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# Relaxation Time for Scattering of Phonons by Substitutional Impurities

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Klemens's method of deriving the relaxation time for the scattering of phonons by substitutional impurities in a Bravais crystal has been examined, with some new results obtained. The Hamiltonian has been expressed in terms of what we call effective atom mass and effective force constants characterizing the crystal. It is seen that in the case of low-frequency phonons, the fractional changes in impurity atom mass and force constants make reinforcing or cancelling contributions to the relaxation rate, according to whether they are of equal or opposite signs. For high-frequency phonons, the situation is the opposite.

## I. INTRODUCTION

Previously, Klemens[1,2] has used time-dependent perturbation theory to study the scattering of phonons by various types of defects in a crystal. He has found that the relaxation time for phonon scattering by substitutional impurities is approximately proportional to the fourth power of the phonon frequency. To some approximation, this result is also given by the Green's-function technique,[3-6] which has received wide application for some time. The Green's-function method is definitely superior to the perturbation method in some respects, but it is also possible to derive certain interesting results using time-dependent perturbation method if one is careful in writing the perturbation part of the Hamiltonian. Recently, Krumhansl and Matthew[3] have shown that in the case of a linear chain of atoms, atomic mass changes and force-constant changes cause reinforcing or cancelling contributions to the relaxation rate according to whether they are of equal or of opposite signs, respectively, in the case of low-frequency phonons. One might expect similar results in the case of a three-dimensional crystal. Klemens's treatment does not indicate clearly any result of this sort. The objective of the present paper is, therefore, to confirm Krumhansl and Matthew's results, employing first-order time-dependent perturbation theory, and to show that in the case of high-frequency phonons, the situation is reversed – the mass change and force-constant changes make reinforcing contributions when they are of opposite signs. These results are easily obtained for a linear atomic chain.[7]

## II. HAMILTONIAN

We consider a three-dimensional Bravais crystal with volume $\Omega$ and total number of atoms $N\Omega$, $N$ being the number of atoms per unit volume. Let us denote the position vector of an atomic site by $\vec{r}$. If the crystal contains a substitutional impurity at site $\vec{x}$, then in the harmonic approximation, the potential energy of the system can be given by

$$\begin{aligned} V_1 = {} & \frac{1}{2} \sum_{\vec{r},\vec{r}\,'\neq\vec{r}}{}' \vec{u}(\vec{r}) \cdot \overleftrightarrow{\Phi}(\vec{r},\vec{r}\,') \cdot \vec{u}(\vec{r}\,') \\ & - \frac{1}{2} \sum_{\vec{r}}{}' \vec{u}(\vec{r}) \cdot \overleftrightarrow{\Phi}{}'(\vec{r},\vec{r}) \cdot \vec{u}(\vec{r}) \\ & + \sum_{\vec{r}}{}' \vec{u}(\vec{r}) \cdot \overleftrightarrow{\Phi}{}'(\vec{r},\vec{x}) \cdot \vec{u}(\vec{x}) \\ & + \tfrac{1}{2} \vec{u}(\vec{x}) \cdot \overleftrightarrow{\Phi}{}'(\vec{x},\vec{x}) \cdot \vec{u}(\vec{x}), \end{aligned} \tag{1}$$

which we have written following Ziman,[8] who defines $\overleftrightarrow{\Phi}(\vec{r},\vec{r}\,')$ as the force-constant tensor[9] between atoms at sites $\vec{r}$ and $\vec{r}\,'$, which satisfies the following:

$$\overleftrightarrow{\Phi}(\vec{r},\vec{r}\,') = \overleftrightarrow{\Phi}(|\vec{r}-\vec{r}\,'|). \tag{2}$$

