PHYSICAL REVIEW VOLUME 122, NUMBER 2 APRIL 15, 1961

Anharmonic Attenuation of Localized Lattice Vibrations

P. G. KLEMENS
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

(Received December 9, 1960)

Lattice modes localized about defects can interchange energy with the continuum of lattice waves by anharmonic interactions. The relaxation time of a localized mode is calculated, taking account of cubic anharmonicities and using perturbation theory analogous to the treatment of three-phonon interactions. At zero temperature the relaxation time is typically of the order of 100 periods, but decreases with increasing temperature.

I. INTRODUCTION

THE vibrations of a perfectly regular and harmonic lattice can be resolved into travelling waves. Montroll and Potts[1] have shown that point defects modify these vibrational modes, and that in some cases there arise normal modes of vibration, localized in the vicinity of the defect and of frequency above the band of frequencies of the travelling waves.

While these localized modes of vibration are true normal modes if the interatomic forces are perfectly harmonic, the anharmonic components of these forces lead to an interchange of energy between a localized mode and travelling waves, just as the anharmonicities give rise to an interchange of energy among the travelling waves themselves. It is of some interest to inquire into the strength of these interactions, because if the relaxation time of the localized mode due to anharmonic interactions would turn out to be shorter than the vibrational period, one could not ascribe physical reality to these modes. One would expect the anharmonic effects to be strong, because much of the energy of a localized mode is concentrated near the defect, where the amplitude of the oscillation is large.

The present paper considers cubic anharmonicities, which lead to three-phonon interactions in perfect crystals and to the elastic scattering of phonons by static strain fields. The formalism for these interactions, developed for calculating thermal resistance,[2] is here adapted to the case when a quantum of the localized oscillation breaks up into two phonons. As surmised above, the resulting relaxation time is short, but not so short as to invalidate the concept of localized modes. At higher temperatures the relaxation time is shortened further, due to enhanced emission of phonons into the travelling wave modes.

II. THE PERTURBATION HAMILTONIAN

The perturbation Hamiltonian due to cubic anharmonicities for three-phonon interactions is of the form[2]

$$H'=\sum_{\mathbf{k},\mathbf{k}',\mathbf{k}''}\frac{1}{V}\int d\mathbf{x}\, e^{i\mathbf{x}\cdot(\mathbf{k}+\mathbf{k}'+\mathbf{k}'')}\times c(\mathbf{k},\mathbf{k}',\mathbf{k}'')a(\mathbf{k})a(\mathbf{k}')a(\mathbf{k}'')\cdots, \tag{1}$$

where V is the volume of the crystal, $\mathbf{x}$ the spatial coordinates, $\mathbf{k},\mathbf{k}',\mathbf{k}''$ the wave-vectors of the three interacting waves, $c(\mathbf{k},\mathbf{k}',\mathbf{k}'')$ a coefficient describing the interaction. The $a(\mathbf{k})$, $a(\mathbf{k}')$, $a(\mathbf{k}'')$ are the matrix elements (creation or annihilation operators) of the time-dependent wave amplitude, given explicitly by

$$a(\mathbf{k})=\left(\frac{\hbar}{M\omega}\right)^{\frac{1}{2}}\begin{bmatrix}N\\N+1\end{bmatrix}^{\frac{1}{2}}, \tag{2}$$

where ω is the frequency, M the atomic mass, N the number of quanta, and the factor N or $N+1$, respectively, is used for annihilation or creation.

In the present problem one of the three travelling waves in (1) is replaced by a localized mode. According to Montroll and Potts[1] the displacement about the defect is given by

$$u(r)=(u_0/kr)e^{-rk+i\omega t}, \tag{3}$$

where r is the radial distance from the impurity, ω the frequency of the localized mode, and k an attenuation length.

