

Anharmonic Forces in the GaP Crystal

D. A. KLEINMAN

Bell Telephone Laboratories, Murray Hill, New Jersey

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The infrared properties and the thermal expansion of gallium phosphide are treated on the basis of a simple model of the anharmonic forces. In this model the anharmonic forces are nearest neighbor central forces characterized by a single parameter. The value of this parameter for GaP is obtained from the integrated absorption recently measured for certain infrared combination bands. It is shown that the observed width of the fundamental resonance (reststrahl) and the observed shift with temperature of the combination bands are consistent with the absorption. This is presented as evidence that the anharmonic mechanism is predominantly responsible for the infrared absorption in the combination bands. It is also shown that the observed thermal expansion is consistent with the same anharmonic model.

1. INTRODUCTION

IN the preceding paper,¹ hereafter referred to as (I), data is presented on the infrared absorption bands of GaP. The bands in the region 12–24 μ are interpreted as two-phonon combination bands, and a scheme based on five lattice frequencies is given which accounts very well for the frequencies observed. From a consideration of the integrated absorption it is concluded that these bands are due primarily to the anharmonic forces in the crystal lattice. The role of anharmonic forces in infrared absorption was first pointed out by Born and Blackman,² who showed on the basis of a one dimensional model that the absorption spectrum of a polar crystal should contain combination frequencies of the form $\omega_1 \pm \omega_2$ as well as the fundamental infrared frequency, the frequency of long wavelength transverse optical vibrations. More elaborate discussions for three dimensional crystals have been given by Blackman³ and by Barnes, Brattain, and Seitz.⁴

It has been pointed out by Born,⁵ Burstein *et al.*,⁶ and Lax and Burstein⁷ that combination bands can also be caused by second order and higher order terms in the electric dipole moment of the crystal as a function of the ionic displacements. The detailed theory for the two phonon processes arising from the second order moment has been given by Lax and Burstein.⁷ On the basis of this theory and a theoretical⁸ vibration spectrum for diamond Stephen⁹ has calculated the shape of the absorption spectrum of diamond. In crystals like diamond which have no ionic charge and no first order moment¹⁰ the interaction of the lattice with the radiation must come (in a perfect crystal) through higher

order terms in the electric moment. In ionic crystals and heteropolar valence crystals like GaP both anharmonic forces and the second order moments could cause two phonon combination bands. Furthermore, both mechanisms predict the same temperature dependence for the absorption (see Sec. 2), and essentially the same shape for the absorption, which is determined primarily by the frequency distribution of the lattice vibrations. Lax and Burstein⁷ have suggested that even in ionic crystals the second order moment mechanism may be important. The question as to the mechanism of the combination bands, except for the homopolar crystals, has therefore not been resolved.

In general neither the anharmonic forces nor the second order electric moments of crystals are quantitatively known. It is not surprising therefore that no quantitative estimates have been published for the absorption coefficient or the integrated absorption of combination bands for either mechanism. And yet it seems probable that only by such quantitative considerations can the question of the mechanism be resolved. The subject was re-opened in (I) by pointing out that the integrated absorption in GaP should only be about twice as great as in silicon if the second order moment mechanism is responsible. In support of this argument it may be mentioned that the lattice constants are about equal, the high-frequency dielectric constants are similar, and the structures are similar if obvious allowance is made for the heteropolar character of GaP. Actually the integrated absorption is about 20 times larger in GaP than in silicon, which suggests that anharmonic forces are the dominant mechanism. In the present paper the argument is carried further by showing that the width of the fundamental resonance and the shift with temperature of the combination bands observed in (I) are consistent with the integrated absorption, on the assumption that all three effects are due to a simple kind of anharmonic force described by a single parameter. An expression is also obtained for the thermal expansion. Unfortunately the velocity of sound which occurs in this expression has not yet been measured. However, by equating the expression to the

¹ D. Kleinman and W. Spitzer, preceding paper [Phys. Rev. **118**, 110 (1960)].

² M. Born and M. Blackman, Z. Physik **82**, 551 (1933).

³ M. Blackman, Z. Physik **86**, 421 (1933).

⁴ L. L. Barnes, R. R. Brattain, and F. Seitz, Phys. Rev. **48**, 582 (1935).

⁵ M. Born, Revs. Modern Phys. **17**, 245 (1945).

⁶ E. Burstein, J. J. Oberly, and E. K. Plyler, Proc. Indian Acad. Sci. **28**, 388 (1948).

⁷ M. Lax and E. Burstein, Phys. Rev. **97**, 39 (1955).

⁸ Helen Smith, Trans. Roy. Soc. (London) **A241**, 105 (1948–9).

⁹ M. Stephen, Proc. Phys. Soc. (London) **71**, 485 (1958).

¹⁰ M. Lax, Phys. Rev. Letters **1**, 131 (1958).

measured thermal expansion a reasonable estimate is obtained for the velocity of sound.

As a material on which to carry out such an analysis GaP presents both advantages and disadvantages. The mechanical and thermal properties are relatively unknown due to the difficulty in obtaining large single crystals. Presumably these disadvantages are only temporary. The advantages are that the fundamental resonance can be accurately described by a single resonance dispersion formula, the combination bands can be accounted for by a simple assignment scheme, and the optical-optical combination bands are separated sufficiently from the other bands (optical-acoustical) to permit the integrated absorption for these bands to be determined. It is especially this last advantage which makes possible a quantitative test of the anharmonic theory of infrared absorption.

2. THE INFRARED ABSORPTION

We consider a single mode of the electromagnetic field in a medium of volume V and dielectric constant ϵ_0 which is the high-frequency dielectric constant of the crystal. The vector potential may be written

$$\mathbf{A}(\mathbf{r}) = V^{-\frac{1}{2}} \mathbf{u} (a e^{i\mathbf{k}\cdot\mathbf{r}} + a^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}}), \quad (1)$$

where \mathbf{u} is a unit vector, \mathbf{k} is a wave vector, and the destruction and creation operators a and a^\dagger have the commutator

$$[a, a^\dagger] = 2\pi\hbar c / k\epsilon_0^{\frac{1}{2}}. \quad (2)$$

We denote the positions of atoms of type σ by \mathbf{r}_σ and the displacements of atoms by $\mathbf{u}(\mathbf{r}_\sigma)$, which can be written¹¹

$$\mathbf{u}(\mathbf{r}_\sigma) = N^{-\frac{1}{2}} \sum_{\mathbf{q}l} (\mathbf{b}_{\sigma q l} \alpha_{q l} e^{i\mathbf{q}\cdot\mathbf{r}_\sigma} + \mathbf{b}_{\sigma q l}^* \alpha_{q l}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}_\sigma}). \quad (3)$$

Here N is the number of unit cells, $\mathbf{q}l$ denotes the wave vector and branch of the phonon, $\alpha_{q l}$ and $\alpha_{q l}^\dagger$ are destruction and creation operators normalized to unit commutator, and the polarization vectors $\mathbf{b}_{\sigma q l}$ satisfy the orthonormality relations

$$\begin{aligned} \sum_{\sigma\sigma'} (b_{\sigma q l})_x (b_{\sigma' q l'})_x m_{\sigma\sigma'} &= (\hbar/2\omega_{q l}) \delta_{ll'}, \\ \sum_l (b_{\sigma q l})_x (b_{\sigma' q l})_x \omega_{q l} &= (\hbar/2m_\sigma) \delta_{\sigma\sigma'} \delta_{xx'}, \end{aligned} \quad (4)$$

where m_σ is the mass of the atoms of type σ and $\omega_{q l}$ is the angular frequency of phonons $\mathbf{q}l$. The momentum conjugate to $\mathbf{u}(\mathbf{r}_\sigma)$ is

$$\mathbf{p}(\mathbf{r}_\sigma) = N^{-\frac{1}{2}} \sum_{\mathbf{q}l} m_\sigma \omega_{q l} i (\mathbf{b}_{\sigma q l}^* \alpha_{q l}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}_\sigma} - \mathbf{b}_{\sigma q l} \alpha_{q l} e^{i\mathbf{q}\cdot\mathbf{r}_\sigma}). \quad (5)$$