The primed $\overleftrightarrow{\Phi}$'s are those which get changed in the presence of the impurity at $\vec{x}$. $\vec{u}(\vec{r})$ denotes the displacement vector of the atom at site $\vec{r}$. The prime over $\sum$ denotes that $\vec{r}$ and $\vec{r}\,'$ do not take the value $\vec{x}$. Notice that $\overleftrightarrow{\Phi}(\vec{r},\vec{r})$ also is changed on account of the following condition[6,9]:

$$\overleftrightarrow{\Phi}(\vec{r},\vec{r}) = -\sum_{\vec{r}\,'} \overleftrightarrow{\Phi}(\vec{r},\vec{r}\,'), \qquad \vec{r}\,'\neq\vec{r}\,. \tag{3}$$

In order to get a simplified expression for $V$, we assume that all the force constants involving the impurity are increased by the same fraction as that by which the nearest-neighbor force constants are increased. This is not a very drastic approximation, first, because in most of the cases the nearest-neighbor interaction is more important than any other, and second, because this is in no way worse than neglecting the other neighbor interactions altogether. This assumption should be particularly valid when the nature of the impurity atom differs only little from that of the normal atom. Thus we write

$$\overleftrightarrow{\Phi}'(\vec{r},\vec{x})-\overleftrightarrow{\Phi}(\vec{r},\vec{x})=\alpha\Phi(\vec{r},\vec{x}),\quad \vec{r}\neq\vec{x}\,. \tag{4}$$

Making use of Eqs. (3) and (4), one can write Eq. (1) as follows:

$$\begin{aligned} V_1=&\frac{1}{2}\sum_{\vec{r},\vec{r}'}\vec{u}(\vec{r})\cdot\overleftrightarrow{\Phi}(\vec{r},\vec{r}')\cdot\vec{u}(\vec{r}')\\ &+\alpha\sum_{\vec{r}}\vec{u}(\vec{r})\cdot\overleftrightarrow{\Phi}(\vec{r},\vec{x})\cdot\vec{u}(\vec{x})\\ &-\frac{\alpha}{2}\sum_{\vec{r}}\vec{u}(\vec{r})\cdot\overleftrightarrow{\Phi}(\vec{r},\vec{x})\cdot\vec{u}(\vec{r}). \end{aligned} \tag{5}$$

Let us now turn our attention to a crystal containing impurities (all similar in nature) at a concentration $n$ per unit volume. If it is assumed that the impurities are distributed randomly, and if $n$ is quite small compared with $N$, then one can assume that the distance between any two impurities is so large that their mutual interaction can be neglected. In this case, the potential energy $V$ can be obtained from (5) by making summation over $\vec{x}$ (impurity site), that is,

$$\begin{aligned} V=&\frac{1}{2}\sum_{\vec{r},\vec{r}'}\vec{u}(\vec{r})\cdot\overleftrightarrow{\Phi}(\vec{r},\vec{r}')\cdot\vec{u}(\vec{r}')\\ &+\alpha\sum_{\vec{x}}\sum_{\vec{r}}\vec{u}(\vec{r})\cdot\overleftrightarrow{\Phi}(\vec{r},\vec{x})\cdot\vec{u}(\vec{x})\\ &-\frac{\alpha}{2}\sum_{\vec{x}}\sum_{\vec{r}}\vec{u}(\vec{r})\cdot\overleftrightarrow{\Phi}(\vec{r},\vec{x})\cdot\vec{u}(\vec{r})\,. \end{aligned} \tag{5'}$$

We now define

$$\overleftrightarrow{\Phi}_0(\vec{r},\vec{r}')=(1+2\alpha f)\overleftrightarrow{\Phi}(\vec{r},\vec{r}'), \tag{6}$$

where $f=n/N$. Then one can write

$$V=V_0+\Delta V, \tag{7}$$

where

$$V_0=\frac{1}{2}\sum_{\vec{r}\,\vec{r}'}\vec{u}(\vec{r})\cdot\overleftrightarrow{\Phi}_0(\vec{r},\vec{r}')\cdot\vec{u}(\vec{r})$$

and

$$\begin{aligned} \Delta V=\sum_{\vec{x}}\frac{\alpha}{(1+2\alpha f)}\Bigg(&\sum_{\vec{r}}\vec{u}(\vec{r})\cdot\overleftrightarrow{\Phi}_0(\vec{r},\vec{x})\cdot\vec{u}(\vec{x})\\ &-\frac{1}{2}\sum_{\vec{r}}\vec{u}(\vec{r})\cdot\overleftrightarrow{\Phi}_0(\vec{r},\vec{x})\cdot\vec{u}(\vec{r})\\ &-f\sum_{\vec{r}\,\vec{r}'}\vec{u}(\vec{r})\cdot\overleftrightarrow{\Phi}_0(\vec{r},\vec{r}')\cdot\vec{u}(\vec{r}')\Bigg)\,. \end{aligned}$$

