

## Influence of isotopic disorder on phonon frequencies and phonon linewidths of an anharmonic crystal

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(Received 13 June 1996)

Based on a perturbation theory using Matsubara functions and a diagrammatic treatment, it is shown that the phonon linewidths of an anharmonic crystal with isotopic impurities include two different contributions, a disorder-induced temperature-independent part, caused by harmonic scattering processes of phonons at isotopic impurities, and a disorder-influenced temperature-dependent part, caused by anharmonic decay processes. Whereas in case of an anharmonic ideal crystal it is usual to restrict the corresponding self-energy on diagonal elements only, this is no longer sufficient in the presence of impurities. For that reason it is shown that only nondiagonal elements of the effective vertex function of the harmonic phonon propagator contribute to the disorder-induced contribution to the phonon linewidth, whereas the corresponding harmonic and the anharmonic frequency shifts are determined by diagonal and nondiagonal elements as well. As an application, numerical results of the disorder-induced temperature-independent as well as the disorder-influenced temperature-dependent contribution to the phonon linewidths of a diatomic linear chain with a single mass defect are presented. [S0163-1829(96)01346-X]

### I. INTRODUCTION

In a recently published article,<sup>1</sup> which is the basis of our further theoretical consideration, the authors have investigated the influence of isotopic disorder on the phonon-phonon interaction in anharmonic crystals and some numerical calculations have been carried out to test the results by application to a diatomic linear chain with a single isotopic impurity. Taking explicitly into account anharmonic contributions of the potential expansion as well as mass changes between impurities and host-lattice particles, it was shown that the anharmonic phonon propagator can be written as a sum of terms, which are added up within a Dyson equation. To get the phonon frequency shifts and linewidths by solving the Dyson equation and subsequently analytical continuation into the complex frequency plane, we made use of the usual approximation to consider the diagonal elements of both the harmonic as well as the anharmonic self-energy matrix only. The harmonic self-energy, which describes the influence of isotopic disorder on the harmonic ideal structure, is known as the effective vertex function and will be denoted in the same way in the following. By making use of the approximation mentioned above, which can be substantiated by no physical reason, the damping and with it the linewidth of a certain lattice mode are determined by anharmonic interactions only in contrast to the corresponding frequency shift, which includes two different contributions, a defect-induced temperature-independent part, caused by harmonic scattering processes of phonons at isotopic impurities and a defect-influenced temperature-dependent part, caused by anharmonic scattering and decay processes. In this paper, however, it is shown that the consideration of nondiagonal elements of the effective vertex function causes a second defect-induced temperature-independent contribution within the damping function and a modification of the defect-induced temperature-independent frequency shift, mentioned

above. Taking into account this contribution of the harmonic crystal to the phonon linewidths of an anharmonic real structure, it is possible to get a more satisfactory description of recent experimental results of relaxation processes in crystals with isotopic impurities.

### II. THEORY

#### A. Model

The starting point of our consideration is the nonprimitive anharmonic crystalline structure with randomly distributed isotopic impurities as recently described in Ref. 1, where the harmonic ideal crystal has been chosen as the reference structure and both anharmonic interactions as well as the influence of isotopic impurities are considered as perturbations.

#### B. The phonon propagator of the harmonic crystalline structure with isotopic impurities

To study the influence of isotopic impurities onto the spectral properties of a crystalline ideal structure we consider the harmonic ideal crystal at first, which is modified by the presence of isotopic impurities. That means that anharmonic interactions are neglected and we restrict ourselves on relaxation processes, caused by the harmonic scattering of phonons at impurities only. Within the context of a perturbation theory using Matsubara functions and a diagrammatic treatment it is possible then to evaluate the phonon propagator  $G_{\lambda\lambda}^h(i\omega_l)$  of the corresponding harmonic crystalline structure with isotopic impurities, as it has been shown in Refs. 1–3. The indices  $\lambda$  and  $\lambda'$  are collective symbols for both the wave vector label  $\vec{q}$  and the branch label  $j$  or  $\vec{q}'$  and

