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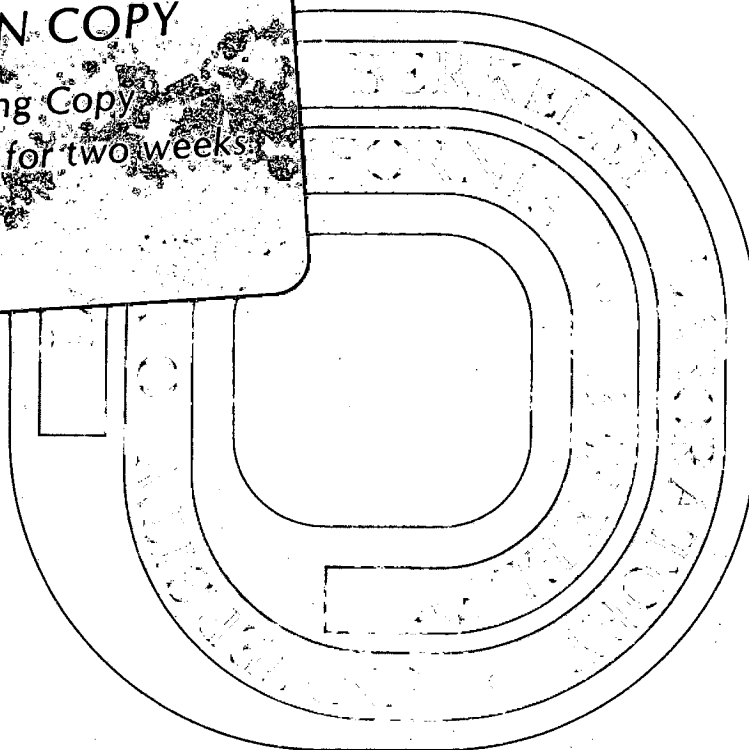
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TEMPERATURE DEPENDENCE OF THE DAMPING
OF NONLINEAR LATTICE RESONANCE IN IONIC CRYSTALS *

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ABSTRACT

A general expression for the n th order nonlinear complex susceptibility tensor is derived by use of many-time temperature-dependent Green's functions. The damping constant for nonlinear absorption is obtained from the susceptibility tensor. It is shown that the n th order nonlinear susceptibility tensor is generated from lower-order Green's functions and that the explicit temperature dependence of the damping constant is not affected by increasing the strength of the applied field. It is found by observing the frequency dependence of the susceptibility, that the frequency, ω , of the applied field is converted into n th harmonic waves of frequency $n\omega$.

I. INTRODUCTION

The phenomenon of infrared absorption in ionic crystals is connected with the dynamics of lattice vibrations. The traditional theory of lattice dynamics was developed mainly by Born and von Karman¹⁻³ more than fifty years ago. In this theory, one may think of a crystalline solid as consisting of a set of coupled springs (forces) and masses (ions). The fundamental assumption is that atomic (ionic) displacements in the lattice from their equilibrium positions are small in comparison with interatomic spacings. Hence, truncation of expansion terms of interatomic potentials in powers of the displacements at the first few anharmonic terms (usually, third or fourth) is valid. This approximation is generally valid for a large class of crystalline solids, but it has recently been discovered that it is not valid for the so-called quantum crystals (for example, solid helium).⁴ We will not consider quantum crystals in this paper.

The process of optical absorption involves the interaction of an electric field with the electric moment of a crystal when one optically active phonon branch is considered. The electric moment may be expanded in powers of the thermal displacements of the ions from their equilibrium positions; the linear term in this expansion is the usual dipole moment. Higher-order terms give rise to continuous absorption.¹ The Hamiltonian of the crystal consists of the sum of harmonic and anharmonic parts; the anharmonic part is obtained by expanding the potential energy of the crystal in powers of the ionic displacements from the equilibrium positions.

An interesting problem in the infrared absorption process is that of explaining the observed temperature dependence of the damping constant of the fundamental lattice vibration absorption peak at high temperature. Measurements carried out by Heilmann⁵ on LiF and by Hass⁶ on NaCl show that the damping constant varies approximately as T^2 at high temperature.

In Born's¹ and the more recent Maradudin-Wallis⁷ classical treatments of this problem, it is found that this damping constant is linearly related to temperature. Jepsen and Wallis⁸ derived results which showed that the damping constant was proportional to T^2 in the classical limit. Their calculation, unlike previous classical treatments, included quartic anharmonic terms in the Hamiltonian. Detailed quantum-mechanical treatments by Born and Huang¹ and Maradudin and Wallis⁹ show that the damping constant should increase as T^3 in the high-temperature limit.

Expressions valid at all temperatures for cubic and quartic anharmonic contributions to the damping constant have been developed by Gurevich and Ipatova¹⁰ and by Kashcheev.¹¹ A detailed numerical calculation, on the basis of a realistic model for ionic crystals, of the cubic and quartic contributions to the damping constant was performed by Ipatova et al.¹²

It has recently been pointed out by Mooij¹³ that the above theoretical considerations of the damping constant neglect the temperature dependence of the thermal expansion coefficient. Using the data for LiF and KBr, it is shown that the quartic anharmonic contribution is very small and the cubic contribution could give rise to a T^2 dependence of the damping constant at high temperature.¹⁴

It is necessary to consider nonlinear effects when the intensity of the external field (perturbation) becomes comparable to the intensity of the internal field acting on the ions in the crystal. The availability of intense light fluxes from laser sources makes possible the experimental observation of these nonlinear effects in the laboratory.

