

Theory of anharmonic processes in crystals with isotopic impurities

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A theory of the influence of isotopic impurities on phonon frequencies and bandwidths, based on the formalism of the retarded Green's functions, is presented. The theory takes into account both harmonic and anharmonic processes in the crystal and yields a proper self-energy that includes impurity-activated contributions depending on the concentration of the impurities and on a parameter λ defined as the ratio of the mass difference to the mass of the impurity atoms. The theory is developed up to second order in the parameter λ and in the concentration of impurities. Central to the theory is the technique of averaging the anharmonic-phonon propagators over the ensemble of impurity configurations. This gives rise to a proper self-energy that includes harmonic and anharmonic contributions to both the phonon shift and damping. The most important result is that processes linear in the quartic anharmonicity, that in the pure crystal contribute only to the phonon shift, in the presence of isotopic impurities give rise also to a contribution to the damping.

INTRODUCTION

It is well known that the presence of randomly distributed impurity sites in a crystal lattice can give rise to significant variations of its mechanical, electrical, thermal, and optical properties with respect to those of the pure solid. All these properties are, more or less, directly related to the structure of the manifold of phonon states and any variation induced in this structure by the presence of the impurities, will produce a corresponding alteration of the physical properties of the material.

If a given number of atoms or molecules of a different chemical nature are randomly substituted at the lattice sites of a crystal to corresponding atoms or molecules of the host crystal, both the kinetic and potential energy of the crystal are locally altered and, depending upon the size and nature of the guest species, the unit cells in which the substitutions take place, experience a deformation that propagates to the neighboring cells and may extend over several unit cells until, by progressive relaxation of the deformation, the original unit-cell structure is eventually recovered. This deformation is sufficient alone to induce changes in the phonon density of states and therefore to affect the physical properties of the material. In addition, however, new levels, associated to the vibrational motions of the guest species, will appear and these may fall in frequency regions where no levels of the host crystal are present, thus giving rise to new bands in the optical spectrum.

Of particular interest is the case in which the impurity species is of the same chemical nature, but with a different mass, i.e., the case of isotopic impurities. In this case no deformation of the unit cells at the substitutional sites occurs and, since the crystal potential remains the same as in the isotopically pure material, only the vibrational kinetic energy is affected by the mass impurities. The mechanisms by which the impurities perturb the phonon distribution will depend on the mass difference between the host and guest species.

Lattice phonons in an atomic crystal are true collective motions of the atoms. The impurity atoms are driven in the collective motion but, owing to their different mass, they will follow the motion with a different amplitude, giving thus rise to a change in the phase of the motion. The impurities play therefore the role of scattering centers for the phonons and their effect can then be described in terms of scattering processes. As a consequence, the collective motion is no longer a pure eigenstate of the harmonic crystal Hamiltonian, but corresponds to a superposition of several eigenstates, with different wave vectors \mathbf{k}_i . In the case of optical phonons this will lead to a broadening of the phonon band in infrared or Raman, since the presence of impurities breaks the translational symmetry and $\mathbf{k} \neq 0$ phonons will acquire optical activity.

If the mass difference is small, the variation in the amplitude of the impurity atoms is also small and the new phonons will have a spread of energy levels $\hbar\Delta\omega_i$ covering a range of wave vectors \mathbf{k}_i which differ very little from the wave vector \mathbf{k} of the unscattered phonon. This situation is often referred to as the "amalgamated band limit" in the sense that the new levels will fall inside the dispersion band of the original phonon. In the amalgamated band limit the scattering then becomes a true resonant scattering process whose efficiency is larger the closer the new levels are to that of the phonon considered.

If, instead, the mass difference is large enough, the impurity atoms will not be able to follow the collective motion and their displacement will be decoupled from those of the neighboring atoms, giving rise to isolated levels (separated band limit) which fall outside the phonon dispersion band and cannot propagate in the crystal. An isolated impurity level can then act as an energy trap in population decay processes, as long as the energy difference ΔE between the host and guest levels can be compensated by creation of another phonon.

In the case of molecular crystals the situation can be

described in exactly the same way as for atomic crystals in the region of the lattice vibrations. For phonons of translational nature the mass difference is between that of the molecule with one or more impurity atoms and that of the isotopically pure molecule. For librational phonons, in which the molecules perform small-angle rotational motions about their inertia axes, what matters is, instead, not the mass of the molecules but their inertia moments.

For high-frequency internal vibrons in molecular crystals the situation is slightly more complex, since the effect depends on the relative amplitude of the motion of the impurity atom with respect to the other atoms of the same molecule. Consider, for instance, a linear triatomic molecule like CO₂. In the symmetric stretching motion ν_1 the carbon atoms is at rest and therefore an isotopic impurity of ¹³C will have no effect on this vibration. In the case of the ν_2 bending and of the ν_3 antisymmetric stretching modes, the carbon atom moves and a molecule with a ¹³C isotopic impurity will possess a different frequency, giving rise to a different Davydov splitting of the crystal modes.

The most significant body of information on the effect of isotopic impurities on the optical phonon spectrum is obtained experimentally from phonon lifetime measurements by time-resolved spectroscopy or from equivalent band-profile measurements by infrared absorption or Raman scattering.¹⁻³ Phonon lifetimes are actually controlled by anharmonic terms of the crystal Hamiltonian which, by coupling together the phonons, give rise to a variety of energy decay or scattering processes. The effect of the impurities is to modify the channels open to phonon decay in the pure crystal, to add new channels as well as to give rise to new scattering processes. Any theoretical treatment of isotopic impurities in a crystal must be, therefore, necessarily carried out at the anharmonic level owing to the fact that the experimental data that can be used to test the theory are dominated by the anharmonic interactions.

The dynamics of crystals with impurities and defects has been the subject of a large number of investigations. Experimental data have been collected for ionic,⁴ molecular,⁵⁻⁷ and covalent crystals⁸ and different theoretical approaches have been proposed. Exhaustive reviews have been given by Maradudin⁹ and by Elliott.^{10,11} Most of the recent work has been concentrated on semiconductors¹² and molecular crystals.⁵⁻⁷ Recently the thermal conductivity of isotopically disordered anharmonic crystals has been discussed by Gairola^{13,14} whereas Gupta and Gairola¹⁵ have treated the problem of the infrared absorption of anharmonic crystals with impurities. Molecular crystals with impurities have been discussed by Klafter and Jortner¹⁶ in the framework of the Frenkel

excitons theory and by Abram and Hochstrasser¹⁷ for time-domain experiments.

