a 640-sec irradiation period) produced the 260°K glow with an integrated emission of 10^{10} photons. The absorption of the crystal at 360 mμ seems to be less than 1%. Assuming that each of the electrons at B will emit a photon during the glow, one gets about 10^{-4} as a lower limit for the efficiency of the excitation. Practically, absorption in the transition from A_1 to A_2 or from A_2 to the conduction band (see Fig. 8) might be much less than 1% and the actual efficiency is probably not far from 1, which is quite surprising for such an unusual process.

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Anharmonic Decay of Optical Phonons*

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An expression is derived from perturbation theory for the lifetime of an optical phonon decaying into two acoustical phonons, and its temperature dependence. The strength of the interaction is expressed in terms of the Grüneisen constant and the effect of a strain, equivalent to the instantaneous strain of an optical mode, on the frequency spectrum of a linear chain with alternating force constants. This interaction depends on the ratio of the acoustical and optical mode frequencies at the zone boundary. Fitting the theory to silicon, the optical mode at $\mathbf{k}=0$ has a calculated half-width at 300°K of about 1.2% of its frequency. This result is compared with experimental data.

I. INTRODUCTION

Because of the anharmonicity of the lattice forces, an optical mode can interchange energy with other lattice modes, and in this way maintain a thermal equilibrium energy content. In this respect, an optical mode behaves similarly to an acoustical mode. The rate at which an acoustic mode approaches equilibrium can be related to the relaxation time which enters the expressions for the thermal conductivity; optical modes, however, do not contribute substantially to thermal conduction. The relaxation time of optical modes does, however, determine such properties as the linewidth in infrared absorption measurements, in Raman scattering, and in inelastic neutron scattering experiments, and theoretical estimates of this lifetime are therefore of interest.

The principal anharmonic interaction is due to the cubic anharmonicities, resulting in the splitting of an optical phonon into two acoustic phonons of opposite momentum. This process will be estimated here from second-order perturbation theory. This method has been used extensively in thermal conductivity problems,[1] and has also been applied to the problem of the lifetime of a local mode.[2] The latter problem has many similarities to that of the optical mode: in one case, the local mode phonon splits into two acoustic phonons; in the other, the optical phonon splits into two acoustic phonons. The main difference is that in the case of the optical phonon one must consider momentum conservation, and in the case of the local mode the interaction is localized and there is no momentum conservation.

From physical intuition one would be led to believe that the lifetime of an optical phonon should be comparable to that of a local mode phonon of the same frequency, since the strain field of a local mode, in a small region about a defect, is similar in character to that of an optical mode. This expectation will indeed be verified. Nevertheless, we shall see that there is an important difference in the theory of these two cases—the method used in the local mode calculation cannot be simply taken over for the optical mode. It is therefore of some interest to describe the calculation for the lifetime of an optical mode.

A calculation of the lifetime of optical phonons has been reported by Cowley.[3] His calculation is based on the same principles as the present one, but differs in the method of estimating the interaction strength, and in that he sums over all interactions numerically by means of a computer. In principle his method is thus capable of greater precision than the present one, but the present calculation can be followed step by step, and has the advantage of greater physical insight and didactic value. It seems difficult to compare the

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

[2] P. G. Klemens, Phys. Rev. **122**, 443 (1961).

[3] R. A. Cowley, J. Phys. (Paris) **26**, 659 (1965).

two calculations except by their final result. Cowley's calculation leads to somewhat shorter lifetimes or wider lines than the present one. In the case of silicon, experimental results on the width of the first-order Raman line of Parker and Feldman[4] seem to support the present calculation. While this is gratifying, it may signify nothing more than a more fortunate choice of parameters.