We have used the method of many-time Green's functions to derive an expression, valid for all temperatures, for the n th order nonlinear complex susceptibility tensor. This expression is a function of the frequency shifts and damping constant for the fundamental absorption peak. Terms smaller than $O(1/N)$ and quartic anharmonic contributions are neglected. It is found that the explicit temperature dependence of the damping constant is T in both the linear and nonlinear cases. However, the implicit temperature dependence of the thermal expansion must be determined for the material under investigation to complete the analysis. The expression for the n th order nonlinear complex susceptibility contains frequency-dependent terms which indicate that the frequency, ω , of the applied field is converted into n th order-harmonic waves with frequency $n\omega$. This is the usual nonlinear frequency-dependent result.

II. MATHEMATICAL FORMULATION

A. Two-Time Temperature Dependent Green's Functions

In this section, we present the essential theory of two-time^{15,16} and many-time^{17,18} temperature-dependent Green's functions, develop a formal expression for the nonlinear complex susceptibility tensor, and express the anharmonic Hamiltonian of an ionic crystal in terms of phonon creation and annihilation operators.

The two-time temperature-dependent retarded Green's function that we will use is defined by

$$\begin{aligned} G(t, t') &= -i\theta(t - t') \langle [A(t), B(t')] \rangle \\ &= \langle \langle A(t); B(t') \rangle \rangle = G(A; B), \end{aligned} \quad (2.1)$$

where

$$\theta(t - t') = \begin{cases} 1, & t - t' > 0 \\ 0, & t - t' < 0 \end{cases}, \quad (2.2)$$

and the canonical ensemble average is denoted by

$$\langle \dots \rangle = \frac{\text{Tr}(e^{-\beta H} \dots)}{\text{Tr} e^{-\beta H}}; \quad \beta = \frac{1}{kT}. \quad (2.3)$$

The operators A and B are second quantized phonon operators in the Heisenberg representation. The Hamiltonian of the isolated (unperturbed) system is denoted by H . The equation of motion of the two-time Green's function is obtained by differentiating Eq. (2.1) with respect to time. On taking the Fourier transform of this equation of motion, we obtain (in the energy representation)

$$E G_2(A; B)_E = \frac{1}{2\pi} \langle [A, B] \rangle_E + G_2([A, H]; B)_E, \quad (2.4)$$

where $E = \omega + i\epsilon$ and $\pi = 1$.

It is well known that the linear complex susceptibility and absorption⁷ coefficient are respectively given by

$$\chi_{\mu\nu}^2(\omega) = -2\pi G_2(M_\mu; M_\nu)_E \quad (2.5)$$

and

$$\alpha_{\mu\nu}^2(\omega) = 4\pi \frac{\omega}{c} \text{Im} \chi_{\mu\nu}(\omega), \quad (2.6)$$

where M is the electric moment of the crystal. The directions of the applied electric field and the response are ν and μ respectively. Equation (2.5) is valid when the volume of the system under consideration is taken to be unity.

B. Many-Time Temperature Dependent Green's Functions

The Fourier transform of the equation of motion of a general many-time Green's function is given by

$$nE G_{n+1}(A; B)_E = \frac{1}{2\pi} G_n([A, B]; B)_E + G_{n+1}([A, H]; B)_E, \quad (2.7)$$

where

$$G_1([A, B]; B)_E = \langle [A, B] \rangle_E, \quad (2.8)$$

$$G_2(A; B)_E = \langle \langle A; B \rangle \rangle_E, \quad (2.9)$$

$$G_3(A; B)_E = \langle \langle [A, B]; B \rangle \rangle_E. \quad (2.10)$$

The usual equation for the two-time Green's function (in the energy representation) may be obtained by setting $n = 1$ in Eq. (2.7). The frequency of the external perturbing field is denoted by ω .

We extend the linear expressions and write the nonlinear complex susceptibility and absorption coefficient as

$$\chi_{\mu\nu}^{n+1}(\omega) = (-2\pi)^n C_{n+1}^{\mu}(\mathbf{M}; \mathbf{M}_\nu) E \quad (2.11)$$

and

$$\alpha_{\mu\nu}^{n+1}(\omega) = 4\pi \frac{\omega}{c} \text{Im} \chi_{\mu\nu}^{n+1}(\omega). \quad (2.12)$$

The susceptibility is a function of the frequency shifts $\Delta(\omega)$ and the damping constant $\Gamma(\omega)$ as will be seen in Sec. III.

