\frac{\omega_{\max}^2-\omega^2}{\lambda_1\lambda_2\lambda_3}\right)^{1/2}\times\Theta(\omega_{\max}^2-\omega^2)\beta_{ij}^{(\vec{h})}\,, \tag{B3}$$

with

$$\beta_{ij}^{(\vec{h})}=\sum_{\nu}4\pi\,e_i^{\sigma}(\vec{k}^{\nu})\,e_j^{\sigma}(\vec{k}^{\nu})\cos(\vec{k}^{\nu}\cdot\vec{R}^{\vec{h}})\,.$$

Contrary to the first order of the low-frequency expansion (A5) this result depends explicitly on $\vec{R}^{\vec{h}}$.

APPENDIX C: BEHAVIOR OF Re^0G NEAR THE BAND EDGES

From the singularities of $\partial_{\omega^2}\mathrm{Im}^0G(\omega)$ at $\omega=0$ and $\omega=\omega_{\max}$ similar singularities of $\partial_{\omega^2}\mathrm{Re}^0G(\omega)$ follow due to the dispersion relation (Kramers-Kronig relation)

$$\mathrm{Re}^0G(\omega)=\frac{1}{\pi}\int_0^{\infty}d\omega'^2P\frac{1}{\omega'^2-\omega^2}\,\mathrm{Im}^0G(\omega')\,. \tag{C1}$$

The same relation holds for the derivatives $\partial_{\omega^2}\mathrm{Re}^0G(\omega)$ and $\partial_{\omega^2}\mathrm{Im}^0G(\omega)$. By using the expressions (A5) and (B3) for $\mathrm{Im}^0G(\omega)$ the results for $\partial_{\omega^2}\mathrm{Re}^0G(\omega)$ near $\omega=0$ and $\omega=\omega_{\max}$ are given by

$$\partial_{\omega^2}\mathrm{Re}^0G_{ij}^{(\vec{h})}(\omega)=\begin{cases}\dfrac{\alpha\delta_{ij}}{2(-\omega^2)^{1/2}}\,\Theta(-\omega^2), & \text{for } \omega^2\lesssim 0\\[2ex] \dfrac{\beta_{ij}^{(\vec{h})}}{2(\omega^2-\omega_{\max}^2)^{1/2}}\,\Theta(\omega^2-\omega_{\max}^2), & \text{for } \omega^2\gtrsim\omega_{\max}^2\,.\end{cases} \tag{C2}$$

(C3)

Due to this singular behavior the low-frequency limit of $\partial_{\omega^2}\mathrm{Re}^0G(\omega)$ exists only in the limit $\omega^2\to 0+$, which is essential for the low-frequency expansion of the defect Green's function and the definition of the effective mass in Sec. III.

APPENDIX D: BREEN'S FUNCTIONS FOR LARGE DISTANCES AND LOW FREQUENCIES

For large distances ($R^m\gg a$) (a is the lattice constant) and small frequencies ($\omega/c_{\sigma}\ll 1/a$) we can replace the perfect lattice Green's function ${}^0G_{ij}^{(\vec{m})}(\omega)$ by the continuum Green's function $G_{ij}(\vec{R}^{\vec{m}},\omega)$, which can be represented as $(1/R)g_{ij}(\hat{R}^{\vec{m}},\omega R^{\vec{m}})$, with $\vec{R}^{\vec{m}}=R^{\vec{m}}\cdot\hat{R}^{\vec{m}}$, and which, e.g., for isotropic crystals is given by[3] (ρ is the mass density)

$$G_{ij}(\vec{R},\omega)=\frac{\delta_{ij}}{4\pi\rho c_t^2R}\exp\left(\frac{i\omega R}{c_t}\right)+\frac{1}{4\pi\rho\omega^2}\,\partial_{R_i}\partial_{R_j}\times\left[\frac{1}{R}\exp\left(\frac{i\omega R}{c_t}\right)-\frac{1}{R}\exp\left(\frac{i\omega R}{c_l}\right)\right]. \tag{D1}$$

The corrections for shorter distances or higher frequencies are of the order of $1/R^3$ or ω^2/R.

The imperfect lattice Green's function is given by Eq. (6) as

$$G_{ij}^{\vec{m}0}={}^0G_{ij}^{\vec{m}0}+\sum_{\substack{\vec{m}',\vec{m}''\\ k,l}}{}^0G_{ik}^{\vec{m}\vec{m}'}V_{kl}^{\vec{m}'\vec{m}''}G_{lj}^{\vec{m}''0}\,. \tag{D2}$$

For large distances ($R^{\vec{m}}\gg a$) we replace ${}^0G_{ik}^{\vec{m}\vec{m}'}$ by the elastic Green's function, which we may expand for $R^{\vec{m}'}\ll R^{\vec{m}}$ according to the short range of $V_{kl}^{\vec{m}'\vec{m}''}$ as

$$G_{ij}(\vec{R}^{\vec{m}}-\vec{R}^{\vec{m}'},\omega)=G_{ij}(\vec{R}^{\vec{m}},\omega)+\vec{R}^{\vec{m}'}\,\partial_{\vec{R}^{\vec{m}}}G_{ij}(\vec{R}^{\vec{m}},\omega)+\cdots\,. \tag{D3}$$

The first term of this expansion gives no contribution to Eq. (D2) since $\sum_{\vec{m}'}V^{\vec{m}\vec{m}'}$ vanishes (exactly for substitutional defects without mass changes and at least as ω^2 for interstitials and mass defects). The second term can be neglected since owing to the derivative it is smaller than ${}^0G_{ij}^{\vec{m}0}$ by a factor $R^{\vec{m}'}/R^{\vec{m}}\ll 1$ or $R^{\vec{m}'}\omega\ll c_{\sigma}$, respectively. Thus for large distances and small frequencies we obtain the result

$$G_{ij}^{\vec{m}0}(\omega)\cong{}^0G_{ij}^{\vec{m}0}(\omega)\,, \tag{D4}$$

i.e., the perfect and imperfect lattice Green's functions agree in this limit.

This result can be understood also by the following consideration: According to Eq. (31) we obtain

$$\partial_{\omega^2}{}^0G_{ij}^{00}(\omega)={}^0M\sum_{\vec{m},k}{}^0G_{ik}^{0\vec{m}}(\omega)\,{}^0G_{kj}^{\vec{m}0}(\omega)\,. \tag{D5}$$

Since all terms in Eq. (D5) are finite the divergence of $\partial_{\omega^2}{}^0G^{00}(\omega)\cong i\alpha/2\omega$ near $\omega=0$ (Appendix A) is due to the behavior of ${}^0G^{0\vec{m}}(\omega)$ for large distances. As shown in Sec. IV $\mathrm{Im}^0G^{00}(\omega)$ and $\mathrm{Im}G^{00}(\omega)$ agree for small frequencies, and the same is true for $\partial_{\omega^2}G(\omega)$ (Appendix C). To obtain the same divergence from (D5) the perfect and imperfect lattice Green's functions should agree for large distances.

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