$j'$ , respectively, whereas  $\omega_l$  denotes the so-called Matsubara frequency. As a result of this, the phonon propagator  $G_{\lambda\lambda'}^h(i\omega_l)$  is given by the following infinite sum of contri-

butions, whereas Eq. (1) obtains the analytical representation of these contributions and Fig. 1 shows the corresponding diagrammatic representation:<sup>1</sup>

$$G_{\lambda\lambda'}^h(i\omega_l) = g_\lambda(i\omega_l)\delta_{\lambda-\lambda'} - 2\beta z_\lambda(i\omega_l)C_{-\lambda-\lambda'}z_{\lambda'}(i\omega_l) + 4\beta^2 \sum_{\lambda_1} z_\lambda(i\omega_l)C_{-\lambda\lambda_1}g_{\lambda_1}(i\omega_l)C_{-\lambda_1-\lambda'}z_{\lambda'}(i\omega_l) - 8\beta^3 \sum_{\lambda_1\lambda_2} z_\lambda(i\omega_l)C_{-\lambda\lambda_1}g_{\lambda_1}(i\omega_l)C_{-\lambda_1\lambda_2}g_{\lambda_2}(i\omega_l)C_{-\lambda_2-\lambda'}z_{\lambda'}(i\omega_l) + \dots, \quad (1)$$

with

$$g_{\lambda\lambda'}(i\omega_l) = g_\lambda(i\omega_l)\delta_{\lambda-\lambda'} = \frac{1}{\beta\hbar} \frac{2\omega_\lambda}{\omega_\lambda^2 + \omega_l^2} \delta_{\lambda-\lambda'}, \quad (2a)$$

$$z_{\lambda\lambda'}(i\omega_l) = z_\lambda(i\omega_l)\delta_{\lambda-\lambda'} = \frac{1}{\beta\hbar} \frac{2i\omega_l}{\omega_\lambda^2 + \omega_l^2} \delta_{\lambda-\lambda'} \quad (2b)$$

and

$$C_{\lambda\lambda'} = \frac{\hbar}{4N} \sqrt{\omega_\lambda\omega_{\lambda'}} \sum_{i\kappa i} \left( \frac{M_\kappa}{M_\kappa^i} - 1 \right) \times e_i(\kappa, \lambda) e_i(\kappa, \lambda') e^{i(\vec{q} + \vec{q}') \cdot \vec{r}^i}. \quad (3)$$

The first term in Eq. (1) describes the harmonic ideal crystal and is known as the harmonic phonon propagator of the ideal structure, whereas the remaining contributions are disorder induced owing to the relative mass change in Eq. (3). Using Eqs. (2a) and (2b) as well as the identity

$$\frac{(i\omega_l)^2}{\omega_\lambda\omega_{\lambda'}} = -\frac{2}{\beta\hbar\omega_\lambda} g_{\lambda'}^{-1}(i\omega_l) + \frac{\omega_{\lambda'}}{\omega_\lambda}, \quad (4)$$

it is possible to rewrite Eq. (1) into the following Dyson equation (matrix representation)

$$\mathbf{G}^h(i\omega_l) = \mathbf{g}(i\omega_l) + \mathbf{g}(i\omega_l)\mathbf{E}(i\omega_l)\mathbf{G}^h(i\omega_l) \quad (5)$$

and

$$G_{\lambda\lambda'}^h(i\omega_l) = g_\lambda(i\omega_l)\delta_{\lambda-\lambda'} + g_\lambda(i\omega_l) \sum_{\lambda_1} E_{-\lambda\lambda_1}(i\omega_l) G_{\lambda_1\lambda'}^h(i\omega_l), \quad (6)$$

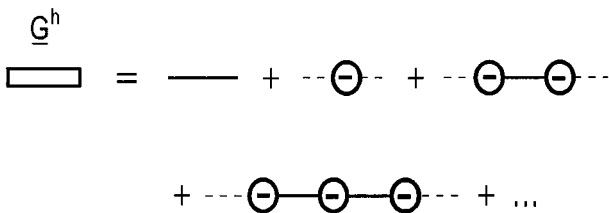


FIG. 1. Diagrammatic representation of Eq. (1).

respectively.<sup>1</sup> According to Eq. (1), Fig. 2 shows the diagrammatic representation of Eq. (5). The nondiagonal matrix  $\mathbf{E}(i\omega_l)$  with

$$E_{\lambda_1\lambda_2}(i\omega_l) = -\beta\hbar \sum_{\lambda_3} [\mathbf{1} + \tilde{\mathbf{C}}]_{\lambda_1\lambda_3}^{-1} \tilde{\mathbf{C}}_{\lambda_3\lambda_2} \frac{(i\omega_l)^2}{2\omega_{\lambda_2}},$$

$$\tilde{\mathbf{C}}_{\lambda_3\lambda_2} = \frac{4}{\hbar\omega_{\lambda_3}} C_{\lambda_3\lambda_2}, \quad (7)$$

usually described as an effective vertex function, corresponds to the complex self-energy  $\mathbf{S}(i\omega_l)$  of an anharmonic crystal and disappears in the case of an ideal structure ( $C_{\lambda\lambda'} = 0$ ). Equation (5) coincides completely with the result of Maradudin and Califano,<sup>4</sup> who used the formalism of the double-time retarded Green's functions to investigate the influence of isotopic impurities onto the spectral properties of a harmonic ideal structure.