C. The Hamiltonian and Electric Moment¹

The system to be placed in a perturbing external electric field is a crystal with N unit cells each containing rigid ions. We impose periodic boundary conditions on this system. The lattice Hamiltonian, to quartic anharmonic terms, in terms of the phonon creation and annihilation operators is

$$H = H^+ = H_0 + H_2 + H_4 \quad (2.13)$$

or

$$H = \sum_{\tilde{\alpha}} \omega_{\tilde{\alpha}} a_{\tilde{\alpha}}^+ a_{\tilde{\alpha}} + \sum_{\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}} v_{\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}}^{(3)} a_{\tilde{\alpha}}^+ a_{\tilde{\beta}}^+ a_{\tilde{\gamma}} + \sum_{\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}, \tilde{\rho}} v_{\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}, \tilde{\rho}}^{(4)} a_{\tilde{\alpha}}^+ a_{\tilde{\beta}}^+ a_{\tilde{\gamma}}^+ a_{\tilde{\rho}} \quad (2.14)$$

where $\mathcal{H} = 1$, and the indices $\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}$, and $\tilde{\rho}$ represent both the wave vector $\tilde{k}$ and polarization index j . For example, $\tilde{\alpha} = \tilde{k}j$ and $\tilde{\rho} = \tilde{k}'j'$. Capital A is defined by

$$A_{\tilde{\alpha}} = a_{-\tilde{\alpha}}^+ + a_{\tilde{\alpha}}, \quad (2.15)$$

where $a_{-\tilde{\alpha}}^+$ and $a_{\tilde{\alpha}}$ are phonon creation and annihilation operators respectively. The frequency of the normal mode of vibration is described by $\omega_{\tilde{\alpha}}$. The $v_{\tilde{\alpha}}^{(3)}$ and $v_{\tilde{\alpha}}^{(4)}$ coefficients which appear in the anharmonic part of the Hamiltonian are Fourier transforms of the third- and fourth-order atomic force constants. These coefficients may be written as

$$v_{\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}}^{(3)} = \frac{1}{6(2^3/2)} \frac{\Delta(\tilde{k} + \tilde{k}' + \tilde{k}'') \phi(\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma})}{(\omega_{\tilde{\alpha}} \omega_{\tilde{\beta}} \omega_{\tilde{\gamma}})^{1/2}} \quad (2.16)$$

and

$$v_{\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}, \tilde{\rho}}^{(4)} = \frac{1}{4(2^4 N)} \frac{\Delta(\tilde{k} + \tilde{k}' + \tilde{k}'' + \tilde{k}''') \phi(\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}, \tilde{\rho})}{(\omega_{\tilde{\alpha}} \omega_{\tilde{\beta}} \omega_{\tilde{\gamma}} \omega_{\tilde{\rho}})^{1/2}}, \quad (2.17)$$

where the force constant is given by ϕ and the v 's are completely symmetric in the indices; for example,

$$v_{\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}}^{(3)} = v_{\tilde{\beta}, \tilde{\alpha}, \tilde{\gamma}}^{(3)}, \quad (2.18)$$

$$v_{\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}}^{(3)} = [v_{-\tilde{\alpha}, -\tilde{\beta}, -\tilde{\gamma}}^{(3)}]^*, \quad (2.19)$$

and

$$v_{-\tilde{\alpha}, -\tilde{\alpha}, \dots}^{(3)} = 0. \quad (2.20)$$

The Δ 's are restricted by the relation

$$\Delta(\tilde{k} + \tilde{k}' + \tilde{k}'') = \begin{cases} 1, & \tilde{k} + \tilde{k}' + \tilde{k}'' = \tilde{k} \\ 0, & \text{otherwise} \end{cases}, \quad (2.21)$$

where $\tilde{k}$ is the primitive translational vector of the reciprocal lattice. Similar relations are valid for $V^{(4)}$ and

$$\Delta(\tilde{k} + \tilde{k}' + \tilde{k}'' + \tilde{k}''').$$

The n th component of the dipole moment of the crystal in terms of phonon creation and annihilation operators is

$$M_\mu = N \sum_{\tilde{Q}} \frac{M_\mu(\tilde{Q})}{(2\omega_{\tilde{Q}})^{\frac{1}{2}}} A_{\tilde{Q}}, \quad (2.22)$$

where $M_\mu(\tilde{Q})$ is the usual expansion coefficient and $A_{\tilde{Q}}$ is defined by

$$A_{\tilde{Q}} = a_{\tilde{Q}}^+ + a_{\tilde{Q}}. \quad (2.23)$$

The index $\tilde{Q}$ equals 0j.