In the present paper we address the general problem of the effect of substitutional isotopic impurities on the optical phonon spectrum of a crystal, presenting a theoretical treatment that allows actual calculations of phonon frequencies and lifetimes in crystals in presence of impurities. The treatment takes into account both harmonic and anharmonic processes involving isotopic impurity centers and, even if designed for crystals made of atoms, is easily extended to the lattice phonons of molecular crystals.

THEORY

In this section we consider an atomic crystal with an arbitrary structure. The positions of the atoms comprising it are given by the vector $r_{l\alpha} = r_l + r_\alpha$, where r_l defines the position of the l th unit cell and r_α ($\alpha = 1, 2, \dots, n$) gives the position of atom α in the l th unit cell. The mass of each atom of the unperturbed crystal is M . In the perturbed crystal a fraction c of all lattice sites is occupied by isotopic impurities of mass M' .

The vibrational crystal Hamiltonian can be written as

$$H = H_{\text{harm}} + H_{\text{imp}} + H_{\text{anh}} . \quad (1)$$

Here H_{harm} is the harmonic Hamiltonian of the unperturbed crystal,

$$H_{\text{harm}} = \sum_{\mu} \sum_{l\alpha} \frac{(P_{\mu}^{l\alpha})^2}{2M} + \frac{1}{2} \sum_{\mu\nu} \sum_{l\alpha} \sum_{l'\beta} \Phi_{\mu\nu} \begin{pmatrix} l & \alpha \\ l' & \beta \end{pmatrix} u_{\mu}^{l\alpha} u_{\nu}^{l'\beta} , \quad (2)$$

where $p_{\mu}^{l\alpha}$ and $u_{\mu}^{l\alpha}$ are the μ th components of the momentum and displacement of atom α in unit cell l , respectively, and the

$$\Phi_{\mu\nu} \begin{pmatrix} l & \alpha \\ l' & \beta \end{pmatrix}$$

are the harmonic force constants. The impurity Hamiltonian H_{imp} can be written in the form

$$H_{\text{imp}} = \sum_{\mu} \sum_{l\alpha} \left[\frac{1}{2M'} - \frac{1}{2M} \right] (P_{\mu}^{l\alpha})^2 c_{l\alpha} , \quad (3)$$

where $c_{l\alpha} = 1$ if $l\alpha$ is an impurity site and $c_{l\alpha} = 0$ if $l\alpha$ is a site of the host atoms. In what follows we shall treat $\{c_{l\alpha}\}$ as independent random variables defined by $c_{l\alpha} = 1$ with probability c , and $c_{l\alpha} = 0$ with probability $1 - c$.

If we retain only cubic and quartic terms, the anharmonic Hamiltonian H_{anh} has the form

$$H_{\text{anh}} = \frac{1}{3!} \sum_{\mu\nu\pi} \sum_{l\alpha} \sum_{l'\beta} \sum_{l''\gamma} \Phi_{\mu\nu\pi} \begin{pmatrix} l & l' & l'' \\ \alpha & \beta & \gamma \end{pmatrix} u_{\mu}^{l\alpha} u_{\nu}^{l'\beta} u_{\pi}^{l''\gamma} + \frac{1}{4!} \sum_{\mu\nu\rho} \sum_{l\alpha} \sum_{l'\beta} \sum_{l''\gamma} \sum_{l'''\delta} \Phi_{\mu\nu\rho} \begin{pmatrix} l & l' & l'' & l''' \\ \alpha & \beta & \gamma & \delta \end{pmatrix} u_{\mu}^{l\alpha} u_{\nu}^{l'\beta} u_{\pi}^{l''\gamma} u_{\rho}^{l'''\delta} , \quad (4)$$

where

$$\Phi_{\mu\nu\pi} \begin{pmatrix} l & l' & l'' \\ \alpha & \beta & \gamma \end{pmatrix}$$

and

$$\Phi_{\mu\nu\pi\rho} \begin{pmatrix} l & l' & l'' & l''' \\ \alpha & \beta & \gamma & \delta \end{pmatrix}$$

are the cubic and quartic force constants, respectively. In these expressions l, l', l'', l''' count unit cells, $\alpha, \beta, \gamma, \delta$ count atoms in the unit cell, and μ, ν, π, ρ label Cartesian components ($\mu, \nu, \pi, \rho = x, y, z$) of the atomic displacements.

The transition to phonon field A_{kj} and momentum B_{kj} operators is carried out through the expressions

$$u_{\mu}^{l\alpha} = \left[\frac{\hbar}{2NM} \right]^{1/2} \sum_{kj} (\omega_{kj})^{-1/2} w_{\mu}(\alpha|kj) e^{i\mathbf{k}\cdot\mathbf{r}_l} A_{kj}, \quad (5a)$$

$$P_{\mu}^{l\alpha} = \frac{1}{i} \left[\frac{\hbar M}{2N} \right]^{1/2} \sum_{kj} (\omega_{kj})^{1/2} w_{\mu}(\alpha|kj) e^{i\mathbf{k}\cdot\mathbf{r}_l} B_{kj}. \quad (5b)$$

Here ω_{kj} is the frequency of the normal mode of the harmonic crystal defined by the wave vector \mathbf{k} and the branch index j , $w(\alpha|kj)$ is the corresponding unit polarization vector and N is the number of primitive unit cells in the crystal. The N values of k allowed by cyclic boundary conditions are uniformly and densely distributed through the first Brillouin zone of the crystal. The operators A_{kj} and B_{kj} can be expressed in terms of creation b_{kj}^{\dagger} and destruction b_{kj} operators of the ω_{kj} phonons as

$$A_{kj} = b_{kj} + b_{-kj}^{\dagger}, \quad (6a)$$

$$B_{kj} = b_{kj} - b_{-kj}^{\dagger}, \quad (6b)$$

and satisfy the commutation relations

$$[A_{kj}, A_{k'j'}] = [B_{kj}, B_{k'j'}] = 0, \quad (7a)$$

$$[A_{kj}, B_{k'j'}] = -2\Delta(\mathbf{k} + \mathbf{k}') \delta_{jj'}. \quad (7b)$$