To simplify the evaluation of the self-energy contributions of the anharmonic crystal, the approximation

$$E_{\lambda_1\lambda_2}(i\omega_l) = E_{\lambda_1-\lambda_1}(i\omega_l)\delta_{\lambda_1-\lambda_2} \quad (8)$$

has been used in Ref. 1 to evaluate the matrix elements of the phonon propagator  $G_{\lambda\lambda'}^h(i\omega_l)$  from Eq. (3). This restriction of the effective vertex function  $E_{\lambda_1\lambda_2}(i\omega_l)$  on diagonal elements only diagonalizes the phonon propagator of the harmonic crystalline real structure and  $G_{\lambda\lambda'}^h(i\omega_l)$  is then given by

$$G_{\lambda\lambda'}^h(i\omega_l) = \frac{\delta_{\lambda-\lambda'}}{g_\lambda^{-1}(i\omega_l) - E_{-\lambda\lambda}(i\omega_l)}. \quad (9)$$

It has to be emphasized here that there is no physical reason for the approximation mentioned above, like the diagonal behavior of the pure anharmonic self-energy contributions in crystals of cubic symmetry or the ratio between the diagonal

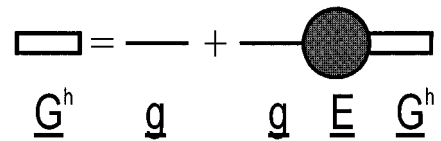


FIG. 2. Diagrammatic representation of Eq. (5).

and the nondiagonal elements. Actually, as it has been made in Ref. 2, the calculation of the effective vertex function elements of simple defect configurations within a diatomic linear chain shows that nondiagonal elements may be as large as the corresponding diagonal elements. Moreover, this assumption is responsible for the vanishing of the disorder-induced temperature-independent damping of phonons, caused by harmonic scattering processes at isotopic impurities, which will be shown in the following. Therefore, to get a sufficient description of the influence of isotopic impurities, one has to take into account diagonal and nondiagonal elements of the effective vertex function as well.

To go beyond the approximation (8), it is necessary to evaluate the nondiagonal inverse matrix  $[1 - \mathbf{g}(i\omega_l)\mathbf{E}(i\omega_l)]^{-1}$ , which appears in

$$\mathbf{G}^h(i\omega_l) = [1 - \mathbf{g}(i\omega_l)\mathbf{E}(i\omega_l)]^{-1}\mathbf{g}(i\omega_l) \quad (10)$$

and

$$G_{\lambda\lambda'}^h(i\omega_l) = \frac{1}{\det[1 - \mathbf{g}(i\omega_l)\mathbf{E}(i\omega_l)]} \times \sum_{\lambda_1} [1 - \mathbf{g}(i\omega_l)\mathbf{E}(i\omega_l)]_{\lambda\lambda_1}^{\text{adj}} g_{\lambda_1\lambda'}(i\omega_l), \quad (11)$$

respectively. This is very complicated in general and leads to a nondiagonal structure of the phonon propagator  $\mathbf{G}^h(i\omega_l)$ . For that reason only a special case of the matrix structure of

$\mathbf{E}(i\omega_l)$  will be discussed in the following to investigate the influence of corresponding nondiagonal elements onto the spectral properties of  $\mathbf{G}^h(i\omega_l)$ , for which is it possible to get a closed form expression of the phonon propagator:

$$\mathbf{E} = \begin{pmatrix} E_{1\bar{1}} & E_{1\bar{2}} & E_{1\bar{3}} & \dots & E_{1\overline{(n-1)}} & E_{1\bar{n}} \\ E_{2\bar{1}} & E_{2\bar{2}} & 0 & \dots & 0 & 0 \\ E_{3\bar{1}} & 0 & E_{3\bar{3}} & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ E_{(n-1)\bar{1}} & 0 & 0 & \dots & E_{(n-1)\overline{(n-1)}} & 0 \\ E_{n\bar{1}} & 0 & 0 & \dots & 0 & E_{n\bar{n}} \end{pmatrix}. \quad (12)$$

Here 1 to  $n$  denote the collective symbols  $\lambda = \vec{q}j = 1$  and  $-\lambda = -\vec{q}j = -1 = \bar{1}$ , respectively, where for a three-dimensional crystal with  $N$  primitive unit cells per periodicity volume and  $s$  lattice particles within the unit cell  $n$  counts to  $3sN$ . The structure of  $\mathbf{E}(i\omega_l)$ , chosen in Eq. (12), corresponds to the case of a defect-induced interaction of the selected mode  $\lambda = 1$ , appropriately the optical-active mode  $\lambda = \vec{0}j_{\text{opt}}$  with all other lattice modes, but no interaction of the modes with  $\lambda \neq 1$  among each other.