The amplitude u_0 is related to the energy of the mode as follows: The kinetic energy is

$$\frac{M}{2}\omega^2\frac{1}{a^3}\int d\mathbf{x}\, u^2(\mathbf{x})=\frac{M\omega^2}{2a^3}4\pi\int_0^\infty\frac{u_0^2}{k^2}e^{-2kr}dr, \tag{4}$$

where a^3 is the volume per atom. The energy of the mode is twice the kinetic energy, and is to be identified to $(N+\frac{1}{2})\hbar\omega$, where N is the number of quanta in the local mode. Thus $u_0e^{i\omega t}$ is replaced by the oscillator matrix

$$u_0e^{i\omega t}=\left(\frac{\hbar}{M\omega}\right)^{\frac{1}{2}}\frac{(ak)^{\frac{3}{2}}}{(2\pi)^{\frac{1}{2}}}\begin{bmatrix}N\\N+1\end{bmatrix}^{\frac{1}{2}}. \tag{5}$$

The displacement due to a travelling wave is given by

$$\mathbf{u}(\mathbf{x})=\frac{1}{\sqrt{G}}\sum_{\mathbf{k}}\boldsymbol{\varepsilon}a(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{x}}, \tag{6}$$

where G is the number of atoms in the crystal, $\boldsymbol{\varepsilon}$ the polarization direction. Thus $a(\mathbf{k})$ in (1) must be replaced by $G^{\frac{1}{2}}u(\mathbf{x})e^{i\omega t}$. Noting that, according to (3),

$$G^{\frac{1}{2}}\int e^{-i\mathbf{q}\cdot\mathbf{x}}u(\mathbf{x})d\mathbf{x}=4\pi\frac{G^{\frac{1}{2}}}{k}\frac{1}{k^2+q^2}u_0, \tag{7}$$

---

[1] E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955).

[2] P. G. Klemens, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1958), Vol. 7, p. 1.

we obtain, after the above replacement,

$$H'=\frac{4\pi}{V}\left(\frac{\hbar}{M}\right)^{\frac{3}{2}}\frac{(ak)^{\frac{3}{2}}}{(2\pi)^{\frac{1}{2}}}\frac{1}{k^3}$$

$$\times\sum_{\mathbf{k}',\mathbf{k}''}c(\mathbf{k},\mathbf{k}',\mathbf{k}'')\frac{k^2}{k^2+q^2}\left(\frac{1}{\omega\omega'\omega''}\right)^{\frac{1}{2}}$$

$$\times\left[\frac{(N+1)N'N''}{N(N'+1)(N''+1)}\right]^{\frac{1}{2}}. \quad (8)$$

Here we have $\mathbf{q}=\mathbf{k}'+\mathbf{k}''$.

The coefficient $c(\mathbf{k},\mathbf{k}',\mathbf{k}'')$ is the same as that used for three-phonon interactions, and is approximately[2]

$$c=-\frac{i}{G^{\frac{1}{2}}}\frac{2M}{\sqrt{3}}\frac{\gamma}{v}\omega\omega'\omega'', \quad (9)$$

where v is the velocity of sound and γ the Grüneisen constant.

III. THE RELAXATION TIME

The perturbation Hamiltonian (8) and (9) can be used in standard second-order perturbation theory. Because of the dependence of (8) on N, N' and N'', the rate of change of N is composed additively of terms each of which contains a factor

$$(N+1)N'N''-N(N'+1)(N''+1)$$
$$=N'N''-N(N'+N''+1). \quad (10)$$

If we write $N=\bar{N}+n$, where $\bar{N}$ is the equilibrium value of N, and n the deviation from equilibrium, then if $n'=n''=0$ the rate of change of N is proportional to terms of the form $-n(\bar{N}'+\bar{N}''+1)$. Thus the inverse of the relaxation time τ is given by

$$\frac{1}{\tau}=-\frac{1}{n}\frac{\partial N}{\partial t}\bigg]=\frac{1}{t}\frac{2}{\hbar^2}\left(\frac{8\pi}{V}\right)^2\frac{\hbar^3}{3M}\frac{\gamma^2}{v^2}\frac{(ak)^3}{2\pi}\frac{1}{k^6}$$