H_{harm} , H_{imp} , and H_{anh} of Eq. (1) assume, in terms of these operators, the form

$$H_{\text{harm}} = \frac{1}{4} \sum_{kj} \hbar \omega_{kj} [B_{kj}^{\dagger} B_{kj} + A_{kj}^{\dagger} A_{kj}], \quad (8a)$$

$$H_{\text{imp}} = \sum_{k_1 j_1} \sum_{k_2 j_2} V_{k_1 j_1, k_2 j_2}^2 B_{k_1 j_1} B_{k_2 j_2}, \quad (8b)$$

$$H_{\text{anh}} = \sum_{k_1 j_1} \sum_{k_2 j_2} \sum_{k_3 j_3} V_{k_1 j_1, k_2 j_2, k_3 j_3}^{(3)} A_{k_1 j_1} A_{k_2 j_2} A_{k_3 j_3} + \sum_{k_1 j_1} \sum_{k_2 j_2} \sum_{k_3 j_3} \sum_{k_4 j_4} V_{k_1 j_1, k_2 j_2, k_3 j_3, k_4 j_4}^{(4)} A_{k_1 j_1} A_{k_2 j_2} A_{k_3 j_3} A_{k_4 j_4}, \quad (8c)$$

where

$$V_{\kappa\kappa'}^{(2)} = -\hbar \frac{\lambda}{4N} (\omega_{\kappa} \omega_{\kappa'})^{1/2} \sum_{l\alpha} c_{l\alpha} \mathbf{w}(\alpha|\kappa') \cdot \mathbf{w}(\alpha|\kappa'') e^{i(\mathbf{k}' + \mathbf{k}'') \cdot \mathbf{r}_l}. \quad (9)$$

In these expressions $\lambda = (M/M') - 1$ and the coefficients $V_{k_1 j_1, k_2 j_2, k_3 j_3}^{(3)}$ and $V_{k_1 j_1, k_2 j_2, k_3 j_3, k_4 j_4}^{(4)}$ are the Fourier transform of the cubic and quartic force constants, respectively. For simplicity we shall use from now on the collective symbol κ for both the wave vector label k and the branch label j . The label $-\kappa$ will mean obviously $-k, j$. Only when necessary shall we specify both labels in the text.

In order to obtain the line shape of the phonon ω_{kj} we solve the equations of motion for the retarded Green's function

$$G(\kappa; \kappa'; t) = -i \Theta(t) \langle [A_{\kappa}(t), A_{\kappa'}^{\dagger}(0)] \rangle, \quad (10)$$

where $\Theta(t)$ is the Heaviside unit step function and the symbol $\langle \dots \rangle$ denotes the average with respect to the canonical ensemble defined by the Hamiltonian.

In the frequency space the equation of motion has the form

$$\begin{aligned} \hbar \omega \langle\langle A_{\kappa}; A_{\kappa'}^{\dagger} \rangle\rangle &= \hbar \langle [A_{\kappa}, A_{\kappa'}^{\dagger}] \rangle + \langle\langle [A_{\kappa}, H]; A_{\kappa'}^{\dagger} \rangle\rangle \\ &= \hbar \langle [A_{\kappa}, A_{\kappa'}^{\dagger}] \rangle + \langle\langle [A_{\kappa}, H_{\text{harm}} + H_{\text{imp}} + H_{\text{anh}}]; A_{\kappa'}^{\dagger} \rangle\rangle, \end{aligned} \quad (11)$$

where the symbols $\langle\langle \dots \rangle\rangle$ and $\langle [\dots] \rangle$ represent the Green's function in the frequency space and the average of commutators respectively. Using the standard commutation properties of the phonon operators we obtain

$$\langle [A_{\kappa}, A_{\kappa'}^{\dagger}] \rangle = 0, \quad (12)$$

$$\langle\langle [A_{\kappa}, H_{\text{harm}}]; A_{\kappa'}^{\dagger} \rangle\rangle = \hbar \omega_{\kappa} \langle\langle B_{\kappa}; A_{\kappa'}^{\dagger} \rangle\rangle, \quad (13)$$

$$\langle\langle [A_{\kappa}, H_{\text{imp}}]; A_{\kappa'}^{\dagger} \rangle\rangle = -4 \sum_{\kappa_1} V_{-\kappa\kappa_1}^{(2)} \langle\langle B_{\kappa_1}; A_{\kappa'}^{\dagger} \rangle\rangle, \quad (14)$$

$$\langle\langle [A_{\kappa}, H_{\text{anh}}]; A_{\kappa'}^{\dagger} \rangle\rangle = 0. \quad (15)$$

By substitution in Eq. (11) we have

$$\hbar\omega \langle\langle A_{\kappa}; A_{\kappa'}^{\dagger} \rangle\rangle = \hbar\omega_{\kappa} \langle\langle B_{\kappa}; A_{\kappa'}^{\dagger} \rangle\rangle + \sum_{\kappa_1} (-4V_{-\kappa\kappa_1}^{(2)}) \langle\langle B_{\kappa_1}; A_{\kappa'}^{\dagger} \rangle\rangle. \quad (16)$$

Equation (16) involves the Green's function $G(\kappa; \kappa'; \omega) = \langle\langle A_{\kappa}; A_{\kappa'}^{\dagger} \rangle\rangle$ and the new Green's functions $F(\kappa; \kappa'; \omega) = \langle\langle B_{\kappa}; A_{\kappa'}^{\dagger} \rangle\rangle$ and $F(\kappa_1; \kappa'; \omega) = \langle\langle B_{\kappa_1}; A_{\kappa'}^{\dagger} \rangle\rangle$. To obtain these new functions we write down their equations of motion and continue the process until we can truncate the resulting system of equations by a decoupling procedure. In this way we obtain

$$G(\kappa; \kappa'; \omega) = g_{\kappa}^0 [\Delta(\mathbf{k} - \mathbf{k}') \delta_{jj'} + U_{\kappa\kappa'}^{(2)}] + g_{\kappa}^0 \sum_{\kappa_1} U_{\kappa\kappa_1}^{(2)} \left[\frac{\omega_{\kappa_1}}{2} \right] G(\kappa_1; \kappa'; \omega) + g_{\kappa}^0 \frac{1}{2\hbar} \sum_{\kappa_1} [\Delta(\mathbf{k} - \mathbf{k}_1) \delta_{jj_1} + U_{\kappa\kappa_1}^{(2)}] \langle\langle [B_{\kappa_1}, H_{\text{anh}}]; A_{\kappa'}^{\dagger} \rangle\rangle, \quad (17)$$