After evaluation of  $\det[1 - \mathbf{g}(i\omega_l)\mathbf{E}(i\omega_l)]$  as well as  $[1 - \mathbf{g}(i\omega_l)\mathbf{E}(i\omega_l)]^{\text{adj}}$ , one obtains for an arbitrary diagonal element of the phonon propagator  $G_{1\bar{1}}^h(i\omega_l)$  of the harmonic crystalline structure:<sup>2</sup>

$$G_{1\bar{1}}^h(i\omega_l) = \frac{1}{g_{1\bar{1}}^{-1}(i\omega_l) - E_{1\bar{1}}(i\omega_l) - \sum_{k=2}^n \{E_{1\bar{k}}(i\omega_l)E_{k\bar{1}}(i\omega_l) / [g_{k\bar{k}}^{-1}(i\omega_l) - E_{k\bar{k}}(i\omega_l)]\}}, \quad (13)$$

$$g_{k\bar{k}}(i\omega_l) = g_k(i\omega_l).$$

The neglect of nondiagonal elements of  $\mathbf{E}(i\omega_l)$  produces the expression (9), discussed in Ref. 1. To connect the results obtained above with the corresponding physical properties (defect-induced frequency shift and damping) one has to analytically continue function (13) into the complex frequency half plane ( $i\omega_l \rightarrow \omega + i\gamma, \gamma > 0$ ).<sup>1</sup> With neglect of terms quadratic in  $\gamma$  or of even higher order in  $\gamma$  and using the abbreviation

$$E_{\lambda_1\lambda_2}(i\omega_l) = -\beta\hbar \sum_{\lambda_3} [1 + \tilde{\mathbf{C}}]_{\lambda_1\lambda_3}^{-1} \tilde{\mathbf{C}}_{\lambda_3\lambda_2} \frac{(i\omega_l)^2}{2\omega_{\lambda_2}} = -\beta\hbar A_{\lambda_1\lambda_2} \frac{(i\omega_l)^2}{2\omega_{\lambda_2}}, \quad (14)$$

$G_{1\bar{1}}^h(\omega + i\gamma)$  is given by

$$G_{1\bar{1}}^h(\omega + i\gamma) = \frac{2\omega_1}{\beta\hbar} \frac{1}{\omega_1^2 - (1 - A_{1\bar{1}})\omega^2 - i(1 - A_{1\bar{1}})2\omega\gamma - \sum_{k=2}^n \{A_{1\bar{k}}A_{k\bar{1}}\omega^4 / [\omega_k^2 - (1 - A_{k\bar{k}})\omega^2 - i(1 - A_{k\bar{k}})2\omega\gamma]\}}. \quad (15)$$

Carrying out the limiting process ( $i\omega_l \rightarrow \omega + i\gamma, \gamma > 0$ ) and some further transformations, the phonon propagator of the harmonic crystalline structure with isotopic impurities  $G_{1\bar{1}}^h(\omega)$  can be written as

$$G_{1\bar{1}}^h(\omega) = \lim_{\gamma \rightarrow 0^+} G_{1\bar{1}}^h(\omega + i\gamma) = \frac{2\omega_1}{\beta\hbar} \frac{\omega_1^2 - \omega^2 + 2\omega_1\Delta_1^h(\omega) + i2\omega_1\Gamma_1^h(\omega)}{[\omega_1^2 - \omega^2 + 2\omega_1\Delta_1^h(\omega)]^2 + [2\omega_1\Gamma_1^h(\omega)]^2} \quad (16)$$

with

$$\begin{aligned}\Delta_1^h(\omega) &= \frac{1}{2\omega_1} \left\{ A_{1\bar{1}}\bar{\omega}^2 - \lim_{\gamma \rightarrow 0^+} \sum_{k=2}^n A_{1\bar{k}}\bar{A}_{k\bar{1}}\bar{\omega}^4 \frac{\omega_k^2 - (1 - A_{k\bar{k}})\omega^2}{[\omega_k^2 - (1 - A_{k\bar{k}})\omega^2]^2 + [(1 - A_{k\bar{k}})2\omega\gamma]^2} \right\} \\ &= \frac{1}{2\omega_1} \left[ A_{1\bar{1}}\bar{\omega}^2 - \sum_{k=2}^n A_{1\bar{k}}\bar{A}_{k\bar{1}}\bar{\omega}^4 P\left(\frac{1}{\omega_k^2 - (1 - A_{k\bar{k}})\omega^2}\right) \right]\end{aligned}\quad (17)$$