The interaction of the crystal with the electromagnetic field is¹²

$$\begin{aligned} H' &= \sum_{\sigma\sigma'} (e_\sigma/m_\sigma c) \mathbf{A}(\mathbf{r}_\sigma) \cdot \mathbf{p}(\mathbf{r}_\sigma) \\ &= V^{-\frac{1}{2}} N^{\frac{1}{2}} \sum_{\sigma} \sum_l (e_\sigma \omega_{k l} / c) i \mathbf{u} \cdot (\mathbf{b}_{\sigma k l}^* \alpha_{k l}^\dagger a \\ &\quad + \mathbf{b}_{\sigma -k l}^* \alpha_{-k l}^\dagger a^\dagger - \mathbf{b}_{\sigma k l} \alpha_{k l} a^\dagger - \mathbf{b}_{\sigma -k l} \alpha_{-k l} a), \end{aligned} \quad (6)$$

¹¹ F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, New York, 1940), Secs. 21, 22.

¹² Reference 11, Sec. 42.

where e_σ is an effective charge so defined¹³ that the electric moment produced in the crystal by displacement of an ion is $e_\sigma \mathbf{u}(\mathbf{r}_\sigma)$. In a crystal with two kinds of atoms the effective charges must be equal in magnitude and opposite in sign, so that we may write $|e_\sigma| = \hat{e}$.

The wave vector \mathbf{k} of the radiation is very small so that we may use H' in the limit $k \rightarrow 0$. In this limit the three acoustical branches satisfy¹⁴

$$\lim_{k \rightarrow 0} (\mathbf{b}_{\sigma k l} - \mathbf{b}_{\sigma' k l}) \rightarrow 0. \quad (7)$$

The acoustical branches therefore do not contribute to H' , because (6) contains the factor $\sum_{\sigma} e_\sigma = 0$ when (7) is satisfied. We now limit the discussion to cubic crystals with two kinds of atoms. In such crystals there are three optical branches which for very small wave vectors may be considered to be one longitudinal and two mutually perpendicular transverse branches. The longitudinal branch cannot interact with the transverse radiation field, and one of the transverse branches may be chosen perpendicular to the field. We shall refer to the transverse optical vibration of zero wave vector polarized in the direction \mathbf{u} as the *fundamental* vibration designated by "f." The polarization vectors for the *f* vibration satisfy¹⁵

$$\mathbf{b}_{\sigma f} - \mathbf{b}_{\sigma' f} = (\hbar/2m\omega_f)^{\frac{1}{2}} \mathbf{u}, \quad (8)$$

where $m = m_\sigma m_{\sigma'} / (m_\sigma + m_{\sigma'})$ is the reduced mass. Thus the interaction of the crystal with the radiation reduces to

$$\begin{aligned} H' &= V^{-\frac{1}{2}} N^{\frac{1}{2}} (\hbar \hat{e}^2 \omega_f / 2mc^2)^{\frac{1}{2}} \\ &\quad \times i (\alpha_f^\dagger a - \alpha_f a^\dagger + \alpha_f^\dagger a^\dagger - \alpha_f a). \end{aligned} \quad (9)$$

For a crystal of the zincblende structure (like GaP) the anharmonic forces can be introduced into an ideal harmonic model by connecting purely anharmonic springs between each atom and its four nearest neighbors of the opposite type. The potential energy of the purely anharmonic spring is $-Gx^3$, where x is the extension and G is a parameter whose value we hope to determine from a comparison of theory and experiment. The anharmonic potential energy of the crystal in this model is

$$H'' = -G \sum_{j\mathbf{r}} \{\mathbf{j} \cdot [\mathbf{u}(\mathbf{r}_j) - \mathbf{u}(\mathbf{r})]\}^3, \quad (10)$$

where \mathbf{r} is the position of one kind of atom and \mathbf{j} is a unit vector in the direction $\mathbf{r}_j - \mathbf{r}$, and the sum is over the four neighbors of atom \mathbf{r} and over all atoms \mathbf{r} . Combining (3) and (10) gives

$$\begin{aligned} H'' &= -GN^{-\frac{3}{2}} \sum_{j\mathbf{r}} [\sum_{\mathbf{q}l} (F_{j q l} \alpha_{q l} e^{i\mathbf{q}\cdot\mathbf{r}} \\ &\quad + F_{j q l}^* \alpha_{q l}^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}})]^3, \end{aligned} \quad (11)$$

¹³ H. Callen, *Phys. Rev.* **76**, 1394 (1949).

¹⁴ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Sec. 26.

¹⁵ Reference 14, Secs. 7, 34.

where

$$F_{jq\ell} = \mathbf{j} \cdot (\mathbf{b}_{jq\ell} e^{i\rho \cdot \mathbf{q}} - \mathbf{b}_{\sigma q\ell}), \quad (12)$$

where $\rho = |\mathbf{r}_j - \mathbf{r}|$ is the interionic distance and σ refers to the atoms \mathbf{r} . It is convenient to define the operators $\beta_{jq\ell}^{(s)}$ where s takes on one of two values (\pm) and

$$\beta_{jq\ell}^{(-)} = F_{jq\ell} \alpha_{q\ell}, \quad \beta_{jq\ell}^{(+)} = F_{jq\ell}^* \alpha_{q\ell}^+. \quad (13)$$

The anharmonic potential can then be written

$$H'' = -6GN^{-\frac{1}{2}} \sum_j \sum_{s,s',s''} \sum_{\Delta}^{(3)} \beta_{jq\ell}^{(s)} \beta_{jq'\ell'}^{(s')} \beta_{jq''\ell''}^{(s'')} \times \Delta(s\mathbf{q} + s'\mathbf{q}' + s''\mathbf{q}''), \quad (14)$$

where

$$\Delta(\mathbf{q}) = 1 \text{ if } \mathbf{q} = \text{zero or any reciprocal lattice vector,} \\ = 0 \text{ otherwise.} \quad (15)$$

The triple summation over phonons has been written $6 \sum^{(3)}$, where 6 is the redundancy factor, and $\sum^{(3)}$ is a nonredundant summation over the phonons $qt, q't', q''t''$ in which each combination without regard to order occurs once. The validity of (14) depends upon N being very large so that terms with repeated indices can be neglected.