$$\times\sum_{\mathbf{k},\mathbf{k}'}\frac{1-\cos(\omega-\omega'-\omega'')t}{(\omega-\omega'-\omega'')^2}\omega\omega'\omega''\frac{k^4}{(k^2+q^2)^2}$$

$$\times[\bar{N}'+\bar{N}''+1]. \quad (11)$$

We must now sum over all $\mathbf{k}'$ and $\mathbf{k}''$. The resonance factor in (11) ensures the conservation of energy, i.e., the only real interactions contributing to (11) are those for which

$$\omega=\omega'+\omega''. \quad (12)$$

Without loss of generality we may assume that $\omega'>\omega''$. Thus in summing over all $\mathbf{k}'$ and $\mathbf{k}''$ we first choose a value of $\mathbf{k}'$ and then a value of $\mathbf{k}''$ consistent with (12). Thus

$$\sum_{\mathbf{k}',\mathbf{k}''}=\frac{V^2}{(2\pi)^6}\int d^3k'\frac{1}{v}\int d\omega''\int d^2k'', \quad (13)$$

and

$$\int d\omega''\frac{1-\cos(\omega-\omega'-\omega'')t}{(\omega-\omega'-\omega'')^2}=\pi t. \quad (14)$$

Hence

$$\frac{1}{\tau}=\frac{64\pi^2}{3(2\pi)^6}\gamma^2\frac{a^3}{k^3v}\frac{\hbar\omega}{Mv^2}\int d^3k'$$

$$\int d^2k''\,\omega'\omega''\frac{k^4}{(k^2+q^2)^2}[\bar{N}'+\bar{N}''+1]. \quad (15)$$

To simplify the integration we make the replacement

$$\begin{aligned}k^4/(k^2+q^2)^2 &\to 0 \quad \text{if } q>k\\ &\to \tfrac{1}{4} \quad \text{if } q<k. \quad (16)\end{aligned}$$

This simplification will cause the scattering to be somewhat underestimated. Let μ be the cosine of the angle between $\mathbf{k}'$ and $-\mathbf{k}''$. Then because of (16) we only count processes such that $q\leqslant k$. In view of the conservation of energy and the condition $\mathbf{q}=\mathbf{k}'+\mathbf{k}''$, this implies that we count only processes such that

$$\mu\geqslant\mu_0=\left(\frac{\omega^2}{v^2}-k^2\right)/2k'k''-1. \quad (17)$$

In general $\omega\simeq vk$, so that $\mu_0=-1$ and hence

$$\int d^2k''=2\pi k''^2\int d\mu=4\pi k''^2. \quad (18)$$

As a further simplification consider the absolute zero of temperature when $\bar{N}'=\bar{N}''=0$. Then the integration in (15) becomes, since $\omega''=\omega-\omega'$

$$\int d^3k'\,4\pi k''^2\omega'\omega''\frac{k^4}{(k^2+q^2)}=\frac{(4\pi)^2}{4}\frac{k_D{}^4}{v}\omega^3I(\omega/\omega_D), \quad (19)$$

where

$$I(x)=\int_0^1 y^3(1-y/x)^3dy, \quad (20)$$

and varies from 1/140 for $x=1$ to about 0.06 for $x=2$. Substituting (19) and (20) into (15), and noting that

$$(4\pi/3)(ak_D)^3=(2\pi)^3, \quad (21)$$

we obtain after some reduction for the relaxation time at absolute zero

$$\frac{1}{\tau_0}=\omega 8\gamma^2I(\omega/\omega_D)\frac{\hbar\omega}{Mv^2}\left(\frac{k_D}{k}\right)^3\left(\frac{\omega}{\omega_D}\right)^2. \quad (22)$$

In most cases of interest $k_D/k=\omega_D/\omega$ and k is comparable to k_D. In a typical case $\gamma=2$ and $\hbar\omega/Mv^2\simeq1/100$. Taking $\omega\simeq1.2\omega_D$, so that $I\simeq0.02$, this implies that $\tau_0\simeq100/\omega$. Hence the anharmonic interaction is not so strong as to destroy the character of the localized mode.