The significance of $\overleftrightarrow{\Phi}_0(\vec{r},\vec{r}')$ will be discussed later.

Let us now calculate the kinetic energy $T$ of the system. If $m$ and $m'$ are the masses of the normal and impurity atoms, respectively, then

$$T={\sum_{\vec{r}}}'\frac{1}{2m}\vec{p}^{\,2}(\vec{r})+\frac{1}{2m'}\sum_{\vec{x}}\vec{p}^{\,2}(\vec{x}) \tag{8}$$

(as before prime over $\sum$ means $r\neq x$). We define $m_0$ by

$$\frac{1}{m_0}=\frac{f}{m'}+\frac{1-f}{m}, \tag{9}$$

that is, $m_0$ is the weighted harmonic mean of the masses of all atoms. We have

$$T=T_0+\Delta T, \tag{10}$$

where

$$T_0=\sum_{\vec{r}}\frac{1}{2m_0}\vec{p}^{\,2}(\vec{r})$$

and

$$\Delta T=\sum_{\vec{r}}\frac{f}{2\mu}\vec{p}^{\,2}(\vec{r})-\sum_{\vec{x}}\frac{1}{2\mu}\vec{p}^{\,2}(\vec{x}),$$

$\mu$ being equal to $mm'/(m'-m)$.

The Hamiltonian of the system can be given by $H=H_0+H'$, where $H_0$ and $H'$ are equal to $T_0+V_0$ and $\Delta T+\Delta V$, respectively. We call $H'$ as the perturbation part of the Hamiltonian which is responsible for the scattering of phonons. $H'$ can be written in terms of the phonon-creation and phonon-annihilation operators[8,10] (see Appendix) as follows:

$$\begin{aligned} H'=&\sum_{\vec{q}j,\vec{q}'j'}\hbar\,\frac{\chi(q'')(\omega\omega')^{1/2}}{N\Omega}\\ &\times\Bigg\{\Bigg[\left(\frac{m_0}{\mu}-\frac{\alpha(\omega^2+\omega'^2)}{(1+2\alpha f)\omega\omega'}\right)\vec{e}\cdot\vec{e}'\\ &+\frac{\alpha}{1+2\alpha f}\sum_{j''}\frac{\omega''^2}{\omega\omega'}(\vec{e}\cdot\vec{e}'')(\vec{e}''\cdot\vec{e}')\Bigg]a^+a'\\ &+\text{terms involving } aa' \text{ and } a^+a'^+\Bigg\},\quad \vec{q}'j'\neq\vec{q}j, \end{aligned} \tag{11}$$

$\chi(q'')$ being equal to $\sum_{\vec{x}}e^{i\vec{q}''\cdot\vec{x}}$. Here we use $\omega$, $\omega'$, and $\omega''$ as shorts for $\omega(\vec{q}j)$, $\omega(\vec{q}'j')$, and $\omega(\vec{q}''j'')$, respectively, $\vec{q}''$ being equal to $(\vec{q}-\vec{q}')$. Likewise, $a=a(\vec{q}j)$, and $\vec{e}=\vec{e}(\vec{q}j)$, etc.