The matrix element $M_{n'n}$ for a process involving several phonons and one photon is

$$M_{n'n} = \sum_{g \neq n', n} \left(\frac{\langle n' | H'' | g \rangle \langle g | H' | n \rangle}{E_n - E_g} + \frac{\langle n' | H' | g \rangle \langle g | H'' | n \rangle}{E_n - E_g} \right), \quad (16)$$

where E_n is the energy of the initial state, E_g the energy of the intermediate state. The transition rate is

$$\Omega_{n'n} = (2\pi/\hbar) |M_{n'n}|^2 \delta(E_{n'} - E_n). \quad (17)$$

The conservation of energy may be written

$$\pm \hbar\omega \pm \hbar\omega_f + \sum s\hbar\omega = 0, \quad (18)$$

where the sum is over the three phonons generated by H'' , and in the other terms (+) refers to emission and (-) to absorption of the respective quanta. In the general process the three H'' phonons are distinct from the f -phonon, so that the general process is a four phonon process. A process of this kind is diagrammed in Fig. 1(a) for the case in which a photon \mathbf{k} is absorbed with creation of phonon f (the H' vertex) followed by the creation of three more phonons (H'' vertex). We shall use the convention that diagrams are to be read from right to left, and arrows pointing into a vertex represent destruction while arrows pointing away represent creation of a particle. The diagram shown corresponds to the left term on the right side of (16); a similar diagram with H'' preceding (to the right of) H' corresponds to the right term. Disconnected diagrams such as Fig. 1(a) do not represent physical

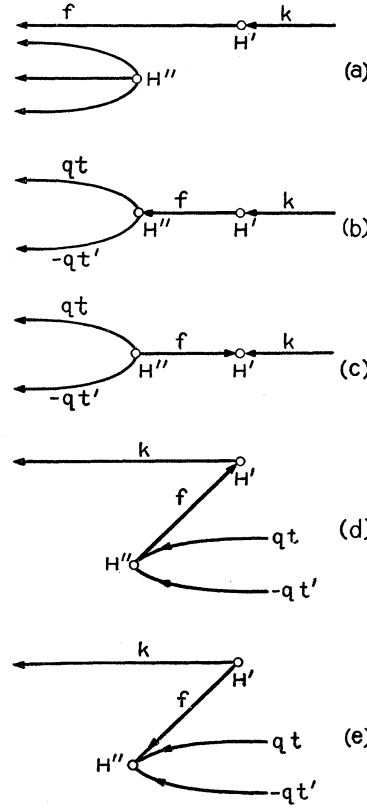


FIG. 1. Diagrams for infrared absorption. (a) Disconnected diagram which cancels. (b), (c) Photon absorption. (d), (e) Photon emission [see Eq. (16)].

effects.¹⁶ In this case the diagram shown is cancelled by its counterpart with H'' preceding H' for processes obeying the conservation of energy (18). This comes about because the matrix elements in the two terms of (16) are the same unless H'' destroys the phonon created by H' or creates the phonon destroyed by H' . Therefore the third order anharmonic potential H'' produces only two-phonon processes in which the fundamental phonon is an intermediate state.

In Figs. 1(b), (c), (d), and (e) are shown diagrams for the two-phonon processes in which both phonons are created or both destroyed. These are the processes which cause the combination bands observed in GaP. Not shown are the counterpart diagrams with H'' preceding H' . As an example consider (b) representing photon absorption through $\beta_f \beta_{qt} + \beta_{-qt'}^+$ in H'' and $\alpha_f^+ a$ in H' . For an initial state with N_ω photons and n_{iq} phonons (prescribed for all qt) and a final state in which a photon is destroyed and phonons $qt, -qt'$ are created the value of the diagram is

$$6ZN_\omega^{\frac{1}{2}} (n_f + 1) X_{qt}^* (n_{qt} + 1)^{\frac{1}{2}} \times (n_{-qt'} + 1)^{\frac{1}{2}} / (\hbar\omega - \hbar\omega_f), \quad (19)$$

where

$$Z = -iGV^{-\frac{1}{2}} [\pi \hbar^3 \epsilon^2 / 2m^2 \omega \epsilon_0]^{\frac{1}{2}} \quad (20)$$

contains the constant factors from (2), (8), (9), and (10). The quantity $\hbar\omega - \hbar\omega_f$ is the energy denominator.

¹⁶ J. Goldstone, Proc. Roy. Soc. (London) A239, 267 (1957).

The sum over j in (10) is contained in the quantity

$$X_{qt'} = \sum_j (\mathbf{j} \cdot \mathbf{u}) F_{jq} F_{j-qt'}. \quad (21)$$

The counterpart diagram to (b) has a similar expression except that (n_f+1) is replaced by n_f and $\hbar\omega - \hbar\omega_f$ by $\hbar\omega_f - \hbar\omega$; the result of adding this to (19) is to cancel the number of fundamental phonons n_f . Diagram (c) representing absorption of radiation through $\beta_f^+ \beta_{qt}^+ \beta_{-qt'}^+$ in H'' and $-\alpha_f a$ in H' has the value

$$-6ZN_\omega^{\frac{1}{2}} n_f X_{qt'}^* (n_{qt}+1)^{\frac{1}{2}} (n_{-qt'}+1)^{\frac{1}{2}} (\hbar\omega + \hbar\omega_f), \quad (22)$$

and its counterpart is obtained by replacing n_f by (n_f+1) and $\hbar\omega + \hbar\omega_f$ by $-\hbar\omega - \hbar\omega_f$. The total matrix element for absorption is

$$M_a(\mathbf{q}t't') = \frac{6Z}{\hbar} \frac{2\omega}{\omega^2 - \omega_f^2} X_{qt'}^* N_\omega^{\frac{1}{2}} (n_{qt}+1)^{\frac{1}{2}} \times (n_{-qt'}+1)^{\frac{1}{2}}. \quad (23)$$

Similarly we find the total matrix element for photon emission

$$M_e(\mathbf{q}t't') = -\frac{6Z}{\hbar} \frac{2\omega}{\omega^2 - \omega_f^2} X_{qt'} (N_\omega + 1)^{\frac{1}{2}} \times (n_{qt})^{\frac{1}{2}} (n_{-qt'})^{\frac{1}{2}} \quad (24)$$

from diagrams (d) and (e).

The total rate of photon absorption is $\Omega = \Omega_a - \Omega_e$ where Ω_a and Ω_e are the rates for absorption and emission processes, respectively. Combining (17), (23) and (24) gives

$$\Omega = 288\pi (|Z|^2/\hbar^3) [\omega^2/(\omega^2 - \omega_f^2)^2] \sum^{(2)} |X_{qt'}|^2 \times [N_\omega (n_{qt}+1)(n_{-qt'}+1) - (N_\omega + 1)n_{qt}n_{-qt'}] \times \delta(\hbar\omega - \hbar\omega_{qt} - \hbar\omega_{-qt'}), \quad (25)$$

where $\sum^{(2)}$ is a nonredundant summation over two phonons $\mathbf{q}t'$ and $-\mathbf{q}t'$. We obtain the real conductivity by equating the classical expression for Joule heating to the quantum mechanical expression for the absorption of energy

$$\sigma \mathbf{E}^2 = \Omega V^{-3} \hbar\omega. \quad (26)$$

The electric field \mathbf{E} can be eliminated by equating the classical and quantum expressions for the energy density

$$(\epsilon_0/4\pi) \mathbf{E}^2 = N_\omega V^{-3} \hbar\omega. \quad (27)$$

Use of the correspondence principle in this way is valid if $\sigma/\omega \ll 1$ and if the polarizability due to the interaction is much less than $\epsilon_0/4\pi$. These conditions are satisfied in the wavelength regions where combination bands are usually observed, i.e., far out on the wings of the fundamental resonance. As pointed out by Schmidt¹⁷ the transition rate Ω in (26) should not contain spontaneous processes, so that in (25) we retain only the part proportional to N_ω . The absorption coefficient¹⁸ $\alpha = 4\pi\sigma/c\epsilon_0^{\frac{1}{2}}$

is then given by

$$\alpha = \frac{288\pi\epsilon_0^{\frac{1}{2}} |Z|^2}{\hbar^3 c} \frac{\omega^2}{(\omega^2 - \omega_f^2)^2} \sum^{(2)} |X_{qt'}|^2 \times (n_{qt} + n_{-qt'} + 1) \delta(\hbar\omega - \hbar\omega_{qt} - \hbar\omega_{-qt'}). \quad (28)$$