and

$$\Gamma_1^h(\omega) = \frac{1}{2\omega_1} \lim_{\gamma \rightarrow 0^+} \sum_{k=2}^n A_{1\bar{k}}\bar{A}_{k\bar{1}}\bar{\omega}^4 \frac{(1 - A_{k\bar{k}})2\omega\gamma}{[\omega_k^2 - (1 - A_{k\bar{k}})\omega^2]^2 + [(1 - A_{k\bar{k}})2\omega\gamma]^2} = \frac{\pi}{2\omega_1} \sum_{k=2}^n A_{1\bar{k}}\bar{A}_{k\bar{1}}\bar{\omega}^4 \delta(\omega_k^2 - (1 - A_{k\bar{k}})\omega^2), \quad (18)$$

where  $P(1/x)$  denotes the principal value of  $1/x$ . From the structure of expression (16),  $\Delta_1^h(\omega)$  has to be interpreted as a defect-induced temperature-independent shift of the frequencies of the harmonic ideal structure and  $\Gamma_1^h(\omega)$  functions as a defect-induced temperature-independent damping of the corresponding lattice mode. It is easy to see now that under restriction on diagonal elements of the effective vertex function only [ $A_{1\bar{k}} = A_{k\bar{1}} = 0, k \neq 1$ ; Eq. (8)], the first contribution of expression (17) remains, whereas the corresponding damping completely disappears. That means both the modification of the defect-induced frequency shift as well as the defect-induced finite phonon lifetime are determined by non-diagonal elements of the effective vertex function  $\mathbf{E}(i\omega_l)$  only. Equation (18) shows that there is not a damping of phonons only in anharmonic structures, but even in a harmonic crystal exists a damping of lattice modes, although defect induced. According to its analytical structure, the damping function  $\Gamma_1^h(\omega)$  corresponds to the spectral density

$$G(\omega^2) = \sum_{\lambda} \delta(\omega_{\lambda}^2 - (1 - A_{\lambda-\lambda})\omega^2), \quad (19)$$

modified by  $A_{ik}(i \neq k)$  and  $\omega^4$ .

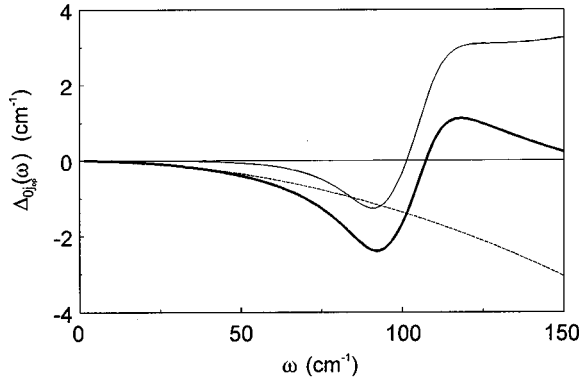


FIG. 3. Defect-induced frequency shift of a diatomic linear chain with a single mass defect ( $M_1^0 = 80$  a.m.u.,  $N = 20, \gamma = 10 \text{ cm}^{-1}$ ). Dotted line: contribution, caused by diagonal elements of  $\mathbf{E}(i\omega_l)$ . Thin line: contribution, caused by nondiagonal elements of  $\mathbf{E}(i\omega_l)$ . Thick line: sum of both contributions.

To summarize it, even in a harmonic crystal a relaxation of lattice modes takes place, which is caused by scattering processes of phonons at impurities. Accordingly,  $\Delta_1^h(\omega)$  and  $\Gamma_1^h(\omega)$  go to zero if the influence of the isotopic disorder vanishes ( $C_{\lambda\lambda} = 0$ ).

As an application Figs. 3 and 4 show the defect-induced temperature-independent frequency shift and damping of the optical active mode ( $\lambda = \tilde{0}j_{\text{opt}}$ ) of the diatomic linear chain with a single mass defect, described in detail with numerical parameters in Ref. 1. As seen from Fig. 3, taking into account of nondiagonal elements of  $\mathbf{E}(i\omega_l)$  modifies considerably the frequency shift of the optical-active mode  $\Delta_{\tilde{0}j_{\text{opt}}}^h(\omega)$ . Whereas the diagonal elements simply produce a pure negative frequency shift determined by  $\omega^2$ , the consideration of nondiagonal elements leads to a frequency shift, which is determined by the frequency distribution of lattice modes of the corresponding harmonic ideal structure and may be positive as well as negative. Figure 4 shows the defect-induced damping function  $\Gamma_{\tilde{0}j_{\text{opt}}}^h(\omega)$  for two sets of numerical parameters, whereas only for the second set with 320 unit cells per periodicity volume and a value of the parameter  $\gamma$  of  $0.5 \text{ cm}^{-1}$ , which is used to deal with the principal values and the Dirac  $\delta$  functions, the structure of the spectral density is really visible. The defect ‘‘concentration’’ (one isotopic impurity per 640 ideal lattice particles),