At higher temperatures the interaction is increased because of the factor $(\bar{N}'+\bar{N}''+1)$. If we define a characteristic temperature

$$T_c=\hbar(\omega-\omega_D)/k, \tag{23}$$

where k is now the Boltzmann constant, then at $T>T_c$ the term in $\bar{N}''$ is dominant. In the integral corresponding to (19) the frequency ω'' now only occurs to second power, and (22) is increased by a factor typically of order $3T/T_c$. Thus τ is substantially decreased at elevated temperatures.

IV. DISCUSSION

Expressions (22) and (24) give an estimate of the rate at which an excitation of the localized lattice vibrations around a defect will return to equilibrium, if excited above the equilibrium value by external means (e.g., optical pumping of an electronic excitation which is coupled to the local mode). Alternatively the quantity $\omega\tau$ is a measure of the relative broadening $\Delta\omega/\omega$ of the defect mode frequency, and $\Delta\omega$ describes the broadening due to anharmonic interaction of any optical spectral line involving the vibrational energy of the local mode.

We have seen that in typical cases at low temperatures $\Delta\omega/\omega\sim 1/100$. The broadening of an optical line due to this cause would in typical cases only be of the order of 10^{-3} ev or less.

The present estimate is probably a lower limit of the anharmonic broadening because in the treatment all approximations were made to underestimate the interaction. Thus expressions (3) for the local mode displacements is only an asymptotic expression for large r, and its Fourier transform (7) holds only for small q. Montroll and Potts[1] obtained an expression for the Fourier transform of the form $A/(B-\cos aq)$, which merges into (7) for low q, but is larger than (7) as q approaches k_D. Again we have underestimated the scattering by the approximations (16), perhaps by a factor 2. Finally, it should be remembered expression (9) for $c(\mathbf{k},\mathbf{k}',\mathbf{k}'')$ is based only on an approximate estimate of the cubic anharmonicities from their effect on the thermal expansion, and it is known that this estimate leads to a value for the thermal resistance due to three-phonon interactions and due to scattering of phonons by dislocations which is somewhat too low. It is not possible to give a reliable estimate of the effect of all these approximations, but in the author's opinion it is quite possible that the interaction has been underestimated by a factor of order 3 to 10.

The author is not aware of any existing spectroscopic data which would test the present theory. Pick[3] has observed an infrared absorption line due to U centers in some alkali halides which has been interpreted by Wallis and Maradudin[4] as being at the frequency of a localized mode. In this case the line is somewhat sharper than the present theory seems to allow. Due to the extremely small mass of the impurity, however, the local mode frequency is about four times the highest frequency of the continuum, so that a local mode quantum cannot split into two phonons. The anharmonic interaction must therefore be due to higher order processes, so that it is weaker at low temperatures than the present theory would predict, and presumably more strongly temperature dependent. Englman[5] has attributed certain sharp details in optical absorption spectra of chromium ions in magnesium oxide and aluminum oxide to the excitation of localized modes. The width of the small peaks is consistent with the present considerations, but this could hardly be regarded as a verification of this theory.

ACKNOWLEDGMENTS

The author wishes to thank his colleagues at Westinghouse who suggested and discussed this problem. Particular thanks are due to Dr. A. A. Maradudin for help in connection with the theory of localized modes, and for spotting a serious error.

---

[3] H. Pick, International Conference on Colour Centers, Oregon State College, Corvallis, Oregon, 1959 (unpublished).

[4] R. F. Wallis and A. A. Maradudin Progr. Theoret. Phys. (Kyoto) **24**, 1055 (1960).

[5] R. Englman, Phil. Mag. **5**, 691 (1960).