The thermal average over initial states can now be carried out simply by giving n_{qt} the value¹⁹

$$n_{qt} = (e^{\hbar\omega_{qt}/kT} - 1)^{-1}. \quad (29)$$

We now restrict ourselves to processes involving two optical phonons. A simple and reasonable approximation is to set

$$|X_{qt'}|^2 \sim (\hbar/2m\omega_{qt})(\hbar/2m\omega_{qt'}), \quad (30)$$

where m is the reduced mass appearing in (8). In this way we obtain

$$\alpha \sim 36\pi^2 \frac{N_0 G^2 \hbar^2 \hat{e}^2}{m^4 c \epsilon_0^{\frac{1}{2}}} \frac{\omega}{(\omega^2 - \omega_f^2)^2} \frac{1}{N} \sum^{(2)} \frac{(n_{qt} + n_{qt'} + 1)}{\omega_{qt} \omega_{qt'}} \times \delta(\hbar\omega - \hbar\omega_{qt} - \hbar\omega_{qt'}), \quad (31)$$

where N_0 is the number of unit cells per unit volume. A dimensionless integrated absorption may be defined as follows

$$P_{tt'} = \int \alpha_{tt'} d\lambda = (2\pi c/\omega^2) \int \alpha_{tt'} d\omega, \quad (32)$$

where $\alpha_{tt'}$ is the absorption coefficient for processes involving a phonon of branch t and one of branch t' . This quantity is of experimental interest in GaP, because it was shown in (I) that the two-optical-phonon combination bands are well separated from the optical-acoustical combination bands permitting their integrated absorption to be measured directly. We may assume that the six possible optical-optical processes have approximately equal integrated absorptions, so that the quantity of experimental interest is $P_{op} \sim 6P_{tt}$. From (31) and (32)

$$P_{op} \sim 24\pi^3 G^2 (N_0 \hbar \hat{e}^2 / m^4 \omega_f^7 \epsilon_0^{\frac{1}{2}}) (1 + 2n), \quad (33)$$

where for the phonon frequencies we have put $\omega_{qt} \sim \omega_{qt'} \sim \omega_f \sim \omega/2$, which is a good approximation in GaP. The effective charge \hat{e} is greater than the ionic charge e^* defined by Szigeti²⁰ by the factor $(\epsilon_0 + 2)/3$. The relevant experimental quantities¹ are

$$\begin{aligned} \omega_f &= 6.90 \times 10^{13} \text{ sec}^{-1}, \\ \epsilon_0 &= 8.457, \\ \hat{e} &= 2.01e, \\ m &= 3.56 \times 10^{-23}, \\ N_0 &= 2.49 \times 10^{22}, \\ P_{op} &= 7 \times 10^{-3}. \end{aligned} \quad (34)$$

¹⁷ H. Schmidt, Z. Physik **139**, 433 (1954).

¹⁸ Reference 11, Sec. 147.

¹⁹ Reference 11, Sec. 18.

²⁰ B. Szigeti, Trans. Faraday Soc. **45**, 155 (1949).

By equating the experimental value of P_{op} to the expression (33) we obtain the estimate

$$G = 3 \times 10^{12} \text{ g cm}^{-1} \text{ sec}^{-2} \quad (35)$$

for the anharmonic parameter. It may be noted that G is of the order of magnitude of an elastic constant, which is what one would expect, since the harmonic and anharmonic energies should be comparable for a displacement of one lattice constant. We shall now use this value to compute theoretical estimates of the width of the fundamental resonance and of the temperature shift of the combination bands.

3. WIDTH OF THE FUNDAMENTAL RESONANCE

In (I) the parameter γ describing the width of the fundamental resonance in GaP was determined from an accurate dispersion analysis of the reflectivity. In terms of γ the relaxation time τ for the decay of energy is $\tau = (\gamma\omega_f)^{-1}$. We shall assume that the principal relaxation mechanism is the anharmonic perturbation H'' . A typical decay process is the destruction of an f phonon and the creation of a pair of phonons having frequencies of sum ω_f and wave vectors of sum zero. For simplicity we shall restrict ourselves to absolute zero temperature, so that no other decay process is possible. The relaxation time may be written

$$1/\tau = (2\pi/\hbar) \sum^{(2)} |H_{qt''}|^2 \delta(\hbar\omega_f - \hbar\omega_{qt} - \hbar\omega_{qt''}), \quad (36)$$

where $H_{qt''}$ is the matrix element of H'' for destroying f and creating qt and $-qt''$ when the initial state has a single f phonon present.

$$H_{qt''} = -6GN^{-\frac{1}{2}}(\hbar/2m\omega_f)^{\frac{1}{2}} X_{qt''}. \quad (37)$$

Thus we find

$$1/\tau = 36\pi(G^2/m\omega_f)(1/N) \sum^{(2)} |X_{qt''}|^2 \times \delta(\hbar\omega_f - \hbar\omega_{qt} - \hbar\omega_{qt''}). \quad (38)$$

The analysis in (I) of the combination bands in GaP shows that critical points²¹ in the vibration spectrum occur at five frequencies, which in terms of wave numbers (cm^{-1}) are 66, 115, 197, 361, and 378. The fundamental resonance is 366. If we imagine simple shapes for the dispersion curves $\omega(\mathbf{q})$, in which the critical points occur at the zone boundary, we conclude that the only decay process is the decay into two longitudinal acoustic phonons of frequency 183. This frequency is far enough from the critical point frequency 197 that the perturbation treatment leading to (38) should be valid. The wave vector \mathbf{q} may also be assumed to be not too near the zone boundary, which permits us to make the approximation

$$\mathbf{b}_{\sigma qt} \sim i\mathbf{q} |q|^{-1} (\hbar/2M\omega_{qt})^{\frac{1}{2}}, \quad (39)$$

where $M = M_\sigma + M_{\sigma'}$ is the mass of the unit cell. We then obtain

$$|X_{qt''}|^2 \sim (\hbar/M\omega_f)^2 \quad (40)$$

²¹ J. Phillips, Phys. Rev. **104**, 1263 (1956).

by considering the sum over j in (21) for several typical directions of \mathbf{q} . The relaxation time can now be written

$$1/\tau \sim 9\pi(G^2\hbar/mM^2\omega_f^3)D(\omega_f/2), \quad (41)$$

where $D(\omega)$ is the normalized frequency distribution for the LA branch defined by

$$D(\omega) = N^{-1} \sum_{q'} \delta(\omega' - \omega). \quad (42)$$

The numerical coefficient in (41) takes account of the fact that the nonredundant summation in (38) is over only half of \mathbf{q} -space for the case $t=t'$.

It is difficult to estimate the value of $D(\omega_f/2)$. In the absence of more accurate information we may suppose that the dispersion relation is of the form $\omega \sim \omega_{\max} \sin(\frac{1}{2}qN_0^{-\frac{1}{2}})$ and identify ω_{\max} with the critical point frequency ω_{LA} , which gives $D(\omega_f/2) \sim 1.6/\omega_{LA}$. Therefore we obtain finally the simple formula

$$1/\tau \sim 45(G^2\hbar/mM^2\omega_f^3\omega_{LA}) \quad (\text{for GaP}). \quad (43)$$

Using $M = 1.7 \times 10^{-22}$ g, the constants given in (34), the critical point frequency 197 cm^{-1} , and G given by (35) we obtain $(1/\tau) \sim 3.7 \times 10^{10} \text{ sec}^{-1}$, which corresponds to the width parameter $\gamma \sim 5 \times 10^{-4}$. This is to be compared with the experimental value 3×10^{-3} . This is satisfactory agreement in view of the uncertainty of estimating $D(\omega)$.