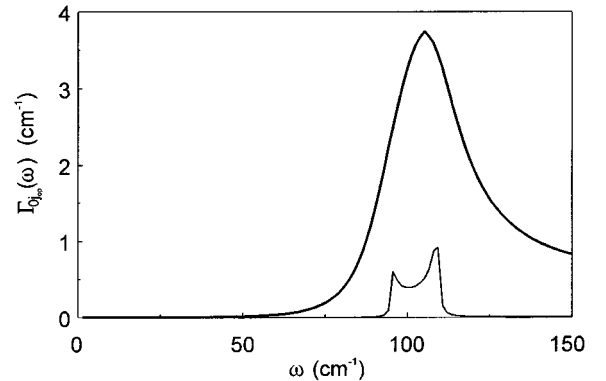


FIG. 4. Defect-induced damping function of a diatomic linear chain with a single mass defect ( $M_1^0 = 80$  a.m.u.). Thin line: calculated with  $N = 320, \gamma = 0.5 \text{ cm}^{-1}$ . Thick line: calculated with  $N = 20, \gamma = 10 \text{ cm}^{-1}$ .

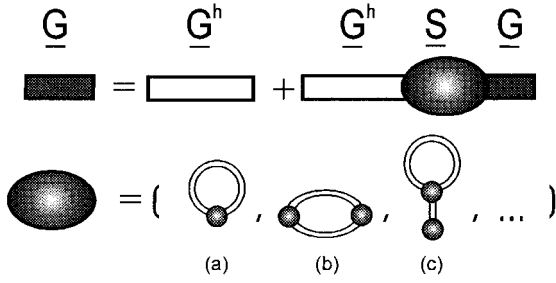


FIG. 5. Diagrammatic representation of the Dyson equation (20) and the corresponding self-energy contributions.

however, is then much lower and according to this the damping values too. Because the defect-induced damping function  $\Gamma_{0j_{\text{opt}}}^h(\omega)$  is explicitly determined by the modified spectral density of the harmonic ideal crystal, damping values different from zero are only possible within the harmonic frequency areas if  $\gamma$  goes to zero. Therefore, localized lattice modes, caused by impurities if the perturbation is large enough, must have infinite lifetimes, what is sufficiently confirmed by other theoretical investigations of a harmonic crystalline structure.

### C. The influence of nondiagonal elements of $E(i\omega_l)$ on frequency shifts and linewidths of an anharmonic crystalline structure

To get the phonon propagator  $\mathbf{G}(i\omega_l)$  of an anharmonic crystalline structure with isotopic impurities, it is possible to renormalize the phonons of the harmonic ideal structure concerning the isotopic disorder by rearranging all connected diagrams and putting them together in a different way, as it was shown in Refs. 1 and 2. Within the diagrammatic representation this means the transition to new diagrams, consisting of one kind of phonon lines only (Fig. 5). The summing up of all diagrams leads to the Dyson equation [Eq. (27) in Ref. 1]:

$$\mathbf{G}(i\omega_l) = \mathbf{G}^h(i\omega_l) + \mathbf{G}^h(i\omega_l)\mathbf{S}(i\omega_l)\mathbf{G}(i\omega_l), \quad (20)$$

where  $\mathbf{S}(i\omega_l)$  is the anharmonic self-energy of the corresponding crystalline *real* structure. As a result of the renormalization, mentioned above, Eq. (20) may be alternatively considered as the perturbation of a harmonic *real* crystal as reference structure by anharmonic scattering and decay processes. In contrast to the harmonic ideal crystal, however, the phonon propagator  $\mathbf{G}^h(i\omega_l)$  of the harmonic ideal structure, modified by the presence of isotopic impurities, possesses a nondiagonal structure, according to Sec. II B.