One has to calculate the modulus square of the matrix element of $H'$ between two different states of the system in order to evaluate the relaxation time (see Sec. III). It is therefore required to calculate the value of $|\chi(\vec{q}'')|^2$. If the number of impurity atoms be sufficiently large, then it can be easily realized that $|\chi(\vec{q}'')|^2$ is almost constant and approximately equal to $n\Omega=fN\Omega$ for $n\ll N$. If we consider the case $n\to N$, then the normal atoms can be taken as impurities; and impurities, as normal atoms. One then writes

$$|\chi(q'')|^2\approx(N-n)\Omega=(1-f)N\Omega\,.$$

This means that as $n$ varies from zero to $N$,

$|\chi(q'')|^2$ varies from $fN\Omega$ to $(1-f)N\Omega$. Clearly, the best average value for $|\chi(q'')|^2$ appears to be $f(1-f)N\Omega$.

We now discuss the significance of defining $m_0$ and $\overleftrightarrow{\Phi}_0$'s. Based on the so-called virtual-crystal approximation, we divide the Hamiltonian into $H_0$ and $H'$ such that the perturbation $H'$ does not contain terms of the form $a^{+}a$. In other words, any diagonal terms that would normally occur in $H'$ have now been included in $H_0$. We achieve this by defining $\overleftrightarrow{\Phi}_0$ and $m_0$ through Eqs. (6) and (9). One might call $\overleftrightarrow{\Phi}_0$'s and $m_0$ as the effective force constants and effective atom mass, respectively, that are seen by the phonons in the crystal. It is seen that these differ from the normal atom force constants and normal atom mass, respectively, by amounts that are determined by the impurity concentration. Furthermore, this sort of division of $H$ into $H_0$ and $H'$ automatically results in the introduction of the factor $1/(1+2\alpha f)$ in the expression for $V$ [Eq. (7)]. Usually, $\alpha f$ is small compared with 1, but it is independent of the crystal volume and is a constant for a given impurity concentration.

## III. RELAXATION TIME

By making use of the expression for $H'$ given by Eq. (11) and employing first-order time-dependent perturbation,[11] one can show that the rate $\partial n/\partial t$, at which phonon occupation number in state $(\vec{q}j)$ increases with time, can be given by

$$\frac{\partial n}{\partial t}=\sum_{j'}\frac{f(1-f)\omega^4}{16\pi^2 N}\int_0^{2\pi}d\varphi\int_0^{\pi}d\theta\,\sin\theta\,\frac{(n'-n)}{v_g'\,v_p'^2}$$
$$\times\left[b^2|\vec{e}\cdot\vec{e}\,'|^2+c^2\left|\sum_{j''}\left(\frac{\omega''}{\omega}\right)^2(\vec{e}\cdot\vec{e}\,'')\,(\vec{e}\,''\cdot\vec{e}\,')\right|^2\right.$$
$$\left.+2bc\sum_{j''}\left(\frac{\omega''}{\omega}\right)^2(\vec{e}\cdot\vec{e}\,'')(\vec{e}\,''\cdot\vec{e}\,')(\vec{e}\,'\cdot\vec{e})\right], \quad (12)$$

where $b=(m_0/\mu-2c)$ and $c=\alpha/(1+2\alpha f)$. $n$ is the phonon occupation number of state $\vec{q}j$. The integration in Eq. (12) is to be carried over constant-energy surfaces (characterized by energy $\hbar\omega$) in the wave-vector space. In other words, the variables involved above correspond to $\vec{q}\,'$ which is a solution of $\omega(\vec{q}\,'j')=\omega(\vec{q}j)\cdot(\theta,\varphi)$ measures the direction of $\vec{q}\,'$ with respect to $\vec{q}$. $\vec{v}_g$ and $\vec{v}_p$ are the group velocity (defined by $\partial\omega/\partial\vec{q}$) and phase velocity (defined by $\omega/\vec{q}$), respectively.