III. LINEAR SUSCEPTIBILITY AND DAMPING

Calculations of the linear complex susceptibility tensor for an ionic crystal, using two-time Green's functions, may be found in various sources.¹¹ However, we present the essential features of this analysis here to clarify the decoupling method to be used in the nonlinear case. It is also found that the nonlinear result is a function of lower-order (linear) results. The equation-of-motion approach for two-time Green's functions can readily be extended to the nonlinear case. To avoid confusion with the nonlinear theory, we use the subscript 2 for linear (or two-time) Green's functions and the subscript 3 to represent the lowest-order nonlinear case. The linear complex susceptibility ($n = 1$) is obtained by substituting Eq. (2.22) into Eq. (2.5); we obtain

$$\chi_{\mu\nu}^2(\omega) = -2\pi \left(\frac{N}{2} \right) \sum_{\tilde{Q}, \tilde{Q}'} \frac{M_\mu(\tilde{Q}) M_\nu(\tilde{Q}')}{(\omega_{\tilde{Q}} \omega_{\tilde{Q}'})^{\frac{1}{2}}} [G_2^1 + G_2^2], \quad (3.1)$$

where

$$G_2^1 = G_2^1(a_{\tilde{Q}}^+; A_{\tilde{Q}'}^+) E \quad (3.2a)$$

and

$$G_2^2 = G_2^2(a_{\tilde{Q}}; A_{\tilde{Q}'}^+) E. \quad (3.2b)$$

Expressions for G_2^1 and G_2^2 are obtained from the Fourier transforms of their respective equations of motions. That is to say,

$$\begin{aligned} EG_2^1 = & \frac{1}{2\pi} \langle [a_{\tilde{Q}}^+, A_{\tilde{Q}'}^+] E + G_2([a_{\tilde{Q}}^+, H_0]; A_{\tilde{Q}'}^+) E \\ & + G_2([a_{\tilde{Q}}, H_3]; A_{\tilde{Q}'}^+) E + G_2([a_{\tilde{Q}}, H_4]; A_{\tilde{Q}'}^+) E \end{aligned} \quad (3.3)$$

and

$$EG_2^2 = \frac{1}{2\pi} \langle [a_0, A_0] \rangle_E + G_2([a_0, H_0]; A_0)_E + G_2([a_0, H_3]; A_0)_E + G_2([a_0, H_4]; A_0)_E. \quad (3.4)$$

Note that the terms in Eqs. (3.3) and (3.4) involving H_4 must be retained and reduced to G_2^1 or G_2^2 at this stage in the approximation since they give rise to contributions of the order $(1/N)$. This is the usual Hartree-Fock approximation to the self energy. Equations (3.3) and (3.4) may be resolved by use of the following relations:

$$[a_0, H_0] = -\omega_0 a_0^+; [a_0, H_0] = -[a_0, H_0]^+ \quad (3.5a)$$

$$[a_0, H_3] \sim -3 \sum_{\alpha, \beta} v_{\alpha, \beta, 0}^{(3)} A_{\alpha, \beta} \quad (3.5b)$$

$$[a_0, H_3] = -[a_0, H_3]^+ \Big|_{0 \rightarrow -0} \quad (3.5c)$$

In Eq. (3.5b) we have omitted certain delta-function terms which involve Green's functions whose evaluation yield zero. Equations (3.3) and (3.4) now become

$$[E - \omega_0 + \sum(Q)]G_2^1 = -\frac{\delta_{0,0'}}{2\pi} - 3 \sum_{\alpha, \beta} v_{\alpha, \beta, 0}^{(3)} (g_2^1 + 2g_2^2 + g_2^3) \quad (3.6)$$

and

$$[E - \omega_0 - \sum(Q)]G_2^2 = \frac{\delta_{0,0'}}{2\pi} + 3 \sum_{\alpha, \beta} v_{\alpha, \beta, -0}^{(3)} (g_2^1 + 2g_2^2 + g_2^3), \quad (3.7)$$

where

$$\sum(Q) = 12 \sum_{\alpha} v_{\alpha, \alpha, 0}^{(4)} (2n_{\alpha} + 1), \quad (3.8a)$$

$$g_2^1 = \langle \langle a_{\alpha}^+ a_{-\beta}^+; A_0 \rangle \rangle, \quad (3.8b)$$

$$g_2^2 = \langle \langle a_{\alpha}^+ a_{\beta}; A_0 \rangle \rangle, \quad (3.8c)$$

$$g_2^3 = \langle \langle a_{-\alpha} a_{\beta}; A_0 \rangle \rangle. \quad (3.8d)$$

Here n_{α} is the usual average boson occupation number.

The expression for $\sum(Q)$ results from retaining only the diagonal terms of the symmetric decoupling of the higher-order Green's functions in the $v^{(4)}$ terms. That is to say, we decoupled in the following way:

$$\langle \langle a_{-\alpha}^+ a_{\beta} a_{-\gamma}^+; A_0 \rangle \rangle \approx [n_{\beta} \delta_{\alpha, \beta} \delta_{-\gamma, 0} + (n_{\beta} + 1) \delta_{\beta, -\gamma} \delta_{-\alpha, 0}] g_2^1. \quad (3.9)$$