To evaluate the total frequency shift  $\Delta^{\text{total}}(\omega)$  and damping function  $\Gamma^{\text{total}}(\omega)$  of the harmonic ideal crystal, caused by isotopic impurities and anharmonic interactions, one has to rearrange Eq. (20) to get the diagonal elements of the anharmonic phonon propagator  $G_{\lambda\lambda'}(i\omega_l)$ . But a closed-form expression is only achievable with the following assumptions: (1) restriction on diagonal elements of  $\mathbf{G}^h(i\omega_l)$ , though modified by nondiagonal elements of  $\mathbf{E}(i\omega_l)$ ,

$$G_{\lambda\lambda'}^h(i\omega_l) = G_{\lambda-\lambda}^h(i\omega_l)\delta_{\lambda-\lambda'}, \quad (21)$$

and (2) restriction on diagonal elements of the anharmonic self-energy matrix  $\mathbf{S}(i\omega_l)$ ,

$$S_{\lambda\lambda'}(i\omega_l) = S_{\lambda-\lambda}(i\omega_l)\delta_{\lambda-\lambda'}. \quad (22)$$

The phonon propagator of the anharmonic crystalline structure with isotopic impurities  $G_{\lambda\lambda'}(i\omega_l)$  is thus given by

$$G_{\lambda\lambda'}(i\omega_l) = \frac{1}{[G_{\lambda-\lambda}^h(i\omega_l)]^{-1} - S_{\lambda-\lambda}(i\omega_l)} \delta_{\lambda-\lambda'}. \quad (23)$$

Using Eq. (13) we get

$$G_{\lambda-\lambda}(i\omega_l) = \frac{1}{g_{\lambda-\lambda}^{-1}(i\omega_l) - U_{\lambda-\lambda}(i\omega_l)} \quad (24)$$

with

$$U_{\lambda-\lambda}(i\omega_l) = E_{\lambda-\lambda}(i\omega_l) + S_{-\lambda\lambda}(i\omega_l) + \sum_{\lambda_1 \neq \lambda} \frac{E_{\lambda-\lambda_1}(i\omega_l)E_{\lambda_1-\lambda}(i\omega_l)}{[g_{\lambda_1-\lambda_1}(i\omega_l)]^{-1} - E_{\lambda_1-\lambda_1}(i\omega_l)}. \quad (25)$$

Obviously, the special case discussed in Ref. 1 [Eqs. (39) and (40)] follows from Eq. (24) by neglecting all nondiagonal elements of  $\mathbf{E}(i\omega_l)$ .

As seen from Eqs. (29)–(31) in Ref. 1, the anharmonic self-energy contributions include phonon propagators of the harmonic real structure in more or less complex combinations, represented by corresponding phonon lines (see Fig. 5). Taking into account here the approximation (8) leads to the contributions (33)–(35) of Ref. 1, where the frequencies of the thermal bath phonons are shifted compared to the frequencies of the corresponding harmonic ideal structure only. Using Eq. (13) instead of Eq. (8) means that the harmonic phonons of the thermal bath in addition to a certain frequency shift possess a finite lifetime now, what additionally modifies the anharmonic self-energy contributions. For example, the energy uncertainty related to this has to give rise to an increasing number of decay channels available and therefore to an enhanced damping of the corresponding phonons. However, the summation over the independent Matsubara frequencies  $\omega_l$ , necessary to evaluate the self-energy contributions in Eqs. (33)–(35) of Ref. 1, is even more complicated and we neglect these modifications in the following numerical calculations.

Finally, the total frequency shift  $\Delta^{\text{total}}(\omega)$  and the total damping function  $\Gamma^{\text{total}}(\omega)$  of the harmonic ideal crystal, caused by isotopic impurities *and* anharmonic interactions, is given by the analytical continuation of Eq. (25) into the complex frequency half plane ( $i\omega_l \rightarrow \omega + i\gamma, \gamma > 0$ ) followed by the limiting process ( $\gamma \rightarrow 0$ ):

$$\begin{aligned} \lim_{\gamma \rightarrow 0^+} U_{\lambda-\lambda}(\omega + i\gamma) &= U_{\lambda-\lambda}(\omega) \\ &= -\beta\hbar[\Delta_{\lambda}^{\text{total}}(\omega) - i\Gamma_{\lambda}^{\text{total}}(\omega)], \end{aligned} \quad (26)$$

with

$$\Delta_{\lambda}^{\text{total}}(\omega, T) = \Delta_{\lambda}^h(\omega) + \Delta_{\lambda}^{\text{anh}}(T) + \Delta_{\lambda}^{\text{anh}}(\omega, T), \quad (27)$$