where

$$U_{\kappa\kappa'}^{(2)} = -\frac{4}{\hbar} \frac{V_{-\kappa\kappa'}^{(2)}}{\omega_{\kappa}}, \quad (18)$$

$$g_{\kappa}^0 = \frac{2\omega_{\kappa}}{\omega^2 - \omega_{\kappa}^2}.$$

For the calculation of the new Green's function $\langle\langle [B_{\kappa_1}, H_{\text{anh}}]; A_{\kappa'}^{\dagger} \rangle\rangle$ we shall limit ourselves to the two lowest-order anharmonic processes, represented in the diagrammatic expression of the self-energy by the two diagrams in Fig. 1. The contribution to the self-energy of these two processes is given in many books and review articles¹⁸ and can be written in the form

$$\frac{1}{2\hbar} \langle\langle [B_{\kappa_1}, H_{\text{anh}}]; A_{\kappa'}^{\dagger} \rangle\rangle = \sum_{\kappa_1\kappa_2} W_{\kappa_1\kappa_2} \langle\langle A_{\kappa_2}; A_{\kappa'}^{\dagger} \rangle\rangle = \sum_{\kappa_1\kappa_2} W_{\kappa_1\kappa_2} G(\kappa_2; \kappa'; \omega), \quad (19)$$

where

$$W_{\kappa_1\kappa_2} = W_{\kappa_1\kappa_2}^{(a)} + W_{\kappa_1\kappa_2}^{(b)} \quad (20)$$

with

$$W_{\kappa_1\kappa_2}^{(a)} = 12\hbar^{-1} \sum_{\kappa_3} V_{-\kappa_1\kappa_2\kappa_3-\kappa_3}^{(4)} (2n_{\kappa_3} + 1), \quad (21a)$$

$$W_{\kappa_1\kappa_2}^{(b)} = 18\hbar^{-2} \sum_{\kappa_3\kappa_4} V_{-\kappa_1\kappa_3\kappa_4}^{(3)} V_{\kappa_2-\kappa_3-\kappa_4}^{(3)} \times \left[\frac{n_{\kappa_3} + n_{\kappa_4} + 1}{\omega - \omega_{\kappa_3} - \omega_{\kappa_4}} + \frac{n_{\kappa_3} - n_{\kappa_4}}{\omega + \omega_{\kappa_3} - \omega_{\kappa_4}} + \frac{n_{\kappa_4} - n_{\kappa_3}}{\omega - \omega_{\kappa_3} + \omega_{\kappa_4}} \right]. \quad (21b)$$

In these expressions n_{κ} is the statistical average of the phonon occupation number given by

$$n_{\kappa} = \left[\exp \frac{\hbar\omega_{\kappa}}{KT} - 1 \right]^{-1}. \quad (22)$$

Inclusion of higher-order diagrams simply requires the addition to $W_{\kappa_1\kappa_2}$ of their contribution to the self-energy which can be found in recent literature.¹⁹ When Eq. (19) is substituted in Eq. (17) we obtain

$$G(\kappa; \kappa'; \omega) = g_{\kappa}^0 [\Delta(\mathbf{k} - \mathbf{k}') \delta_{jj'} + U_{\kappa\kappa'}^{(2)}] + g_{\kappa}^0 \sum_{\kappa_1} U_{\kappa\kappa_1}^{(2)} \left[\frac{\omega_{\kappa_1}}{2} \right] G(\kappa_1; \kappa'; \omega) + g_{\kappa}^0 \sum_{\kappa_1\kappa_2} [\Delta(\mathbf{k} - \mathbf{k}_1) \delta_{jj_1} + U_{\kappa\kappa_1}^{(2)}] \times W_{\kappa_1\kappa_2} G(\kappa_2; \kappa'; \omega). \quad (23)$$

Equation (23) is a stochastic equation because the coefficients $U_{\kappa\kappa'}^{(2)}$ and $U_{\kappa\kappa_1}^{(2)}$ are stochastic quantities. We need thus to average these quantities over the ensemble of impurity configurations, i.e., we do not need $G(\kappa; \kappa'; \omega)$ itself but its average $\langle G(\kappa; \kappa'; \omega) \rangle$. From this averaged Green's function we can extract the proper self-energy

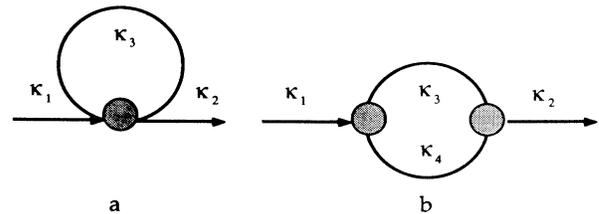


FIG. 1. Diagrammatic expression of the self-energy.

which determines the frequency shift and width of the phonon ω_κ due to the combined effect of anharmonicity and disorder. We begin by introducing the Green's function

$$G^0(\kappa; \kappa'; \omega) = \langle\langle A_\kappa; A_{\kappa'}^\dagger \rangle\rangle_{\text{harm}}, \tag{24}$$

which is the solution of Eq. (23) when the effect of anharmonicity is neglected. It therefore satisfies the equation

$$G^0(\kappa; \kappa'; \omega) = g_\kappa^0 [\Delta(\mathbf{k} - \mathbf{k}') \delta_{jj'} + U_{\kappa\kappa'}^{(2)}] + g_\kappa^0 \sum_{\kappa_1} U_{\kappa\kappa_1}^{(2)} \left[\frac{\omega_{\kappa_1}}{2} \right] G^0(\kappa_1; \kappa'; \omega). \tag{25}$$

In order to obtain $\langle G^0(\kappa; \kappa'; \omega) \rangle$ we rewrite Eq. (25) in the standard form of Dyson's equation:

$$G^0(\kappa; \kappa'; \omega) = g_\kappa^0 \Delta(\mathbf{k} - \mathbf{k}') \delta_{jj'} + g_\kappa^0 \sum_{\kappa_1} \hat{U}_{\kappa\kappa_1}^{(2)} G^0(\kappa_1; \kappa'; \omega). \tag{26}$$