From Eq. (12), one can determine the single-mode relaxation time,[1] by putting $n'=n_0$ (Planck distribution). The relaxation time $\tau$ is defined by

$$\frac{\partial n}{\partial t}=\frac{n_0-n}{\tau}\quad . \quad (13)$$

An exact calculation of $\tau$ is almost impossible. One has, therefore, to resort to some specific model for the phonon dispersion. However, a good deal of information can be easily obtained by a careful study of Eq. (12). The integrand of this equation is seen to contain three types of terms; two of these are proportional to the squares of $m_0/\mu$ and $\alpha/(1+2\alpha f)$, respectively. In other words, these are proportional to the squares of the mass and force-constant changes, respectively. The third term involves the product of $m_0/\mu$ and $\alpha(1+2\alpha f)$. Contributions to this term come from the first and third terms inside the square brackets in Eq. (12). Since the phonon frequency does not increase monotonically with phonon wave vector, but rather increases gradually at first, when the wave vector lies in the first Brillouin zone, and then begins to decrease, the contribution of the latter term varies strongly with phonon frequency $\omega$. In fact, it happens that, for $\omega$ small, its contribution exceeds that of the former term, and this results in a positive coefficient for

$$(m_0/\mu)[\alpha/(1+2\alpha f)].$$

For large values of $\omega$, the situation is exactly opposite, and we get a negative coefficient for

$$(m_0/\mu)[(\alpha/(1+2\alpha f)].$$

These results can be interpreted to mean that for $\omega$ small, the contributions to $\tau^{-1}$ of $\alpha$ and $\mu$ reinforce each other when they are of the same sign, and interfere destructively when they have opposite signs. For large values of $\omega$, their contributions are of opposite nature compared to above. To elaborate this point, we assume a highly simplified dispersion model in the following and calculate $\tau$.

If it is assumed that the direction dependence of $v_g'\,v_p'^2$ is not very pronounced, then one can write a weighted average $v_{gj'}\,v_{gj'}^2$ for this in Eq. (12) and then take it out of the integral. It is obvious that the contribution to $\tau^{-1}$ of the second and third terms inside the square brackets in Eq. (12) is much more difficult to calculate than that of the first term. Let us denote them by $\tau_2^{-1}$ and $\tau_1^{-1}$, respectively, so that $\tau^{-1}=\tau_1^{-1}+\tau_2^{-1}$. Taking the direction average of $|\vec{e}\cdot\vec{e}\,'|^2$ to be equal to $\frac{1}{3}$ as done by Klemens,[1] we get

$$\tau_1^{-1}=\frac{b^2\omega^4}{12\pi N}f(1-f)\sum_{j'}\frac{1}{v_{gj'}\,v_{pj'}^2}\quad . \quad (14)$$

We now turn our attention to the evaluation of $\tau_2$. To achieve this, we introduce a number of simplifying assumptions. The crystal is assumed to be isotropic so that the Brillouin zone is spherically symmetric. In the case of an isotropic body, the longitudinal polarization vector is along the phonon wave vector, and the transverse polarization vectors are oriented in a plane perpendicular to the phonon wave vector. In order to take account of the periodic nature of the phonon frequency $\omega$ as a function of the phonon wave vector $q$, we assume that $\omega$ increases linearly with $q$ up to a maximum value $q_m$ of $q$, and then decreases linearly, being zero when $q = 2q_m$. Evidently, $q_m$ defines the Debye sphere. The phase velocity is then the same as the group velocity. Let us call either of them phonon velocity, denoted by $v$. Since the transverse polarization vectors can be in any direction in a plane perpendicular to the phonon wave vector, the integrand in the expression for $\tau_2^{-1}$ is to be averaged over the corresponding directions. The main difficulty in evaluating $\tau_2^{-1}$ arises in expressing $\omega''$ in terms of $\omega$. If it is assumed that the phonon velocity is the same for all polarization branches, then one can write

$$q'' = 2q \sin\tfrac{1}{2}\theta \ , \tag{15}$$

and consequently

$$\omega'' = 2\omega \sin\tfrac{1}{2}\theta \ , \tag{16}$$

when the phonon frequency is sufficiently small such that $q < \frac{1}{2}q_m$. If $q$ does not satisfy this condition, then $q''$ will exceed $q_m$. In such cases

$$\omega'' = 2\omega(1 - \sin\tfrac{1}{2}\theta), \tag{17}$$

in accordance with the assumed periodicity of the phonon frequency.