II. THE PERTURBATION CALCULATION

Let us consider an optical phonon at $\mathbf{k}=0$ of frequency ω_0 which interacts by anharmonic three-phonon processes with two acoustic phonons of frequency ω', ω'' and wave vector $\mathbf{k}'$ and $\mathbf{k}''$, respectively. Conservation of energy and momentum requires

$$\omega_0=\omega'+\omega'', \tag{1}$$

and

$$\mathbf{k}=\mathbf{k}'+\mathbf{k}''=0. \tag{2}$$

The strength of the interaction is governed by the perturbation Hamiltonian

$$H'=\sum_{\mathbf{k},\mathbf{k}',\mathbf{k}'',\mathbf{x}}\frac{1}{G}e^{i(\mathbf{k}-\mathbf{k}'-\mathbf{k}'')\cdot\mathbf{x}}c(\mathbf{k},\mathbf{k}',\mathbf{k}'')\times a(\mathbf{k})a^*(\mathbf{k}')a^*(\mathbf{k}''), \tag{3}$$

where the coefficient $c(\mathbf{k},\mathbf{k}',\mathbf{k}'')$ is related to the cubic anharmonicities, G is the number of atoms in the crystal, and the coefficients a, a^* are creation and annihilation operators given by

$$\begin{aligned}a_{N,N+1}{}^*&=(\hbar/M\omega)^{1/2}(N+1)^{1/2},\\ a_{N,N-1}&=(\hbar/M\omega)^{1/2}N^{1/2}.\end{aligned} \tag{4}$$

In (4) N is the number of phonons and M the atomic mass. Since $\mathbf{k}=0$ we can disregard umklapp processes and H' vanishes unless $\mathbf{k}'=-\mathbf{k}''$, leading to (2).

From standard perturbation theory the rate of change of the occupation number N of mode $\mathbf{k}$ is given by

$$t\left.\frac{dN}{dt}\right]=2\sum_{j',j'',\mathbf{k}'}\frac{c^2\hbar^3}{M^3\omega\omega'\omega''}\frac{1-\cos\Delta\omega t}{\hbar^2\,\Delta\omega^2}\times[(N+1)N'N''-N(N'+1)(N''+1)], \tag{5}$$

when $\Delta\omega=\omega_0-\omega'-\omega''$, and the summation is over all modes $\mathbf{k}'$, and all polarizations of $\mathbf{k}'$ and $\mathbf{k}''$.

If $N=N^0+n$, when N^0 is the equilibrium value of N, and if N', N'' are in equilibrium, then the expression in square brackets on the right-hand side of (5) becomes $-n(N'+N''+1)$. At $T=0$ this becomes $-n$. Now

$$\int\frac{1-\cos\Delta\omega t}{\Delta\omega^2}d(\Delta\omega)=\pi t \tag{6}$$

and picks out contributions from processes for which $\Delta\omega=0$. Also

$$\Delta\omega=\omega-(1+\alpha)vk', \tag{7}$$

where v is the velocity of wave $\mathbf{k}'$, and αv is that of wave $\mathbf{k}''$. Without loss of generality we can choose $\omega'>\omega''$. In the case when $\mathbf{k}''$ and $\mathbf{k}'$ belong to the same polarization branch, $\alpha=1$, and we shall adopt that simplification.

Now $\sum_{j',j''}=6$ if interactions with all polarizations are allowed, i.e., $(j',j'')=(L,L)$, (L,T_1), (L,T_2), (T_1,T_1), (T_1,T_2), (T_2,T_2). But not all these possibilities are consistent with $\omega=\omega'+\omega''$; this depends on the nature of the dispersion curves. For example in Si, a case of experimental interest, energy conservation only permits (L,L), since the $\mathbf{k}=0$ optical mode is 1.6×10^{13} cps, while the top of longitudinal acoustic (LA) is 1.1 and transverse acoustic (TA) is below 0.4, so that LA+TA cannot reach the optical mode at $\mathbf{k}=0$. Let $\sum_{j',j''}=J$, a number between 1 and 6.