A comparison of Eqs. (25) and (26) shows that the effective vertex function $\hat{U}_{\kappa\kappa_1}^{(2)}$ is given in terms of the vertex function $U_{\kappa\kappa_1}^{(2)}$ by

$$\hat{U}_{\kappa\kappa'}^{(2)} = \sum_{\kappa_1} [\vec{I} + \vec{U}^{(2)}]_{\kappa\kappa'}^{-1} U_{\kappa_1\kappa'}^{(2)} \frac{\omega^2}{2\omega_{\kappa'}} \cong \left[U_{\kappa\kappa'}^{(2)} - \sum_{\kappa_1} U_{\kappa\kappa_1}^{(2)} U_{\kappa_1\kappa'}^{(2)} \right] \frac{\omega^2}{2\omega_{\kappa'}}. \tag{27}$$

We can now apply the smoothing method²⁰ to obtain from Eq. (27) the equation satisfied by $\langle G^0(\kappa; \kappa'; \omega) \rangle$. The result can be written in the form

$$\langle G^0(\kappa; \kappa'; \omega) \rangle = \Delta(\mathbf{k} - \mathbf{k}') \delta_{jj'} g_\kappa^0 + g_\kappa^0 \sum_{\kappa_1} \langle M_{\kappa\kappa_1}^0(\omega) \rangle \langle G^0(\kappa_1; \kappa'; \omega) \rangle, \tag{28}$$

where the averaged proper self-energy $\langle M_{\kappa\kappa_1}^0(\omega) \rangle$ is given by

$$\langle M_{\kappa\kappa'}^0(\omega) \rangle = \langle \hat{U}_{\kappa\kappa'}^{(2)} \rangle + \sum_{\kappa_1\kappa_2} \{ \langle \hat{U}_{\kappa\kappa_1}^{(2)} \langle G^0(\kappa_1; \kappa_2; \omega) \rangle \hat{U}_{\kappa_2\kappa'}^{(2)} \rangle - \langle \hat{U}_{\kappa\kappa_1}^{(2)} \rangle \langle G^0(\kappa_1; \kappa_2; \omega) \rangle \langle \hat{U}_{\kappa_2\kappa'}^{(2)} \rangle \} + O(\hat{U}^{(2)})^3. \tag{29}$$

Equations (28) and (29) must be solved together to yield both $\langle G^0(\kappa; \kappa', \omega) \rangle$ and $\langle M_{\kappa, \kappa'}^0(\omega) \rangle$. Since we are primarily interested in qualitative rather than in quantitative results, we can simplify the solution of these equations by making the assumption, well satisfied by most isotopic impurities, that the parameter λ is small compared to unity and working only to second order in λ . We also use the result that the restoration of periodicity to the disordered crystal has the consequence that both $\langle G^0(\kappa; \kappa', \omega) \rangle$ and $\langle M_{\kappa, \kappa'}^0(\omega) \rangle$ are diagonal in \mathbf{k} and \mathbf{k}' :

$$\langle G^0(\kappa; \kappa', \omega) \rangle = \Delta(\mathbf{k} - \mathbf{k}') G^0(kj j', \omega), \tag{30a}$$

$$\langle M_{\kappa, \kappa'}^0(\omega) \rangle = \Delta(\mathbf{k} - \mathbf{k}') M_{kj j'}^0(\omega). \tag{30b}$$

The fact that $G^0(kj j', \omega)$ and $M_{kj j'}^0(\omega)$ are not diagonal in j and j' is referred to as polarization mixing:

$$G^0(kj j'; \omega) = [(\vec{g}_k^0)^{-1} - \vec{M}_k^0]_{jj'}^{-1}. \tag{31}$$

From Eqs. (27), (29), and (30) we find that the equation for $M_{kj j'}^0(\omega)$ takes the form

$$M_{kj j'}^0(\omega) = \delta_{jj'} c \frac{\omega^2}{2\omega_{kj}} \lambda(1 - \lambda) + \frac{\omega^4 \lambda^2}{4} c(1 - c) \sum_{\alpha} \sum_{\mu\nu} \frac{w_\mu^*(\alpha|kj)}{\omega_{kj}^{1/2}} \left[\frac{1}{N} \sum_{k_1} \sum_{j_1 j_2} \frac{w_\mu(\alpha|k_1 j_1)}{\omega_{k_1 j_1}^{1/2}} G^0(k_1 j_1 j_2; \omega) \frac{w_\nu^*(\alpha|k_1 j_2)}{\omega_{k_1 j_2}^{1/2}} \right] \frac{w_\nu(\alpha|kj')}{\omega_{kj'}^{1/2}}. \tag{32}$$

When Eq. (31) is substituted in Eq. (32) the result is a nonlinear integral equation for $M_{kj j'}^0(\omega)$, which can only be solved numerically. The solution of Eq. (32) yields a proper self-energy that gives rise to a frequency-dependent shift and damping of the phonon ω_{kj} . This can be seen from the result for $M_{kj j'}^0(\omega)$ that is obtained when $G^0(kj j', \omega)$ is replaced by its unperturbed value

$$G^0(kj_1 j_2; \omega) = \delta_{j_1 j_2} \frac{2\omega_{k_1 j_1}}{\omega^2 - \omega_{k_1 j_1}^2}, \tag{33}$$

$$M_{kj j'}^{(0)}(\omega) = \delta_{jj'} c \frac{\omega^2}{2\omega_{kj}} \lambda(1 - \lambda) + \frac{\omega^4 \lambda^2}{2} c(1 - c) \sum_{\alpha} \sum_{\mu\nu} \frac{w_\mu^*(\alpha|kj)}{\omega_{kj}^{1/2}} \left[\frac{1}{N} \sum_{k_1 j_1} \frac{w_\mu(\alpha|k_1 j_1) w_\nu^*(\alpha|k_1 j_1)}{\omega^2 - \omega_{k_1 j_1}^2} \right] \frac{w_\nu(\alpha|kj')}{\omega_{kj'}^{1/2}}. \tag{34}$$

This result could serve as the starting point for the iterative solution of Eq. (32). It is clear that the first term on the right-hand side of Eq. (34) contributes only to the shift of the phonon frequency due to the isotopic disorder, while the second term contributes to both the shift and width of the phonon.