We have evaluated (2) when $\omega < \frac{1}{2}\omega_m$, and also when $\omega \approx \omega_m$; the results are

$$\begin{aligned} \tau_2^{-1} &\approx K(\tfrac{3}{2}c^2 + bc) \ , && \omega < \omega_m/2 \\ &\approx K(\tfrac{19}{280}\, c^2 + \tfrac{59}{280}\, bc), && \omega \approx \omega_m \end{aligned} \tag{18}$$

for the longitudinal phonons, and

$$\begin{aligned} \tau_2^{-1} &\approx K(\tfrac{23}{12}\, c^2 + bc), && \omega < \omega_m/2 \\ &\approx K(\tfrac{37}{560}\, c^2 + \tfrac{317}{1680}\, bc), && \omega \approx \omega_m \end{aligned} \tag{19}$$

for the transverse phonons, $K$ being equal to $f(1-f)\,\omega^4/\pi N v^3$.

## IV. DISCUSSION

We have found that the inverse relaxation time $\tau^{-1}$ for the phonon scattering due to a substitutional defect in a Bravais crystal can be expressed as the sum of two terms, $\tau_1^{-1}$ and $\tau_2^{-1}$. It can be seen that $\tau^{-1}$ is approximately proportional to the fourth power of the phonon frequency. The first term $\tau_1^{-1}$ is similar to what Klemens[1] has obtained. In obtaining $\tau$ we have taken proper account of the simultaneous changes in mass and force constants when an atom is replaced by an impurity. Krumhansl and Matthew[3] have pointed out that it is essential to superimpose different matrix-element contributions to the scattering amplitude before squaring to compute the scattering relaxation rate. They have shown that in the case of a linear atomic chain with a nearest-neighbor force constant, $\Phi$, $m' - m$ and $(\Phi' - \Phi)/\Phi$ make reinforcing or cancelling contributions depending on whether they have similar or opposite signs. Similar results are also obtained in the present case. This is clear when $\tau$ is expressed explicitly in terms of $m_0/\mu$ and $\alpha$. It is found that in the case of low-frequency phonon, $m_0/\mu$ and $\alpha$ make reinforcing contributions when they are of similar signs, and cancelling contributions when they are of opposite signs. In the case of high-frequency phonons, the situation is different, reinforcing contributions are obtained when $m_0/\mu$ and $\alpha$ are of opposite signs. Obviously, there can be certain phonon frequencies for which the contribution of the force-constant changes is expected to be negligibly small. It is to be emphasized that these results are essentially due to the occurrence of the second term in the perturbation part of the Hamiltonian [Eq. (11)].

We summarize the results by saying that the relaxation time is approximately proportional to the fourth power of phonon frequency $\omega$. The proportionality constant, however, depends strongly on $\omega$, and decides how $\alpha$ and $\mu$ make contributions to $\tau^{-1}$. The results we have derived by making simplifying assumptions are also expected to hold for real crystals and appear to be plausible on the basis of short-range order effects. In fact, the second term inside the braces in Eq. (11) is responsible for such results, which arise because of the periodic dependence of $\omega$ on $q$. The extent to which our results can be reliable depends on the validity on the perturbation approach. The situation becomes somewhat complicated when there are resonances. Nevertheless, we believe in the qualitative features of the present results, which are expected to hold at least when $\alpha$ and $m' - m$ are small. For large $\omega$, these results should not be taken to be quantitatively correct.

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## APPENDIX

The normal coordinate $\vec{Q}(\vec{q})$ and conjugate momentum $\vec{P}(\vec{q})$ are defined by

$$\begin{aligned} \vec{u}(\vec{r}) &= (N\Omega)^{-1/2} \textstyle\sum_{\vec{q}} \vec{Q}(\vec{q})\, e^{i\vec{q}\cdot\vec{r}}, \\ \vec{p}(\vec{r}) &= (N\Omega)^{-1/2} \textstyle\sum_{\vec{q}} \vec{P}(\vec{q})\, e^{-i\vec{q}\cdot\vec{r}} \ , \end{aligned} \tag{A1}$$

where $\vec{q}$ is the phonon wave vector that can take only a limited number of discrete values confined to the first Brillouin zone. It is well known that

$$\textstyle\sum_{\vec{r}} e^{i\vec{q}\cdot\vec{r}} = N\Omega\,\delta(\vec{q}),$$

$$\sum_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} = N\Omega\delta(\vec{r}), \tag{A2}$$

where $\delta(\vec{x}) = 1$, when $\vec{x} = 0$, and 0 otherwise.