The higher-order Green's functions g_2^1 , g_2^2 , and g_2^3 must be determined from their respective equations of motion. In the energy representation, we obtain

$$E g_2^1 = \langle \langle a_{\alpha}^+ a_{-\beta}^+; A_0 \rangle \rangle_E + \langle \langle [a_{\alpha}^+ a_{-\beta}^+; H_0]; A_0 \rangle \rangle_E + \langle \langle [a_{\alpha}^+ a_{-\beta}^+; H_3]; A_0 \rangle \rangle_E, \quad (3.10a)$$

$$E g_2^2 = \langle [a_{\tilde{\alpha}}^+ a_{\tilde{\beta}}, A_0] \rangle_E + \langle \langle [a_{\tilde{\alpha}}^+ a_{\tilde{\beta}}, H_0]; A_0 \rangle \rangle_E \\ + \langle \langle [a_{\tilde{\alpha}}^+ a_{\tilde{\beta}}, H_3]; A_0 \rangle \rangle_E, \quad (3.10b)$$

and

$$E g_2^3 = \langle [a_{\tilde{\alpha}} a_{\tilde{\beta}}, A_0] \rangle_E + \langle \langle [a_{\tilde{\alpha}} a_{\tilde{\beta}}, H_0]; A_0 \rangle \rangle_E \\ + \langle \langle [a_{\tilde{\alpha}} a_{\tilde{\beta}}, H_3]; A_0 \rangle \rangle_E. \quad (3.10c)$$

Equations (3.10 a-c) reduce to

$$E g_2^1 = -(\omega_{\tilde{\alpha}} + \omega_{\tilde{\beta}}) g_2^1 - 6 V_{\tilde{\alpha}, \tilde{\alpha}, \tilde{\alpha}, \tilde{\alpha}}^{(3)} (n_{\tilde{\alpha}} + n_{\tilde{\beta}} + 1) g_2^1 \\ - 6 V_{\tilde{\alpha}, \tilde{\beta}, \tilde{\alpha}, \tilde{\alpha}}^{(3)} (n_{\tilde{\alpha}} + n_{\tilde{\beta}} + 1) g_2^2, \quad (3.11a)$$

$$E g_2^2 = (\omega_{\tilde{\beta}} - \omega_{\tilde{\alpha}}) g_2^2 + 6 V_{\tilde{\alpha}, \tilde{\alpha}, \tilde{\alpha}, \tilde{\alpha}}^{(3)} (n_{\tilde{\alpha}} - n_{\tilde{\beta}}) g_2^1 \\ + 6 V_{\tilde{\alpha}, \tilde{\alpha}, \tilde{\beta}, \tilde{\alpha}}^{(3)} (n_{\tilde{\alpha}} - n_{\tilde{\beta}}) g_2^2, \quad (3.11b)$$

and

$$E g_2^3 = (\omega_{\tilde{\alpha}} + \omega_{\tilde{\beta}}) g_2^3 + 6 V_{\tilde{\alpha}, \tilde{\alpha}, \tilde{\alpha}, \tilde{\alpha}}^{(3)} (n_{\tilde{\alpha}} + n_{\tilde{\beta}} + 1) g_2^1 \\ + 6 V_{\tilde{\alpha}, \tilde{\alpha}, \tilde{\beta}, \tilde{\alpha}}^{(3)} (n_{\tilde{\alpha}} + n_{\tilde{\beta}} + 1) g_2^2. \quad (3.11c)$$

To obtain Eqs. (3.11 a-c), we evaluated the indicated commutation relations in Eqs. (3.10 a-c) and symmetrically decoupled the Green's functions associated with the $V^{(3)}$ terms. Again, we have retained only the diagonal terms. By solving Eqs. (3.11 a-c) for the g

Green's functions and substituting the results into Eqs. (3.6) and (3.7) we find that Eq. (3.1) becomes

$$\chi_{\mu\nu}^2(\omega) = N \sum_{\tilde{\alpha}, \tilde{\beta}} \frac{M_{\mu}(\tilde{\alpha}) M_{\nu}(\tilde{\beta})}{\omega_{\tilde{\alpha}}} \left\{ \frac{\omega_{\tilde{\alpha}} + \sum(\tilde{\alpha})}{\omega_0^2 - \omega^2 + 2 \sum(0) + 2\omega_0 r_2^2(E)} \right\}, \quad (3.12)$$

where

$$r_2^2(E) = 18 \sum_{\tilde{\alpha}, \tilde{\beta}} |V_{\tilde{\alpha}, \tilde{\alpha}, \tilde{\alpha}, \tilde{\beta}}^{(3)}|^2 \left\{ \frac{n_{\tilde{\alpha}} + n_{\tilde{\beta}} + 1}{E - \omega_{\tilde{\alpha}} - \omega_{\tilde{\beta}}} - \frac{(n_{\tilde{\alpha}} + n_{\tilde{\beta}} + 1)}{E + \omega_{\tilde{\alpha}} + \omega_{\tilde{\beta}}} \right. \\ \left. + \frac{2(n_{\tilde{\alpha}} - n_{\tilde{\beta}})}{E + \omega_{\tilde{\alpha}} - \omega_{\tilde{\beta}}} \right\}. \quad (3.13)$$