We now turn to a consideration of Eq. (23). Using Eq. (25) we can rewrite Eq. (23) in the more convenient form

$$G(\kappa; \kappa'; \omega) = G^0(\kappa; \kappa'; \omega) + \sum_{\kappa_1 \kappa_2} G^0(\kappa; \kappa_1; \omega) W_{\kappa_1 \kappa_2} G(\kappa_2; \kappa'; \omega) \quad (35)$$

from which we see that, if we seek the proper self-energy to no higher than the first in $W_{\kappa \kappa'}$, it suffices to solve Eq. (35) by iteration to first order in $W_{\kappa \kappa'}$ and to study the equation

$$\langle G(\kappa; \kappa'; \omega) \rangle = \langle G^0(\kappa; \kappa'; \omega) \rangle + \sum_{\kappa_1 \kappa_2} \langle G^0(\kappa; \kappa_1; \omega) W_{\kappa_1 \kappa_2} G^0(\kappa_2; \kappa'; \omega) \rangle, \quad (36)$$

which requires the evaluation of the average $\langle G^0(\kappa; \kappa_1; \omega) G^0(\kappa_2; \kappa'; \omega) \rangle$. For this we make use of the fact that $W_{\kappa_1 \kappa_2}$ vanishes unless $\mathbf{k}_1 = \mathbf{k}_2$, which has the consequence that the average we need to consider is $\langle G^0(kj; k_1 j_1; \omega) G^0(k_1 j_2; k' j'; \omega) \rangle$. If we denote the transpose by a tilde $G^0(k_1 j_2; k' j'; \omega) = \tilde{G}^0(k' j'; k_1 j_2; \omega)$, the average of interest is thus $\langle G^0(kj; k_1 j_1; \omega) \tilde{G}^0(k' j'; k_1 j_2; \omega) \rangle$ which satisfies the following Bethe-Salpeter equation.²⁰

$$\begin{aligned} \langle G^0(kj; k_1 j_1) \tilde{G}^0(k' j'; k_1 j_2) \rangle &= \langle G^0(kj; k_1 j_1) \rangle \langle \tilde{G}^0(k' j'; k_1 j_2) \rangle \\ &+ \sum_{k_3 j_3} \sum_{k_4 j_4} \sum_{k_5 j_5} \sum_{k_6 j_6} \langle G^0(kj; k_3 j_3) \rangle \langle \tilde{G}^0(k' j'; k_4 j_4) \rangle \langle \Gamma_{k_3 j_3 k_4 j_4 k_5 j_5 k_6 j_6} \rangle \\ &\quad \times \langle G^0(k_5 j_5; k_1 j_1) \tilde{G}^0(k_6 j_6; k_1 j_2) \rangle, \end{aligned} \quad (37)$$

where, to simplify the notation, we have dropped explicit reference to the frequency ω . The function $\langle \Gamma_{k_3 j_3 k_4 j_4 k_5 j_5 k_6 j_6} \rangle$ is the irreducible vertex function. It is given, in general, by²¹

$$\langle \Gamma_{k_3 j_3 k_4 j_4 k_5 j_5 k_6 j_6} \rangle = \frac{\delta \langle M_{k_3 j_3 k_4 j_4}^0 \rangle}{\delta \langle G^0 k_5 j_5; k_6 j_6 \rangle}. \quad (38)$$

This relation, which has the nature of a Ward identity, shows that one cannot consistently approximate $\langle \Gamma_{k_3 j_3 k_4 j_4 k_5 j_5 k_6 j_6} \rangle$ independently of the approximations made in obtaining the proper self-energy $\langle M_{k_3 j_3 k_4 j_4}^0 \rangle$. If we use the approximation of Eq. (29) for the latter function, our approximation to the former must be

$$\langle \Gamma_{k_3 j_3 k_4 j_4 k_5 j_5 k_6 j_6} \rangle \cong \langle \hat{U}_{k_3 j_3 k_5 j_5}^{(2)} \hat{U}_{k_4 j_4 k_6 j_6}^{(2)} \rangle - \langle \hat{U}_{k_3 j_3 k_5 j_5}^{(2)} \rangle \langle \hat{U}_{k_4 j_4 k_6 j_6}^{(2)} \rangle. \quad (39)$$

However, since we have approximated $\hat{U}_{kj k' j'}^{(2)}$ by $(U_{kj k' j'}^{(2)}) (\omega^2 / 2\omega_{kj'})$ in evaluating the second term on the right-hand side of Eq. (29) to obtain Eq. (32), our consistent approximation to the irreducible vertex function is

$$\langle \Gamma_{k_3 j_3 k_4 j_4 k_5 j_5 k_6 j_6} \rangle = \frac{\lambda^2 \omega^4}{4N} \frac{c(1-c) \Delta(\mathbf{k}_3 - \mathbf{k}_5 + \mathbf{k}_6 - \mathbf{k}_4)}{(\omega_{k_3 j_3} \omega_{k_4 j_4} \omega_{k_5 j_5} \omega_{k_6 j_6})^{1/2}} \sum_{\alpha} \sum_{\mu \nu} e_{\mu}^*(\alpha | k_3 j_3) e_{\mu}(\alpha | k_5 j_5) e_{\nu}^*(\alpha | k_6 j_6) e_{\nu}(\alpha | k_4 j_4), \quad (40)$$

where $e_{\mu}(\alpha | kj) = \omega_{\mu}(\alpha | kj) \exp(i\mathbf{k} \cdot \mathbf{r}_{\alpha})$. The proportionality of $\langle \Gamma_{k_3 j_3 k_4 j_4 k_5 j_5 k_6 j_6} \rangle$ to $\Delta(\mathbf{k}_3 - \mathbf{k}_5 + \mathbf{k}_6 - \mathbf{k}_4)$ is general and not specific to the approximation made in obtaining Eq. (40). Equation (37) can now be written as

$$\begin{aligned} \langle G^0(kj; k_1 j_1) \tilde{G}^0(k' j'; k_1 j_2) \rangle &= \Delta(\mathbf{k} - \mathbf{k}_1) \Delta(\mathbf{k}' - \mathbf{k}_1) G^0(kj j_1) \tilde{G}^0(k' j' j_2) \\ &+ \frac{\lambda^2 \omega^4}{4} c(1-c) \sum_{j_3 j_4} \frac{G^0(kj j_3)}{(\omega_{k_3 j_3})^{1/2}} \frac{\tilde{G}^0(k' j' j_4)}{(\omega_{k_4 j_4})^{1/2}} \frac{1}{N} \\ &\quad \times \sum_{k_5 j_5} \sum_{k_6 j_6} \frac{\Delta(\mathbf{k} - \mathbf{k}_5 + \mathbf{k}_6 - \mathbf{k}')}{(\omega_{k_5 j_5} \omega_{k_6 j_6})^{1/2}} \\ &\quad \times \sum_{\alpha} \sum_{\mu \nu} e_{\mu}^*(\alpha | k j_3) e_{\mu}(\alpha | k_5 j_5) e_{\nu}^*(\alpha | k_6 j_6) e_{\nu}(\alpha | k' j_4) \\ &\quad \times \langle G^0(k_5 j_5; k_1 j_1) \tilde{G}^0(k_6 j_6; k_1 j_2) \rangle. \end{aligned} \quad (41)$$