We define the relaxation time τ by

$$\frac{1}{\tau}=-\frac{1}{n}\left.\frac{dN}{dt}\right]. \tag{8}$$

Since

$$\sum_{\mathbf{k}'}=\frac{V}{(2\pi)^3}\int d^3k'=\frac{Ga^3}{(2\pi)^3}4\pi\int(k')^2dk', \tag{9}$$

where V is the volume of the crystal and a^3 the volume per atom, the summation (5) can be carried out. We note that $d\Delta\omega/dk'=-2v$, and $\omega'=\omega''=\omega_0/2$. After some rearrangement one obtains the following result:

$$\frac{1}{\tau}=\frac{J}{32\pi}\hbar\omega_0\frac{g^2G}{M^3}\frac{a^3\omega_0{}^2}{v^3}\omega_0, \tag{10}$$

where g is defined by $c(\mathbf{k},\mathbf{k}',\mathbf{k}'')=g\omega\omega'\omega''$. This relaxation time pertains to zero temperature. A similar result has been given by Weinreich.[5]

We must now estimate the coefficient c in (3) or (5), or the coefficient g. We could make use of the following standard result[1,2] in terms of the Grüneisen constant γ

$$c(\mathbf{k},\mathbf{k}',\mathbf{k}'')=-\frac{i}{\surd G}\gamma\frac{2M}{\surd 3}\frac{1}{v}\omega\omega'\omega'' \tag{11}$$

although we shall show below that this result is not applicable to the present case. With this form of g, Eq. (10) becomes

$$\frac{1}{\tau}=\omega_0\frac{J}{24\pi}\gamma^2\frac{\hbar\omega_0}{Mv^2}\frac{a^3\omega_0{}^3}{v^3}. \tag{12}$$

This can be simplified somewhat. If we take the fre-

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[4] J. H. Parker and D. W. Feldman (private communications).

[5] G. Weinreich, *Solids—Elementary Theory for Advanced Students* (John Wiley & Sons, New York, 1965), p. 94.

quency of the optical mode to be the Debye frequency of the corresponding monatomic lattice, which is of course only an approximation,

$$a^3\omega_0{}^3/v^3 = a^3k_D{}^3 = (3/4\pi)(2\pi)^3 \simeq 60\,, \tag{13}$$

where k_D is the Debye wave number. If we further take $\gamma=2$, $J=1$

$$\frac{1}{\tau}=\frac{60\times4}{24\pi}\omega_0\frac{\hbar\omega_0}{Mv^2}=3\omega_0\frac{\hbar\omega_0}{Mv^2}\,. \tag{14}$$

Taking for the typical case of silicon $Mv^2/K=30\,000$°K, $\hbar\omega_0/K=600$°K, we obtain for the inverse lifetime at zero temperature

$$1/\tau=0.06\omega_0\,. \tag{15}$$

III. THE INTERACTION HAMILTONIAN

The linewidth predicted from (15) is considerably greater than the width of the first-order Raman line of silicon observed by Parker and Feldman.[4] We must therefore examine the choice of the interaction Hamiltonian (11). The argument used to derive (11) proceeded as follows.

The unperturbed Hamiltonian can be written

$$H_0=\frac{1}{G}\sum_{\mathbf{x},\mathbf{k},\mathbf{k}'} M\omega\omega' e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}}a^*(\mathbf{k}')a(\mathbf{k}) \tag{16}$$

which, after summation over $\mathbf{x}$, has nonvanishing terms only for $\mathbf{k}'=\mathbf{k}$. A dilation Δ changes ω to $\omega(1-\gamma\Delta)$, so that H_0 is appropriately changed. If Δ, instead of being independent of $\mathbf{x}$, varies slowly with position, the perturbation is

$$H'=\frac{1}{G}\sum_{\mathbf{k},\mathbf{k}'} 2M\omega\omega' a^*(\mathbf{k}')a(\mathbf{k})\sum_{\mathbf{x}}\Delta(\mathbf{x})e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}}\,. \tag{17}$$

If now Δ is due not to a static strain, but to that of a third lattice wave, one readily obtains (11), except that a factor $1/\sqrt{3}$ has been included to consider the possibility that $\mathbf{k}$ and $\mathbf{k}'$ may belong to different polarization branches: In that case H' should include a trigonometric factor whose root mean square value is $1/\sqrt{3}$, when the different polarization directions are so complex as to be almost random.