We now write $r_2^2(E)$ as

$$r_2^2(E) = r_2^2(\omega + i\epsilon) = \Delta(\omega) - i\Gamma^2(\omega), \quad (3.14)$$

where $\Delta(\omega)$ denotes the frequency shifts and $\Gamma(\omega)$ is the corresponding damping constant. On using the well-known relation

$$\frac{1}{x \pm i\epsilon} = P\left(\frac{1}{x}\right) \mp i\pi\delta(x), \quad (3.15)$$

we obtain

$$\Delta(\omega) = 18 \sum_{\tilde{\alpha}, \tilde{\beta}} |V_{\tilde{\alpha}, \tilde{\alpha}, \tilde{\alpha}, \tilde{\beta}}^{(3)}|^2 \left\{ (n_{\tilde{\alpha}} + n_{\tilde{\beta}} + 1) P\left(\frac{1}{\omega - \omega_{\tilde{\alpha}} - \omega_{\tilde{\beta}}}\right) \right. \\ \left. - (n_{\tilde{\alpha}} + n_{\tilde{\beta}} + 1) P\left(\frac{1}{\omega + \omega_{\tilde{\alpha}} + \omega_{\tilde{\beta}}}\right) + 2(n_{\tilde{\alpha}} - n_{\tilde{\beta}}) P\left(\frac{1}{\omega + \omega_{\tilde{\alpha}} - \omega_{\tilde{\beta}}}\right) \right\} \quad (3.16)$$

and

$$\Gamma^2(\omega) = 18\pi \sum_{\alpha, \beta} |v_{\alpha, 0, \beta}^{(3)}|^2 \{ (n_{\alpha} + n_{\beta} + 1) \delta(\omega - \omega_{\alpha} - \omega_{\beta}) - (n_{\alpha} + n_{\beta} + 1) \delta(\omega + \omega_{\alpha} + \omega_{\beta}) + 2(n_{\alpha} - n_{\beta}) \delta(\omega + \omega_{\alpha} - \omega_{\beta}) \}, \quad (3.17)$$

where $P(\dots)$ indicates principal part.

We note that the damping constant in the cubic anharmonic approximation, Eq. (3.17), is a linear function of T ($n \rightarrow kT$) if the temperature dependence of the expansion coefficient is neglected for high temperature. Note also that we have retained only diagonal contributions of the decoupling since only one optically active branch is assumed. The frequency dependence of the susceptibility is indicated in Eq. (3.12). A model for the specific material under investigation must be developed to obtain more detailed information.

IV. NONLINEAR SUSCEPTIBILITY AND DAMPING

In this section, we extend the linear equation of motion technique and derive an expression for the nonlinear complex susceptibility tensor. On substituting Eq. (2.22) into Eq. (2.11), we find the n th order nonlinear complex susceptibility tensor becomes

$$\chi_{\mu\nu}^{n+1}(\omega) = (-2\pi)^n \frac{1}{2} \sum_{0, 0'} \frac{M(0) M(0')}{(\omega_0 \omega_{0'})^{\frac{n}{2}}} [G_{n+1}^1 + G_{n+1}^2], \quad (4.1)$$

where

$$G_{n+1}^1 = G_{n+1}(a_0^+; A_0')_E \quad (4.2a)$$

and

$$G_{n+1}^2 = G_{n+1}(a_0; A_0')_E. \quad (4.2b)$$

The G_{n+1} Green's functions are determined for the following equations (in the energy representation):

$$nE G_{n+1}^1 = \frac{1}{2\pi} G_n([a_0^+, A_0']; A_0')_E + G_{n+1}([a_0^+, H]; A_0')_E \quad (4.3)$$

and

$$nE G_{n+1}^2 = \frac{1}{2\pi} G_n([a_0, A_0']; A_0')_E + G_{n+1}([a_0, H]; A_0')_E. \quad (4.4)$$

Equations (4.3) and (4.4) reduce to

$$[nE + \omega_0 + \sum(0)] G_{n+1}^1 = -\frac{8(G_n)}{2\pi} - 3 \sum_{\alpha, \beta} v_{\alpha, \beta, 0}^{(3)} \{ g_{n+1}^1 + 2g_{n+1}^2 + g_{n+1}^3 \} \quad (4.5)$$

and

$$[nE - \omega_0 - \sum(\tilde{0})]G_{n+1}^2 = \frac{\delta(G_n)}{2\pi} + 3 \sum_{\tilde{\alpha}, \tilde{\beta}} V_{\tilde{\alpha}, \tilde{\beta}, -\tilde{0}}^{(3)} (E_{n+1}^1 + 2E_{n+1}^2 + E_{n+1}^3),$$

(4.6)

where

$$E_{n+1}^1 = E_{n+1}(a_{\tilde{\alpha}\tilde{\beta}}^+; A_{\tilde{0}'}), E, \quad (4.7a)$$

$$E_{n+1}^2 = E_{n+1}(a_{\tilde{\alpha}\tilde{\beta}}^+; A_{\tilde{0}'}), E, \quad (4.7b)$$

$$E_{n+1}^3 = E_{n+1}(a_{\tilde{\alpha}\tilde{\beta}}^+; A_{\tilde{0}'}), E, \quad (4.7c)$$

and

$$\delta(G_n) = \begin{cases} 1; & n = 1 \\ 0; & n > 1 \end{cases} \quad (4.7d)$$