If we make the ansatz

$$\langle G^0(kj; k_1 j_1) \tilde{G}^0(k' j'; k_1 j_2) \rangle = \Delta(\mathbf{k} - \mathbf{k}') G^1(kj j_1 | k_1 j' j_2), \quad (42)$$

the equation satisfied by $G^1(kj j_1; k_1 j' j_2)$ is

$$\begin{aligned}
 G^1(kjj_1|k_1j'j_2) &= \Delta(\mathbf{k}-\mathbf{k}_1)G^0(kjj_1)\tilde{G}^0(kj'j_2) \\
 &+ \frac{\lambda^2\omega^4}{4}c(1-c)\sum_{j_3j_4}\frac{G^0(kjj_3)\tilde{G}^0(kj'j_4)}{(\omega_{kj_3}\omega_{kj_4})^{1/2}}\frac{1}{N} \\
 &\quad \times \sum_{k_5j_5j_6}\sum_{\alpha}\sum_{\mu\nu}e_{\mu}^*(\alpha|kj_3)e_{\nu}(\alpha|kj_4)\frac{e_{\mu}(\alpha|k_5j_5)}{(\omega_{k_5j_5})^{1/2}}\frac{e_{\nu}^*(\alpha|k_5j_6)}{(\omega_{k_5j_6})^{1/2}}G^1(k_5j_5j_1|k_1j_6j_2).
 \end{aligned}
 \tag{43}$$

This is an integral equation with a separable kernel whose solution is

$$\begin{aligned}
 G^1(kjj_1|k_1j'j_2) &= \Delta(\mathbf{k}-\mathbf{k}_1)G^0(kjj_1)\tilde{G}^0(kj'j_2) \\
 &+ \frac{\lambda^2\omega^4}{4}c(1-c)\sum_{j_3j_4}\sum_{j_5j_6}G^0(kjj_3)\frac{1}{N} \\
 &\quad \times \sum_{\alpha\beta}\sum_{\mu\nu}\sum_{\sigma\tau}\frac{e_{\mu}^*(\alpha|kj_3)e_{\nu}(\alpha|kj_4)}{(\omega_{kj_3}\omega_{kj_4})^{1/2}}\left[\vec{I}-\frac{\lambda^2\omega^4}{4}c(1-c)\vec{D}\right]_{\alpha\beta}^{-1}{}_{\mu\nu\rho\sigma}G^0(k_1j_5j_1) \\
 &\quad \times \frac{e_{\sigma}(\beta|k_1j_5)}{(\omega_{k_1j_5})^{1/2}}\frac{e_{\tau}^*(\beta|k_1j_6)}{(\omega_{k_1j_6})^{1/2}}G^0(kj_2j_6)G^0(kj_2j').
 \end{aligned}
 \tag{44}$$

In writing Eq. (44) we have used the matrices

$$I\begin{pmatrix} \alpha & \beta \\ \mu\nu & \sigma\tau \end{pmatrix} = \delta_{\alpha\beta}\delta_{\mu\nu}\delta_{\sigma\tau}, \tag{45a}$$

$$D\begin{pmatrix} \alpha & \beta \\ \mu\nu & \sigma\tau \end{pmatrix} = \frac{1}{N}\sum_k f_{\mu\sigma}(\alpha\beta|k)\tilde{f}_{\nu\tau}(\alpha\beta|k), \tag{45b}$$

where

$$f_{\mu\sigma}(\alpha\beta|k) = \sum_{jj'}\frac{e_{\mu}(\alpha|kj')}{(\omega_{kj'})^{1/2}}G^0(kjj')\frac{e_{\sigma}^*(\beta|kj')}{(\omega_{kj'})^{1/2}}. \tag{46}$$

With the use of Eqs. (42) and (44) we find that

$$\sum_{k_1}\sum_{j_1j_2}\langle G^0(kj;k_1j_1)W_{k_1j_1j_2}G^0(k_1j_2;k'j') \rangle = \Delta(\mathbf{k}-\mathbf{k}')\sum_{j_1j_2}G^0(kjj_1)M_{k_1j_1j_2}^1(\omega)G^0(kj_2j'), \tag{47}$$

where

$$\begin{aligned}
 M_{k_1j_1j_2}^1(\omega) &= W_{k_1j_1j_2} + \frac{\lambda^2\omega^4}{4}c(1-c)\sum_{j_3j_4}\sum_{j_5j_6}\frac{1}{N}\sum_{k_1}\sum_{\alpha\beta}\sum_{\mu\nu}\sum_{\sigma\tau}\frac{e_{\mu}^*(\alpha|kj_1)e_{\sigma}(\beta|k_1j_5)}{(\omega_{kj_1}\omega_{k_1j_5})^{1/2}}\left[\vec{I}-\frac{\lambda^2\omega^4}{4}c(1-c)\vec{D}\right]_{\alpha\beta}^{-1}{}_{\mu\nu\rho\sigma} \\
 &\quad \times G^0(k_1j_5j_3)W_{k_1j_3j_4}G^0(k_1j_4j_6)\frac{e_{\tau}^*(\beta|k_1j_6)e_{\nu}(\alpha|kj_2)}{(\omega_{k_1j_6}\omega_{kj_2})^{1/2}}.
 \end{aligned}
 \tag{48}$$