It can be shown that (Ziman[8])

$$H_0 = \sum_{\vec{q}} [(1/2m_0)\vec{P}(\vec{q}) \cdot \vec{P}^*(\vec{q}) + \tfrac{1}{2}\vec{Q}(\vec{q}) \cdot \overleftrightarrow{E}(\vec{q}) \cdot \vec{Q}^*(\vec{q})], \tag{A3}$$

where

$$\overleftrightarrow{E}(\vec{q}) = \sum_{\vec{h}} \overleftrightarrow{\Phi}_0(\vec{h})\, e^{i\vec{q}\cdot\vec{h}} .$$

From Eq. (A3), one can derive equations of motion for $\vec{Q}(\vec{q})$'s, for example,

$$m_0\omega^2\, \vec{Q}(\vec{q}) = \overleftrightarrow{E}(\vec{q}) \cdot \vec{Q}(\vec{q}). \tag{A4}$$

Equation (A4) is an eigenvalue equation. It can be proved that there exist three eigenvectors as solutions of Eq. (A4). We denote an eigenvector by $\vec{e}(\vec{q}j)$ (called polarization vector), which is chosen to be a unit vector, and the corresponding eigenfrequency by $\omega(qj)$. The index $j$ can take three values and is called the polarization index. We have

$$\overleftrightarrow{E}(\vec{q}) \cdot \vec{e}(\vec{q}j) = m_0\omega^2(\vec{q}j)\, \vec{e}(\vec{q}j). \tag{A5}$$

These eigenvectors are orthonormal,

$$\vec{e}(\vec{q}j) \cdot \vec{e}(\vec{q}j') = \delta_{jj'} , \tag{A6}$$

$\delta_{jj'}$ being the Kronecker $\delta$.

The phonon-creation operator $a^+(\vec{q}j)$ and the phonon-annihilation operator $a(\vec{q}j)$ are defined by[10]

$$\vec{Q}(\vec{q}) = \sum_j [\hbar/2m_0\omega(\vec{q}j)]^{1/2} [a(\vec{q}j) + a^+(-\vec{q}j)]\vec{e}(\vec{q}j), \tag{A7}$$

$$P(q) = \sum_j i[\hbar m_0\omega(\vec{q}j)/2]^{1/2} [a^+(\vec{q}j) - a(-\vec{q}j)]\, \vec{e}(\vec{q}j).$$

These operators satisfy the usual commutation relations.

Making use of the above results, we can express $H$ in terms of $a^+$'s and $a$'s. In particular, we need to simplify the expression

$$[\vec{e}(\vec{q}j) \cdot \overleftrightarrow{E}(\vec{q}\,'') \cdot \vec{e}(\vec{q}\,'j')]$$

that occurs in $H'$. We have

$$\vec{e}(\vec{q}\,'j') = \sum_{j''} \vec{e}(\vec{q}\,''j'')[\vec{e}(\vec{q}\,''j'') \cdot \vec{e}(\vec{q}\,'j')] \tag{A8}$$

from Eq. (A6). Using Eqs. (A5) and (A8) one can show that

$$\vec{e}(\vec{q}j) \cdot \overleftrightarrow{E}(\vec{q}\,'') \cdot \vec{e}(\vec{q}\,'j')$$
$$= \sum_{j''} m_0\, \omega^2(\vec{q}\,''j'')[\vec{e}(\vec{q}j) \cdot \vec{e}(\vec{q}\,''j'')]$$
$$\times[\vec{e}(\vec{q}\,''j'') \cdot \vec{e}(\vec{q}\,'j')]. \tag{A9}$$

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