This method of deriving $c(\mathbf{k},\mathbf{k}',\mathbf{k}'')$ applies strictly speaking to the case when one wave, say $\mathbf{k}$, is long so that its strain is only slowly varying, and where the other waves $\mathbf{k}'$ and $\mathbf{k}''$ are nearly equal. Equation (8) has frequently been applied to cases where the strain field of the first wave was no longer varying slowly, and although then no longer valid, the extrapolation from the case of uniform strain seems to give order of magnitude agreement, as seen from thermal conductivity studies.

In the present case, however, we have $\mathbf{k}'$ and $\mathbf{k}''$ of the same frequency, albeit moving in opposite direction, but the strain of the optical mode, even though it is of magnitude $(\omega/v)a(\mathbf{k})$, is not uniform, but changes sign even more rapidly than that of the other waves. Under these circumstances it seems questionable to use an approximation based on uniform strain.

The following alternative procedure will be used to estimate H': We consider the energy $M(\omega')^2a^*(\mathbf{k}')a(\mathbf{k}')$ of the mode $\mathbf{k}'$, and impose a *static* strain field identical to the instantaneous strain field of an optical mode. This causes a change in energy $2M\omega'\delta\omega'a^*(\mathbf{k}')a(\mathbf{k}')$. We now equate this change with $c(\mathbf{k},\mathbf{k}',-\mathbf{k}')a(\mathbf{k}=0)a(-\mathbf{k}')a(\mathbf{k}')$, i.e.,

$$c(\mathbf{k},\,\mathbf{k}',\,-\mathbf{k}')a(\mathbf{k})=2M\omega'\delta\omega'\,, \tag{18}$$

where $\delta\omega'$ is calculated for the same strain as that produced by $a(\mathbf{k})$.

As a model for the calculation of $\delta\omega'$ we take a linear chain with alternating force constants. The dispersion relation for this model is obtained explicitly. An optical mode, in virtue of the anharmonicity, perturbs the force constants—the perturbation alternates in sign from linkage to linkage. We can explicitly calculate $\delta\omega'$ for this model for the mode $\omega'=\omega_0/2$ and determine the perturbation. We shall find that c is reduced by about $\sqrt{8}$.

Consider a linear chain of atoms, all of the same mass, distant a from each other, with harmonic linkages of force constant α and β, alternatively. The frequency of a lattice wave of wave vector k is then readily shown to be

$$\omega^2=\frac{\alpha+\beta}{M}\pm\left[\frac{(\alpha+\beta)^2}{M^2}-\frac{4\alpha\beta}{M^2}\sin^2ka\right]^{1/2}. \tag{19}$$

When $k=0$ the frequency of the optical mode is

$$\omega_0{}^2=2(\alpha+\beta)/M\,, \tag{20}$$

while that of the acoustical branch for small k is given by

$$\omega^2=2\alpha\beta/(\alpha+\beta)M\,\sin^2ka\,. \tag{21}$$

At the zone boundary, when $\sin ka=1$, the frequencies of the two branches are given respectively by

$$\omega^2=2\alpha/M\quad\text{or}\quad 2\beta/M\,. \tag{22}$$

Now impose strain ϵ which is $+\epsilon$ on every α link and $-\epsilon$ on every β link. The force constants are now

$$\begin{aligned}\alpha&=\alpha_0(1+2\gamma\epsilon)\,,\\ \beta&=\beta_0(1-2\gamma\epsilon)\,,\end{aligned} \tag{23}$$

where γ is the same Grüneisen constant as in Eq. (11).