4. TEMPERATURE SHIFT OF THE COMBINATION BANDS

The contribution of the anharmonic potential to the energy of the crystal according to ordinary second order perturbation theory is

$$W^{(2)} = \sum_{q \neq n} \frac{|H_{qn''}|^2}{E_n - E_q}, \quad (44)$$

where an average is to be taken over the thermal distribution of initial states n . We shall define the frequency shift $\delta\omega_q$ of a phonon q as follows

$$\hbar\delta\omega_q = W^{(2)}(n_q+1) - W^{(2)}(n_q), \quad (45)$$

where all phonon occupation numbers except for q are the same in $W^{(2)}(n_q+1)$ and $W^{(2)}(n_q)$. We shall obtain an expression for $\delta\omega_q$ on the basis of a one dimensional model, since the three dimensional treatment leads to formidable difficulty.

The frequencies of the longitudinal vibrations of a linear chain¹¹ are given by the so-called "normal dispersion" relation

$$\omega_q = (K/M)^{\frac{1}{2}} |f_q|, \quad (46)$$

where M is the mass of the particles and K the constant of the connecting springs, and

$$\begin{aligned} f_q &= 1 - e^{-iq\rho}, \\ |f_q| &= 2 \sin \frac{1}{2}q\rho, \end{aligned} \quad (47)$$

where ρ is the interparticle distance. The anharmonic potential can be written in the form (14) except that

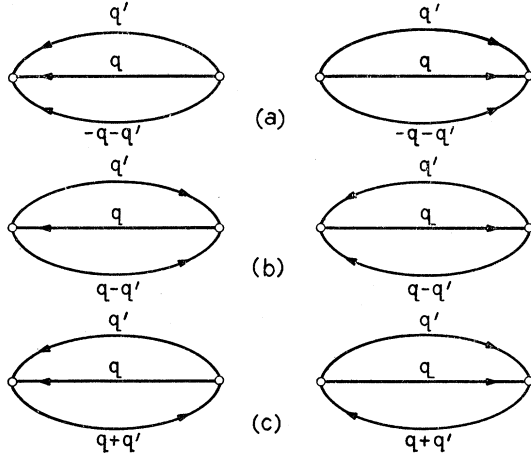


FIG. 2. Diagrams for the shift of phonon frequencies [see Eq. (49)].

the sum over j is omitted, and

$$\begin{aligned}\beta_a^{(-)} &= (\hbar/2M\omega_a)^{1/2} f_q \alpha_a, \\ \beta_a^{(+)} &= (\hbar/2M\omega_a)^{1/2} f_q^* \alpha_a^+.\end{aligned}\quad (48)$$

The intermediate states $|g\rangle$ which contribute to $\delta\omega_a$ are those in which a q phonon is created or destroyed. From (14), (44), (45), (46), (47), and (48) we obtain

$$\begin{aligned}\delta\omega_a &= -\frac{9G^2\hbar\omega_a}{4K^3} \frac{1}{N} \sum_{q'} \omega_{q'} \left(\frac{\omega_{q+q'}(1+n_{q'}+n_{q+q'})}{-\omega_{q-q'}-\omega_{q'}-\omega_{q+q'}} \right. \\ &\quad \left. + \frac{\omega_{q-q'}(1+n_{q'}+n_{q-q'})}{\omega_{q-q'}-\omega_{q'}-\omega_{q-q'}} + \frac{2\omega_{q+q'}(n_{q+q'}-n_{q'})}{-\omega_{q-q'}-\omega_{q'}+\omega_{q+q'}} \right),\end{aligned}\quad (49)$$

where the summation is over all q' (first Brillouin Zone), and the redundancy of this summation has been taken into account in the numerical coefficient. We may regard (49) as the sum of the diagrams of Fig. 2. The two diagrams of Fig. 2(a) give the first term in brackets; the diagrams on the right and left differ only in the order of creation and destruction of phonons. Likewise Figs. 2(b) and (c) show the processes of the second and third terms, respectively, in (49). Henceforth the temperature independent part of $\delta\omega_a$ will be dropped, since it would not be observable in the experiments described in (I).

The combination bands in GaP exhibit maxima which can be related as shown in (I) to five frequencies corresponding to critical points. We may presume that these critical points occur at or near the boundary of the Brillouin Zone. Therefore we consider the case $q=q_{\max}=\pi/\rho$ for which (49) may be readily reduced to a simpler form. For q on the boundary of the Brillouin Zone the wave vectors $q+q'$ and $q'-q$ are equivalent, so that $\omega_{q+q'}=\omega_{q-q'}=\omega_q|\cos\frac{1}{2}\rho q'|$. We denote $\omega_{q'}=\omega'$, $\omega_{q\pm q'}=\omega''$, $n_{q'}=n'$, $n_{q\pm q'}=n''$ and note the identity

$$(\omega' \pm \omega'')^2 - \omega_q^2 = \pm 2\omega'\omega''.$$

The sum of the first two terms in (49) is then found to be $-(n'+n'')(\omega'+\omega'')$ while the third term reduces to $-(n''-n')(\omega''-\omega')$. Therefore we obtain for the frequency shift

$$\delta\omega_a/\omega_a = -9(G^2\hbar/K^3)N^{-1} \sum_{q'} n_{q'} \omega_{q'}. \quad (50)$$

There is no difficulty in this case with the convergence of the sum (49). The method breaks down, however, when one tries to calculate $\delta\omega_a/\omega_a$ in the limit $\omega_a \rightarrow 0$. The difficulty arises because of the presence of intermediate states which conserve energy and cause (49) to diverge. Since the combination bands are due to phonons at or near the boundary of the Brillouin Zone, the present treatment is adequate.

The frequency shifts are closely related to the phenomenon of thermal expansion.²² The Hamiltonian of the linear chain is

$$H = (K/2) \sum_i (x_i - x_{i-1})^2 + \sum_i (\mathbf{p}_i^2/2M) - G \sum_i (x_i - x_{i-1})^3, \quad (51)$$

where x_i is the displacement, \mathbf{p}_i the momentum of the i th particle. If we now displace the equilibrium positions by adding δ to the interparticle spacing, the new Hamiltonian is

$$H(\delta) = \frac{1}{2}(K-6G\delta) \sum_i (x_i - x_{i-1})^2 + \sum_i (\mathbf{p}_i^2/2M) - G \sum_i (x_i - x_{i-1})^3 + N(\frac{1}{2}K\delta^2 - G\delta^3), \quad (52)$$

where now x_i is the displacement from the new equilibrium positions. Periodic boundary conditions $x_i = x_{i+N}$ are assumed in (52), which cause the terms in $\delta^2 x_i$ to cancel out; in any case we would not want linear terms in x_i in the Hamiltonian if x_i represents a displacement from equilibrium. The first three terms of (52) represent a set of oscillators with anharmonic coupling similar to the undistorted crystal (51) except for a modified spring constant. The frequency shift resulting from the modified spring constant is

$$\delta\omega/\omega = -3G\delta/K, \quad (53)$$

which is constant for all q . To relate δ to thermal expansion we compute the free energy of the distorted crystal. The free energy to the lowest order in δ and G is

$$\psi = \sum_q [\frac{1}{2}\hbar\omega_q + kT \ln(1 - e^{-\hbar\omega_q/kT})] + \frac{1}{2}NK\delta^2, \quad (54)$$

where the summation is the free energy of the crystal oscillators with the anharmonic interaction neglected except for the frequency shift (53), and the second term is the energy of stretching the springs. The equilibrium condition $\partial\psi/\partial\delta=0$ reduces to the formula

$$\delta = (3G/K^2)(1/N) \sum_q (n_q + \frac{1}{2})\hbar\omega_q \quad (55)$$

²² E. Gruneisen, Ann. Physik **39**, 257 (1912); *Handbuch der Physik*, edited by S. Flügge (Verlag Julius Springer, Berlin, 1926), Vol. 10, p. 1; M. Born, *Atomtheorie des festen Zustandes* (B. G. Teubner, Leipzig, 1923); J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939); R. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1954); J. S. Dugdale and D. K. C. MacDonald, Phys. Rev. **96**, 57 (1954); **89**, 832 (1953).