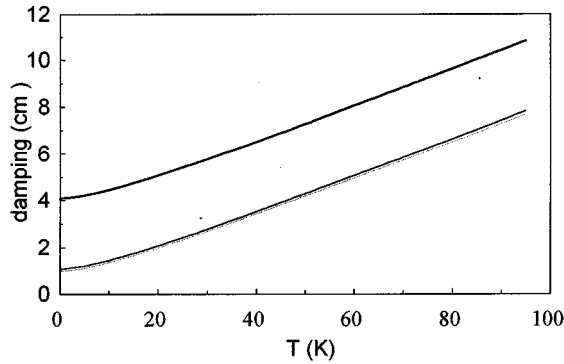


FIG. 6. Damping of the optical-active mode of the diatomic linear chain, described in Ref. 1. Dotted line: damping of the corresponding ideal structure  $\Gamma^{\text{anh,ideal}}(\omega_{\tilde{0}j_{\text{opt}}}, T)$ . Thin line: anharmonic damping contribution of the crystalline structure with a single mass defect  $\Gamma^{\text{anh}}(\omega_{\tilde{0}j_{\text{opt}}}, T)$  ( $M_1^0 = 80$  a.m.u.). Thick line: total damping  $\Gamma^{\text{total}}(\omega_{\tilde{0}j_{\text{opt}}}, T)$ .

and

$$\Gamma_{\lambda}^{\text{total}}(\omega, T) = \Gamma_{\lambda}^h(\omega) + \Gamma_{\lambda}^{\text{anh}}(\omega, T). \quad (28)$$

Therefore, in contrast to well-known results of phonon frequency shifts and linewidths of an anharmonic ideal crystal, both the frequency shift as well as the damping function include different contributions, if isotopic disorder is present. The first contribution of Eqs. (27) and (28), respectively, describes the defect-induced temperature-independent frequency shift and damping function, caused by scattering processes at isotopic impurities, whereas the remaining contributions correspond to the defect-influenced temperature-dependent frequency shift and damping function, caused by anharmonic scattering and decay processes, given, within the approximation mentioned above and up to  $O(\alpha^2)$ , by analytical continuation of Eqs. (33)–(35) of Ref. 1. Because the influence of isotopic disorder on phonons of the thermal bath is temperature-independent, the general temperature dependence of the anharmonic frequency shift and damping function is equal to that of an anharmonic ideal crystal, for example, the linear behavior in the high-temperature region up to  $O(\alpha^2)$ , but with changed values. This is clearly supported by the results of experimental investigations of frequencies and linewidths in natural and pure sulfur,<sup>5,6</sup> which show for both crystals and corresponding bands the same high-temperature behavior with different values. Additionally, the fitting attempts, made by Becucci *et al.*,<sup>6</sup> indicate the pres-

ence of a defect-induced temperature-independent contribution to the linewidth, which of course affects the linewidth most at low temperatures and sometimes even dominates it. According to the results obtained in Ref. 1 and discussed here, the temperature-independent contribution of the phenomenological description of Becucci *et al.*<sup>6</sup> [Eq. (10) of Ref. 6] is caused by scattering processes of phonons at isotopic impurities, whereas the second contribution has to be attributed to anharmonic scattering and decay processes, modified by the isotopic disorder. But the attempt of evaluating the defect-influenced anharmonic damping contribution from the corresponding contribution of the anharmonic ideal structure by multiplying it with a defect-determined parameter only cannot be supported from the point of view of a microscopic theory. Moreover, in contrast to the supposition of Becucci *et al.*,<sup>6</sup> that the modification of anharmonic decay processes by isotopic impurities may be described by a dressing of the usual cubic and quartic anharmonic coupling constants by mass-change coefficients only, we have obtained instead a modification of the harmonic bath phonons by the isotopic disorder and therefore a modification of the decay channels itself.

As an application Fig. 6 shows the total damping  $\Gamma^{\text{total}}(\omega_{\tilde{0}j_{\text{opt}}}, T)$  as well as the anharmonic damping contribution  $\Gamma^{\text{anh}}(\omega_{\tilde{0}j_{\text{opt}}}, T)$  of the diatomic linear chain mentioned in Sec. II B as a function of temperature.

### III. CONCLUSIONS

Using the theoretical formalism described in Ref. 1 and further developed within this paper it has been shown that the frequency shifts as well as the linewidths of an anharmonic crystal with isotopic impurities include two different contributions, a defect-induced temperature-independent one, caused by harmonic scattering processes of phonons at isotopic impurities and a defect-influenced temperature-dependent one, caused by anharmonic scattering and decay processes. Additionally, it could be demonstrated that nondiagonal elements of the effective vertex function have to be considered as well to get a sufficient description of the influence of isotopic impurities on relaxation processes in anharmonic crystals.

As an application both damping contributions of a diatomic linear chain with a single mass defect has been calculated, which clearly indicates the importance of the temperature-independent contribution especially at low temperatures, what is supported by experimental investigations.

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