The basic equations for E_{n+1}^1 , E_{n+1}^2 , and E_{n+1}^3 reduce to

$$(nE + \omega_{\tilde{\alpha}} + \omega_{\tilde{\beta}})E_{n+1}^1 = -\Gamma_n^1(a_{\tilde{\alpha}\tilde{\beta}}^+; A_{\tilde{0}'}), E \delta_{\tilde{0}', \tilde{\alpha}} - \Gamma_n^1(a_{\tilde{\alpha}\tilde{\beta}}^+; A_{\tilde{0}'}), E \delta_{\tilde{0}', \tilde{\beta}}$$

$$- 6V_{\tilde{\alpha}, \tilde{\beta}, -\tilde{0}}^{(3)}(n_{\tilde{\alpha}} + n_{\tilde{\beta}} + 1)G_{n+1}^1 - 6V_{\tilde{\alpha}, \tilde{\beta}, -\tilde{0}}^{(3)}(n_{\tilde{\alpha}} + n_{\tilde{\beta}} + 1)G_{n+1}^2, \quad (4.8a)$$

$$(nE + \omega_{\tilde{\alpha}} - \omega_{\tilde{\beta}})E_{n+1}^2 = \Gamma_n^2(a_{\tilde{\alpha}\tilde{\beta}}^+; A_{\tilde{0}'}), E \delta_{\tilde{0}', \tilde{\beta}} - \Gamma_n^2(a_{\tilde{\alpha}\tilde{\beta}}^+; A_{\tilde{0}'}), E \delta_{\tilde{0}', \tilde{\alpha}}$$

$$+ 6V_{\tilde{\alpha}, -\tilde{0}, -\tilde{\beta}}^{(3)}(n_{\tilde{\alpha}} - n_{\tilde{\beta}} + 1)G_{n+1}^1 + 6V_{\tilde{\alpha}, -\tilde{0}, -\tilde{\beta}}^{(3)}(n_{\tilde{\alpha}} - n_{\tilde{\beta}} + 1)G_{n+1}^2, \quad (4.8b)$$

and

$$(nE - \omega_{\tilde{\alpha}} - \omega_{\tilde{\beta}})E_{n+1}^3 = \Gamma_n^3(a_{\tilde{\alpha}\tilde{\beta}}^+; A_{\tilde{0}'}), E \delta_{\tilde{0}', -\tilde{\alpha}} + \Gamma_n^3(a_{\tilde{\alpha}\tilde{\beta}}^+; A_{\tilde{0}'}), E \delta_{\tilde{0}', \tilde{\beta}}$$

$$+ 6V_{\tilde{\alpha}, -\tilde{0}, -\tilde{\beta}}^{(3)}(n_{\tilde{\alpha}} + n_{\tilde{\beta}} + 1)G_{n+1}^1 + 6V_{\tilde{\alpha}, -\tilde{0}, -\tilde{\beta}}^{(3)}(n_{\tilde{\alpha}} + n_{\tilde{\beta}} + 1)G_{n+1}^2. \quad (4.8c)$$

On solving Eqs. (4.8 a-c) for E_{n+1}^1 , E_{n+1}^2 , and E_{n+1}^3 and substituting the results into Eqs. (4.5) and (4.6), we obtain

$$[nE + \omega_0 + \sum(\tilde{0}) + r_3(E)]G_{n+1}^1 = -\frac{\delta(G_n)}{2\pi} - r_3(E)G_{n+1}^2 - K_n(E) \quad (4.9)$$

and

$$[nE - \omega_0 - \sum(\tilde{0}) - r_3(E)]G_{n+1}^2 = \frac{\delta(G_n)}{2\pi} + r_3(E)G_{n+1}^1 + K_n(E), \quad (4.10)$$

where

$$r_3(E) = r_2(E)|_{E \rightarrow nE} \quad (4.11)$$

and

$$K_n(E) = 3 \sum_{\tilde{\alpha}, \tilde{\beta}} V_{\tilde{\alpha}, \tilde{\beta}, -\tilde{0}}^{(3)} \left\{ \frac{\Gamma_n^3(a_{\tilde{\alpha}\tilde{\beta}}^+; A_{\tilde{0}'}), E \delta_{\tilde{0}', -\tilde{\alpha}} + \Gamma_n^3(a_{\tilde{\alpha}\tilde{\beta}}^+; A_{\tilde{0}'}), E \delta_{\tilde{0}', \tilde{\beta}}}{nE - \omega_{\tilde{\alpha}} - \omega_{\tilde{\beta}}} \right. \\ \left. - \frac{[\Gamma_n^1(a_{\tilde{\alpha}\tilde{\beta}}^+; A_{\tilde{0}'}), E \delta_{\tilde{0}', \tilde{\alpha}} + \Gamma_n^1(a_{\tilde{\alpha}\tilde{\beta}}^+; A_{\tilde{0}'}), E \delta_{\tilde{0}', \tilde{\beta}}]}{nE + \omega_{\tilde{\alpha}} + \omega_{\tilde{\beta}}} \right. \\ \left. + \frac{2[\Gamma_n^2(a_{\tilde{\alpha}\tilde{\beta}}^+; A_{\tilde{0}'}), E \delta_{\tilde{0}', \tilde{\beta}} - \Gamma_n^2(a_{\tilde{\alpha}\tilde{\beta}}^+; A_{\tilde{0}'}), E \delta_{\tilde{0}', \tilde{\alpha}}]}{nE + \omega_{\tilde{\alpha}} - \omega_{\tilde{\beta}}} \right\}. \quad (4.12)$$