giving the expansion of the unit cell in the linear chain. When δ is substituted back into (53) the frequency shift becomes

$$\delta\omega/\omega = -9(G^2\hbar/K^3)N^{-1}\sum_q(n_q + \frac{1}{2})\hbar\omega_q. \quad (56)$$

In obtaining the perturbation result (50) we neglected the temperature independent terms, so that (50) and (56) are in agreement. The derivation of (50), however, applies only to the zone boundary, whereas (56) applies to all phonons.

The analysis presented shows that (50) is equivalent to (53) when δ represents the thermal expansion. For comparison with experiment we therefore use (53) since the thermal expansion coefficient of GaP is known. The spring constant K may be eliminated by the relation $\omega_{\max} = 2(K/M)^{1/2}$ and ω_{\max} identified with ω_{LA} reported in (I), which gives the result [however, see comments above (60)]

$$\frac{1}{\omega} \frac{\Delta\omega}{\Delta T} \sim -12 \frac{Ga\alpha}{M\omega_{\text{LA}}^2}, \quad (57)$$

where a denotes the lattice constant and α the coefficient of linear thermal expansion. Using the same M and ω_{LA} as in (43), G from (35), and the values²³ $\alpha = 5.3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and²⁴ $a = 5.4 \times 10^{-8} \text{ cm}$ we obtain $-\omega^{-1}(\Delta\omega/\Delta T) \sim 4 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$. This is in agreement with the experimental value¹ $(5 \pm 2) \times 10^{-5} \text{ }^\circ\text{C}^{-1}$. Therefore the anharmonic mechanism for the infrared absorption seems to be in agreement with the temperature shift of the combination bands. This conclusion, however, is based upon the simple model of a linear crystal with nearest neighbor interactions.

It will be recognized that (53) is equivalent to the relation

$$\gamma_\omega = 3Ga/K \quad (57)$$

for the one dimensional Gruneisen constants²² $\gamma_\omega = -d(\log\omega)/d(\log a)$ of the linear chain. When the Gruneisen constants of a system are all equal to a single constant γ the thermal expansion coefficient is given by the Gruneisen relation²²

$$\alpha = \gamma C_v \beta / V, \quad (58)$$

where C_v is the specific heat of the crystal at constant volume and β is the isothermal compressibility. This relation holds in one, two, or three dimensions with appropriate definitions of γ and β . In three dimensions γ is defined

$$\gamma = -d \log \omega / d \log V. \quad (59)$$

From the observed frequency shift and the coefficient of linear thermal expansion we obtain $\gamma \sim 3 \pm 1$ for the Gruneisen constant. This is a reasonable result, but data are lacking to compare (58) with experiment. The

thermal expansions of germanium, silicon, and indium antimonide have recently been measured by Gibbons²⁵ from 4.2° to 300°K. Silicon has a very pronounced *negative* thermal expansion in the neighborhood of 80°K, with normal behavior setting in above 120°K, although the expansion coefficient is quite small. The Gruneisen parameter γ defined by (58) is found to be negative for silicon below 120°K. These results are a dramatic demonstration of the limitations and shortcomings of the linear chain model for anharmonic effects in real crystals. It is quite clear that the linear chain model can only account for normal thermal expansion and positive Gruneisen parameters. Blackman²⁶ has observed that reasonable choices for the interatomic forces in ionic crystals can give negative γ_ω for the low-frequency transverse waves. Barron²⁷ has carried out detailed analyses of cubic lattices and shown that the resultant γ which should appear in (58) can be negative at temperatures below $0.3\theta_D$ (θ_D = Debye temperature). We may conclude that qualitative features can come into the thermal expansion which are essentially three dimensional. We may still expect that the linear chain model is applicable to well behaved cases in which the thermal expansion is positive, normal in magnitude, and the Gruneisen parameter is approximately constant. One might anticipate just from the abnormally small thermal expansion of silicon at room temperature that it is an abnormal material. But in general the abnormal materials cannot be recognized so easily, because InSb has a normal expansion coefficient at room temperature and negative expansion below 50°K. Therefore we can only hope at this writing that GaP is a normal material to which the linear chain model may be applied. The fact that (57) agrees with experiment using a G obtained from infrared absorption may be used as an argument in favor of the anharmonic mechanism for the absorption, which is the position taken here, or as an argument in favor of the linear chain model.

The very close agreement obtained is apparently fortuitous, however, because the quantities G , δ , K appearing in (53) refer to a linear chain whereas in (57) G , a , M , ω_{LA} refer to GaP. Somewhat poorer agreement is obtained if one proceeds in the following way which actually seems more plausible. We see that (53) is proportional to the ratio of the anharmonic potential energy to the harmonic potential energy stored in the restoring springs. The same expression will apply to GaP if δ is the extension of the nearest neighbor distance, G is given by (35), and K is the spring constant for the nearest neighbor forces assumed to be the predominant restoring forces. It is true that a crystal of the GaP structure with only nearest neighbor springs would be unstable with respect to shear along (111) type planes, but we may still imagine

²³ H. Welker and H. Weiss, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 3, p. 51.

²⁴ G. Geiscke and H. Pfister, *Acta Cryst.* **11**, 369 (1958).

²⁵ D. F. Gibbons, *Phys. Rev.* **112**, 136 (1958).

²⁶ M. Blackman, *Proc. Phys. Soc. (London)* **B70**, 827 (1957).

²⁷ T. H. K. Barron, *Ann. Physik* **1**, 77 (1957).

longitudinal waves in the [111] direction in such a structure. Accordingly we regard the particles of the linear chain as the planes of Ga atoms and planes of P atoms. One can show that the spring constant between neighboring planes is then just K and the masses are M_{Ga} and M_{P} . The frequency at the zone boundary for such a chain of two kinds of atoms is¹¹ $\omega_{\text{LA}} = (2K/M_{\text{Ga}})^{1/2}$. In this way one obtains

$$\frac{1}{\omega} \frac{\Delta\omega}{\Delta T} \sim \frac{3\sqrt{3}}{2} \frac{Ga\alpha}{M_{\text{Ga}}\omega_{\text{LA}}^2}, \quad (60)$$

which has the value $1.4 \times 10^{-5} \text{ } ^\circ\text{C}$ (experimental¹ $5 \times 10^{-5} \text{ } ^\circ\text{C}$). The conclusion already reached on the basis of (57) that the anharmonic mechanism for the infrared absorption is consistent with the temperature shift of the combination bands still holds, at least insofar as a one dimensional model can be used to discuss the problem.