In the expression (19), terms in $\alpha\beta$ are unchanged to first order in ϵ, and

$$\alpha+\beta=(\alpha_0+\beta_0)[1+[(\alpha-\beta)/(\alpha+\beta)]2\gamma\epsilon]. \qquad (24)$$

Substituting this into (19) for the case $\omega'=\omega_0/2$, where ω_0 is now the optical mode frequency (20) at $\mathbf{k}=0$, one finds the following change in ω' due to the changes (23):

$$\frac{\delta(\omega')^2}{(\omega')^2}=\frac{4}{3}\left(\frac{\alpha-\beta}{\alpha+\beta}\right)\gamma\epsilon. \qquad (25)$$

This may be compared with the interaction coefficient (11), which is equivalent to

$$\delta(\omega')^2/(\omega')^2=(2/\sqrt{3})\gamma\epsilon. \qquad (26)$$

Hence the present model leads to an interaction which is reduced by a factor

$$(2/\sqrt{3})([\alpha-\beta]/[\alpha+\beta]) \qquad (27)$$

and the expressions (12) to (15) for $1/\tau$ are reduced by the square of this factor.

The present model yields a relaxation rate which is very sensitive to the ratio of the force constants $\alpha:\beta$. This ratio, in the case of the linear chain, can be related to the dispersion curve. In Eq. (22) the frequencies of the acoustical and optical branch at the zone boundary were in the ratio $(\beta/\alpha)^{1/2}$. If we assume that the same ratio of frequencies gives an effective value of $(\beta/\alpha)^{1/2}$ also in the case of three dimensions, we can estimate the ratio $\alpha:\beta$, and hence the strength of the interaction.

Thus in the case of silicon in the [111] direction, where the dispersion curve resembles that of a linear chain,[6] the frequencies of the two branches at the zone boundary are in the ratio 11/15, so that $\alpha/\beta=1.85$. This makes $(\alpha-\beta)/(\alpha+\beta)=0.30$ and the square of the ratio (27) becomes 0.12. Thus the relaxation rate at $T=0$ for the optical mode can be expressed in the same form as (15) and becomes

$$1/\tau=0.007\omega_0. \qquad (28)$$

IV. TEMPERATURE DEPENDENCE OF THE INVERSE LIFETIME

The relaxation rate (5) contains the factor

$$[1+N'+N''], \qquad (29)$$

where N' and N'' are the equilibrium occupation numbers of the modes $\mathbf{k}'$ and $\mathbf{k}''$ interacting with the optical mode. In the approximation when $\omega'=\omega''=\omega_0/2$, the relaxation rate at temperature T is given by the rate at $T=0$, multiplied by the factor

$$1+2/(e^x-1), \qquad (30)$$

where $x=\hbar\omega_0/2KT$.

V. COMPARISON WITH OBSERVATION

Parker and Feldman[4] observed the first-order Raman line in silicon, situated at 522 cm^{-1}, to have a half-width of 5 cm^{-1} at room temperature. In other words, the half-width is a little less than 1% of the frequency.

A simple theory of line broadening[7] leads to a half-width, when frequencies are expressed in rad/sec, of

$$\Delta\omega=1/\tau. \qquad (31)$$

Multiplying $1/\tau$ of (28) by the factor (30), one obtains a theoretical half-width

$$\Delta\omega=1/\tau=1.74\times7\times10^{-3}\omega_0=0.012\omega_0, \qquad (32)$$

so that the theoretically predicted half-width is a little more than 1% of frequency. In view of the crude approximations involved in the present calculations, this agreement, while satisfactory, is certainly fortuitous.

Cowley[3] had similarly calculated the half-width of this line at 300°K to be about 4% of its frequency. Since his calculations are apparently quite different in detail, even though the basic principles are naturally the same, the disagreement between the two calculations cannot be regarded as very serious.

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[6] G. Dolling, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. II, p. 37.

[7] See, e.g., W. Heitler, *Quantum Theory of Radiation* (Oxford University Press, New York, 1936).