On solving Eqs. (4.9) and (4.10) for G_{n+1}^1 and G_{n+1}^2 and substituting the results into Eq. (4.1), we find that the n th order nonlinear complex susceptibility tensor becomes

$$\chi_{\mu\nu}^{n+1}(\omega) = (-2\pi)^n N \sum_{\tilde{Q}, \tilde{Q}'} \frac{M_\mu(\tilde{Q}) M_\nu(\tilde{Q}')}{(\omega_0 \omega_0')^{\frac{n}{2}}} \left\{ 2\pi \left[\frac{\omega_0 + \sum(\tilde{Q})}{Y Y^2} \right] + K_n(E) \left[\frac{\omega_0 + \sum(\tilde{Q})}{Y Y^2} \right] \right\}, \quad (4.13)$$

where

$$Y^1 = nE + \omega_0 + \sum(\tilde{Q}) + r_3(E)$$

and

$$Y^2 = nE - \omega_0 - \sum(\tilde{Q}) - r_3(E). \quad (4.14)$$

The lowest-order nonlinear susceptibility results from setting $n = 2$ in Eq. (4.13). The result is¹⁹

$$\chi_{\mu\nu}^3(\omega) = \frac{3(2\pi)}{2} N \sum_{\tilde{Q}} \frac{M_\mu(\tilde{Q}) M_\nu(\tilde{Q}) v_{\tilde{Q}, \tilde{Q}, \tilde{Q}}^{(3)}}{Y Y^2 Y_1 Y_2} \left\{ Y_2 + r_2(E) \frac{Y_2 - \omega_0}{E - \omega_0} + \frac{Y_1 - r_2(E)}{E + \omega_0} + \frac{2(Y_2 + Y_1)}{E} \right\}, \quad (4.15)$$

where

$$Y_1 = E + \omega_0 + \sum(\tilde{Q}) + r_2(E) \quad (4.16a)$$

and

$$Y_2 = E - \omega_0 - \sum(\tilde{Q}) - r_2(E). \quad (4.16b)$$

or

$$\chi_{\mu\nu}^3(\omega) = \frac{3(2\pi)}{2} N \sum_{\tilde{Q}} \frac{M_\mu(\tilde{Q}) M_\nu(\tilde{Q}) v_{\tilde{Q}, \tilde{Q}, \tilde{Q}}^{(3)}}{Y Y^2 Y_1 Y_2} \times \left\{ \frac{\omega - \omega_0 - \sum(\tilde{Q})}{\omega - \omega_0} + \frac{\omega + \omega_0 + \sum(\tilde{Q})}{\omega + \omega_0} + 4 \right\}, \quad (4.17)$$

where

$$Y Y^2 Y_1 Y_2 \approx [(2\omega)^2 - \omega_0^2][\omega^2 - \omega_0^2] - 2\omega_0 \sum(\tilde{Q})[5\omega^2 - 2\omega_0^2] - 2\omega_0[(2\omega)^2 - \omega_0^2]r_2(E) - 2\omega_0(\omega^2 - \omega_0^2)r_3(E). \quad (4.18)$$

On neglecting $\sum(\tilde{Q})$, we find that

$$\chi_{\mu\nu}^3(\omega) = (2\pi)(9) N \sum_{\tilde{Q}} M_\mu(\tilde{Q}) M_\nu(\tilde{Q}) v_{\tilde{Q}, \tilde{Q}, \tilde{Q}}^{(3)} \times \left\{ \frac{1}{[(2\omega)^2 - \omega_0^2][\omega^2 - \omega_0^2] + 2\omega_0[\omega_0^2 - (2\omega)^2]r_2(E) + 2\omega_0[\omega_0^2 - \omega^2]r_3(E)} \right\}. \quad (4.19)$$

From Eq. (4.19) we note that the damping consists of the following two additive parts:

$$\Gamma(\omega) = \Gamma^2(\omega) + \Gamma^3(\omega), \quad (4.20)$$

where

$$\Gamma^3(\omega) = \Gamma^2(\omega) \Big|_{\omega \rightarrow 2\omega} \quad (4.21)$$

The explicit temperature dependence of the damping constant, Eq. (4.20), is not altered by increasing the strength of the applied field. Here, the damping constant varies explicitly as T ($n \rightarrow kT$) in the high-temperature limit. However, the frequency dependence of the susceptibility is altered; the frequency, ω , of the applied field is converted into second-harmonic waves with frequency 2ω . This is characteristic of nonlinear response coefficients.

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FOOTNOTES AND REFERENCES

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14. We have shown, using a two-time Green's function method, that the quartic anharmonic contribution is of the order $O(1/N^2)$ compared to a $O(1/N)$ contribution from the cubic term for large N . The details of this work will be presented in a separate paper.
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19. Here we have made use of the linear results developed in Sec. III.

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