5. THE THERMAL EXPANSION

We have already made use of both the theory and the observed magnitude of the thermal expansion in the preceding section. Although there we were concerned with the temperature shift of frequencies rather than the thermal expansion itself, it is clear that there is no violent disagreement between the observed thermal expansion and theoretical predictions based on (35). For we would expect that if such a disagreement exists it would show up in (57) or (60). In this section we shall calculate the thermal expansion on the basis of the three dimensional GaP anharmonic model described in Sec. 2.

We shall use a direct perturbation method which does not require explicit knowledge of the dependence of phonon frequencies on volume. Consider a simple anharmonic oscillator with the potential energy $\frac{1}{2}Kx^2 - Gx^3$, and define the expansion δ by the relation

$$\delta_n = \langle \psi_n^{(1)} | x | \psi_n^{(1)} \rangle, \quad (61)$$

where $\psi_n^{(1)}$ is the wave function to first order in the perturbation $-Gx^3$ corresponding to the n th quantum state of the harmonic oscillator. A simple calculation gives

$$\delta_n = (3G/K^2)(n + \frac{1}{2})\hbar\omega. \quad (62)$$

When δ_n is averaged over the thermal equilibrium distribution of quantum states it may be called the thermal expansion of the oscillator. According to this view an expansion can be defined for each quantum state; if the perturbation could be turned on adiabatically one would expect to observe the expansion δ_n for any initial state n . This approach can be readily applied to the linear chain by defining

$$\delta_n = N^{-1} \sum_i \langle \psi_n^{(1)} | x_i - x_{i-1} | \psi_n^{(1)} \rangle, \quad (63)$$

where the sum is over the N atoms of the chain. A simple calculation gives the result (55) for an arbitrary assignment of occupation number n_q . The thermal expansion is obtained by assigning the equilibrium values (29) to n_q .

For the GaP structure the expansion of the cube edge is

$$\delta_n = (4/\sqrt{3})N^{-1} \sum_r \langle \psi_n^{(1)} | \mathbf{j}' \cdot [\mathbf{u}(\mathbf{r}_{j'}) - \mathbf{u}(\mathbf{r})] | \psi_n^{(1)} \rangle, \quad (64)$$

where the notation is that of Sec. 2, and \mathbf{j}' may be any one of the four nearest neighbor directions. In terms of unperturbed states this becomes

$$\delta_n = \frac{4}{\sqrt{3}} N^{-1} \sum_t \sum_{g \neq n} \frac{\langle n | (\beta_{j'0t} + \beta_{j'0t^+}) | g \rangle \langle g | H'' | n \rangle}{E_n - E_g} + \frac{\langle n | H'' | g \rangle \langle g | (\beta_{j'0t} + \beta_{j'0t^+}) | n \rangle}{E_n - E_g}, \quad (65)$$

where H'' is given by (10). For each branch t there are two intermediate states corresponding to creation and destruction of a phonon of zero wave vector.

Diagrams for the processes responsible for expansion are shown in Fig. 3, with (a) representing the first term in (65) and (b) the second. The intermediate states are single phonon states (i.e., differ by one phonon from the initial state), so that two of the H'' phonons must be the same phonon created and destroyed at the H'' vertex as indicated by the closed loops. The single phonon vertices are labelled δ to represent the "expansion operator" $(\beta_0 + \beta_0^+)$. The relevant part of H'' which contributes to δ_n is

$$H'' = -3GN^{-1} \sum_j \sum_{ss'} \sum_{q'v'} \beta_{j0t}^{(s)} \beta_{jq'v'}^{(s')} \beta_{jq'v'}^{(-s')}. \quad (66)$$

It may be noted that (14) is not valid for repeated indices such as occur in this case.

A simple calculation involving (13), (65) and (66) gives

$$\delta_n = \frac{4}{\sqrt{3}} \frac{3G}{N} \sum_{tj} \frac{[F_{j'0t} F_{j0t}^* + F_{j'0t}^* F_{j0t}]}{\hbar\omega_{0t}} \times \sum_{q'v'} |F_{jq'v'}|^2 (2n_{q'v'} + 1). \quad (67)$$

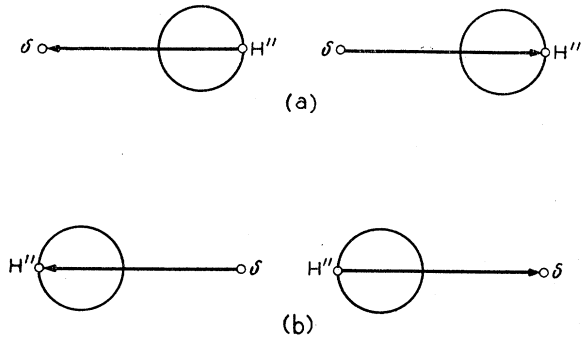


FIG. 3. Diagrams for thermal expansion [see Eq. (65)].

From (7), (8), and (12) we have

$$F_{j0t} = (\mathbf{j} \cdot \mathbf{u}) (\hbar/2m\omega_{0t})^{\frac{1}{2}} \text{ optical branches} \\ = (\mathbf{j} \cdot \mathbf{u}) (\hbar/2M\omega_{0t})^{\frac{1}{2}} i\rho \mathbf{q} \cdot \mathbf{j} \text{ acoustic branches.} \quad (68)$$

This shows that the optical branches make no contribution to the sum \sum_{ij} in (67) because the sum $\sum_{q'v}$ is independent of \mathbf{j} while $\sum(\mathbf{j} \cdot \mathbf{u}) = 0$ for any phonon polarization \mathbf{u} . The optical branches still contribute to $\sum_{q'v}$, but the occupation numbers $n_{q'v}$ strongly favor the acoustical branches at ordinary temperatures. In order to obtain the linear thermal expansion we neglect the optical branches entirely and make the high-temperature approximation $n_{qt} \sim kT/\hbar\omega_{qt}$ for the acoustic branches. The thermal expansion then becomes

$$\delta = \frac{4}{\sqrt{3}} \frac{3G\rho^4 kT}{M^2} N^{-1} \sum_{q'v} \frac{(\mathbf{j} \cdot \mathbf{u}')^2 (\mathbf{j} \cdot \mathbf{q}')^2}{\omega_{q'v}^2} \\ \times \lim_{q \rightarrow 0} \frac{1}{4} \left(\sum_{jt} \frac{(\mathbf{j} \cdot \mathbf{u})(\mathbf{j} \cdot \mathbf{q})}{\omega_{qt}} \right), \quad (69)$$

where \mathbf{j} has been summed and a compensating factor $\frac{1}{4}$ supplied. In (69) the unit polarization vectors \mathbf{u} are functions of $\mathbf{q}t$. A simple formula can be obtained if it be assumed that the acoustic branches can be represented by a single velocity of sound c_s

$$\omega_{qt} \sim c_s q. \quad (70)$$

This is the simplest Debye approximation. The summation over phonons then reduces to

$$N^{-1} \sum_{q'v} \frac{(\mathbf{j} \cdot \mathbf{u})^2 (\mathbf{j} \cdot \mathbf{q}')^2}{\omega_{q'v}^2} = \frac{1}{3c_s^2}, \quad (71)$$

where c_s is related to the longitudinal and transverse velocities by the formula

$$\frac{1}{3c_s^4} = \frac{1}{5c_L^2} \left[\frac{2}{3c_T^2} + \frac{1}{c_L^2} \right]. \quad (72)$$

The summation over \mathbf{j} is carried out by means of the identity

$$\sum_j (\mathbf{j} \cdot \mathbf{u})(\mathbf{j} \cdot \mathbf{q}) = 4\mathbf{u} \cdot \mathbf{q}, \quad (73)$$

which shows that only the longitudinal branch contributes to this summation. The final formula is

$$\delta = \frac{3\sqrt{3}}{16} \frac{Ga^4 kT}{M^2 c_s^4}, \quad (74)$$

where $a = 4\rho/\sqrt{3}$ is the cube edge or lattice constant. This gives

$$\alpha = \frac{3\sqrt{3}}{16} \frac{Ga^3 k}{M^2 c_s^4} \quad (75)$$

for the coefficient of linear thermal expansion, which must be compared with the observed value²³ $5.3 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$.