We can now combine the result given by Eqs. (36), (30), (31), and (47) to write

$$\begin{aligned}
 \langle G(kj;k'j';\omega) \rangle &= \Delta(\mathbf{k}-\mathbf{k}')\left[G^0(kjj';\omega) + \sum_{j_1j_2}G^0(kjj_1;\omega)M_{k_1j_1j_2}^1(\omega)G^0(kj_2j';\omega) + \dots\right] \\
 &\cong \Delta(\mathbf{k}-\mathbf{k}')[(\vec{G}_k^0)^{-1} - \vec{M}_k^1(\omega)]_{jj'}^{-1} \\
 &= \Delta(\mathbf{k}-\mathbf{k}')[(\vec{G}_k^0)^{-1} - \vec{M}_k^0(\omega) - \vec{M}_k^1(\omega)]_{jj'}^{-1}.
 \end{aligned}
 \tag{49}$$

The essential new result obtained here is the contribution to the proper self-energy that is obtained when the vertex $W_{k_1 j_3 j_4}$ in the second term on the right-hand side of Eq. (48) is replaced by $W_{k_1 j_3 j_4}^{(a)}$ [see Eqs. (20) and (21)]. The imaginary part of this contribution that results from replacing ω by $\omega - i\eta$ [Eq. (52)] is a frequency-dependent contribution to the damping constant $\Gamma_{kj}(\omega)$ that is *linear* in the quartic anharmonicity and is nonzero only because of the presence of the impurities. From Eq. (21a) it follows that this defect-activated contribution is a linear function of the absolute temperature T in the classical regime of high temperatures. The contribution to the proper self-energy that is obtained when $W_{k_1 j_3 j_4}$ in the second term on the right-hand side of Eq. (48) is replaced by $W_{k_1 j_3 j_4}^{(b)}$ [see Eqs. (20) and (21)] yields a defect-activated contribution to $\Gamma_{kj}(\omega)$ that is of second order in the cubic anharmonicity. However, inasmuch as the first term in $M_{kjj'}^{(a)}(\omega)$ [Eq. (48)] already yields a contribution to $\Gamma_{kj}(\omega)$ of the same order in the anharmonicity independent of the presence of impurities, the defect-activated contribution is a small addition to the latter.

Thus, the proper self-energy matrix $M_{kjj'}(\omega)$ is given by

$$M_{kjj'}(\omega) = M_{kjj'}^0(\omega) + M_{kjj'}^1(\omega) . \quad (50)$$

The contribution $M_{kjj'}^0(\omega)$ is that from the isotopic impurities alone; the first term in $M_{kjj'}^1(\omega)$ is the contribution from the cubic and quartic anharmonicity alone; the second term in $M_{kjj'}^1(\omega)$ is the contribution that arises from the combined effect of the anharmonicity and of the isotopic impurities.

If we approximate $M_{kjj'}(\omega)$ by its diagonal part, to obtain a qualitative feeling for the content of these results

$$M_{kjj}(\omega) = \delta_{jj'} M_{kjj}(\omega) = \delta_{jj'} M_{kj}(\omega) \quad (51)$$

and define

$$M_{kj}(\omega \pm i\eta) = \Delta_{kj}(\omega) \mp \Gamma_{kj}(\omega) , \quad (52)$$

where η is a positive infinitesimal, then the spectral density $\rho_{kj}(\omega)$ of the phonon ω_{kj} , defined as

$$\begin{aligned} \rho_{kj}(\omega) &= \int_{-\infty}^{+\infty} dt e^{i\omega t} \langle A_{kj}(t) A_{kj}(0) \rangle \\ &= \frac{i}{1 - e^{-\hbar\omega/KT}} [\langle G(kj; kj; \omega + i\eta) \rangle \\ &\quad - \langle G(kj; kj; \omega - i\eta) \rangle] \quad (53) \end{aligned}$$

becomes

$$\begin{aligned} \rho_{kj}(\omega) &= \frac{i}{1 - e^{-\hbar\omega/KT}} \\ &\times \left[\frac{2\Gamma_{kj}(\omega)}{(\omega - \omega_{kj} - \Delta_{kj}(\omega) + \Gamma_{kj}^2(\omega))} \right. \\ &\quad \left. + \frac{2\Gamma_{kj}(\omega)}{\omega + \omega_{kj} + \Delta_{kj}(\omega) + \Gamma_{kj}^2(\omega)} \right] . \quad (54) \end{aligned}$$

The corresponding spectral density $\rho_{kj}^0(\omega)$ for the perfect crystal in the harmonic approximation is

$$\rho_{kj}^0(\omega) = \frac{2\pi}{1 - e^{-\hbar\omega/KT}} [\delta(\omega - \omega_{kj}) - \delta(\omega + \omega_{kj})] . \quad (55)$$

In the perfect harmonic crystal the spectral density has δ -function peaks at $\omega = \pm\omega_{kj}$. In the presence of disorder and/or anharmonicity the spectral density has quasi-Lorentzian peaks centered at values of ω that differ from $\pm\omega_{kj}$ [quasi-Lorentzian because both $\Delta_{kj}(\omega)$ and $\Gamma_{kj}(\omega)$ are frequency dependent]. If both $\Delta_{kj}(\omega)$ and $\Gamma_{kj}(\omega)$ are small, we can set $\omega = \omega_{kj}$ in $\Delta_{kj}(\omega)$ and $\Gamma_{kj}(\omega)$, in which case the former describes the shift in the frequency ω_{kj} of the phonon induced by the disorder and the anharmonicity, while the latter gives the uncertainty in the frequency of the phonon ω_{kj} caused by the disorder and the anharmonicity. $\Gamma_{kj}(\omega_{kj})$ is the reciprocal of the lifetime of the phonon amplitude, according to the uncertainty principle. Consequently, the full width at half maximum of the peak in the spectral density centered at $\omega = \omega_{kj} + \Delta_{kj}(\omega)$ is the reciprocal of the lifetime of the phonon ω_{kj} , since the energy of the phonon is proportional to the square of the modulus of its amplitude, at least approximately.

Finally, we notice that the contribution to $\Gamma_{kj}(\omega)$ and to $\Delta_{kj}(\omega)$ from $M_{kjj'}^0(\omega)$ is temperature independent, while the contributions from the two terms of $M_{kjj'}^1(\omega)$ are both temperature dependent, and are linear functions of the absolute temperature T in the classical regime of high temperatures. The application of this theoretical treatment to a linear chain with mass impurities and the comparison with a computer simulation are in progress and will be published later.

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