In making the comparison between theory and experiment it is necessary to estimate the effective velocity of sound c_s , which comes into (75) as the inverse fourth power. In the absence of experimental information on the velocities of sound or the elastic constants we can only make rough estimates of c_T and c_L from the critical point frequencies¹ ω_{TA} and ω_{LA} (we shall ignore ω_{TA2}). If the critical points are at $(111)\pi/a$ on the Brillouin Zone and the normal dispersion relation (46) holds we have $c_T = 3.4 \times 10^5$, $c_L = 5.8 \times 10^5$ cm/sec, and (72) gives

$$c_s \sim 5.0 \times 10^5 \text{ cm/sec.} \quad (76)$$

The use of the normal dispersion approximation probably²⁸ underestimates c_T and overestimates c_L , although this is not certain and little can be said about the error made in ignoring ω_{TA2} . If the theoretical expansion coefficient (75) is to agree with experiment the required value of c_s is 6.1×10^5 cm/sec which is probably not in disagreement with (76). As best we can tell at present, therefore, the thermal expansion is consistent with the infrared absorption on the basis of the same anharmonic model.

6. SUMMARY

A summary of results is shown in Table I. The first column lists in order the infrared absorption (I.A.), the width γ of the fundamental resonance, the temperature shift of frequencies $\omega^{-1}(\Delta\omega/\Delta T)$, the coefficient α of linear thermal expansion, and the effective velocity of sound c_s defined by (72). The second and third columns give, respectively, the experimental and theoretical values. When these two agree it means a parameter in the theory listed in the fourth column has been determined. The parameters so determined are the anharmonic parameter G determined from (I.A.) and the effective sound velocity c_s determined from α . The experimental c_s is not a direct measurement, and represents only a guess based on an assumed dispersion relation. This investigation has been carried out to

TABLE I. Summary of results.

	Exp.	Theor.	Parameter fitted
I.A.	7×10^{-3}	7×10^{-3}	$G = 3 \times 10^{12}$ cgs
γ	3×10^{-3}	5×10^{-4} (0°K)	...
$\frac{1}{\omega} \frac{\Delta\omega}{\Delta T}$	$(5 \pm 2) \times 10^{-5}$	1.4×10^{-5}	...
α	5.3×10^{-6}	5.3×10^{-6}	$c_s = 6 \times 10^5$ cm/sec
c_s	$\sim 5 \times 10^5$	6×10^5	

²⁸ M. Lax, Phys. Rev. Letters **1**, 133 (1958).

ascertain whether or not a single anharmonic model could account for the infrared absorption and a number of other anharmonic effects. On the basis of the results summarized in Table I we reach an affirmative conclusion. A consequent conclusion is that in the case of GaP it is not *necessary* to invoke the second order

electric moment mechanism (charge deformation) to explain the observed infrared combination bands.

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Critical Field Curve of Superconducting Mercury*

D. K. FINNEMORE, D. E. MAPOTHER,† AND R. W. SHAW
Physics Department, University of Illinois, Urbana, Illinois

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The critical field curve of mercury has been precisely measured in a range of reduced temperature, $t=T/T_c$, from 1 to 0.27. The observed H_c values show an appreciable deviation from a parabolic temperature dependence, lying above the parabola which passes through the experimental values of H_0 and T_c . The general behavior is similar to that previously observed in the case of lead. Values of the temperature coefficient of the normal electronic specific heat, γ , are derived, but are somewhat uncertain since the H_c data indicate an appreciable entropy contribution from the superconducting electrons at the lowest temperature of measurement. The qualitative behavior of $H_c(T)$ for lead and mercury is in accord with recent infrared measurements which give direct indication that the energy gap value for these elements is anomalously large.

ONE of the best known regularities of superconductivity is the fact that the critical field curves of all superconducting elements can be approximately represented by the "parabolic law"

$$H_c(T) = H_0(1 - t^2); \quad t = T/T_c, \quad (1)$$

where H_0 and T_c are, respectively, the critical field at $T=0^\circ\text{K}$ and the critical temperature. Precise measurements of $H_c(T)$ for a particular element generally exhibit small deviations from (1) which may be described by the function

$$D(T) = [H_c(T) - H_c^p(T)]/H_0, \quad (2)$$

where $H_c(T)$ is the experimentally observed critical field and $H_c^p(T)$ is the value computed for the same temperature from (1) using the experimental constants, H_0 and T_c . The maximum value of $D(T)$ is never greater than a few percent and, until recently, $D(T)$ also seemed to be negative for all superconducting elements—a circumstance attributed to the fact that the superconducting electronic specific heat, C_{es} , had an exponential dependence on T [rather than the well known T^3 dependence which follows thermodynamically from (1)].¹

Recent measurements of Pb show this element to be exceptional in exhibiting a positive $D(T)$.² From this

behavior it follows that C_{es} for Pb cannot be exponential above a reduced temperature $t=T/T_c \sim 0.3$. It was also noted that the maximum value of $D(T)$ for various elements shows a correlation with the ratio T_c/θ_D , where θ_D is the limiting value of the Debye temperature as $T \rightarrow 0^\circ\text{K}$. The same correlation indicated that Hg, hitherto considered to be the one true "parabolic" superconductor,³ should also show a positive $D(T)$. We have measured $D(T)$ for Hg and find it to be not only positive but of greater maximum amplitude than expected from the empirical correlation with T_c/θ_D .

Specimens of reagent grade Hg⁴ were cast in graphite molds as nearly single crystals in the form of cylinders (0.160 cm diam \times 3.05 cm long). After removal from the mold, the specimens were annealed for 8 hours about 20°K below the melting point of Hg. The specimens were freely suspended in a liquid helium bath and the critical field measured by a ballistic induction method.⁵ Values were obtained down to a temperature of about 1.1°K ($t \sim 0.27$) by pumping over the helium bath. The specimen temperature was determined from a vapor pressure thermometer bulb with large copper fins which sampled the temperature of the helium bath immediately adjacent to the specimen. This procedure eliminates some of the uncertainty due to the hydrostatic head correction required when the vapor pressure

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† Alfred P. Sloan Foundation Fellow.

¹ W. S. Corak and C. B. Satterthwaite, *Phys. Rev.* **102**, 662 (1956); also M. A. Biondi, A. T. Forrester, M. P. Garfunkel, and C. B. Satterthwaite, *Revs. Modern Phys.* **30**, 1109 (1958).

² D. L. Decker, D. E. Mapother, and R. W. Shaw, *Phys. Rev.* **112**, 1888 (1958).

³ E. Maxwell and O. S. Lutes, *Phys. Rev.* **95**, 333 (1954).

⁴ Obtained from Goldsmith Brothers Smelting & Refining Company, of Chicago, Illinois. Stated purity: Au, Ag, less than 0.0005%, other base metals less than 0.0001%.

⁵ J. F. Cochran, D. E. Mapother, and R. E. Mould, *Phys. Rev.* **103**, 1657 (1956).