

## Infrared Lattice Absorption of GaP

D. A. KLEINMAN AND W. G. SPITZER

*Bell Telephone Laboratories, Murray Hill, New Jersey*

(Received October 29, 1959)

Transmission and reflectivity measurements on GaP in the wavelength region 1 to  $40\mu$  have been analyzed to obtain information on the lattice vibrations. The fundamental reflection band has been fitted by dispersion theory and the strength, width, and resonance wavelength ( $27.3\mu$ ) determined. The dielectric constant is found to be  $8.5 \pm 0.2$  in the range  $1 < \lambda < 12\mu$  and  $10.2$  for  $\lambda > 40\mu$ . The background absorption in *n*-type samples due to free carriers was reduced by copper diffusion to make possible accurate transmission measurements of the lattice combination bands. An assignment scheme using five frequencies is proposed to explain the combination bands. The temperature dependence of the bands is consistent with theory for two-phonon processes. One band is observed which appears to be due to molecular vibrations of an impurity not yet identified. From the integrated absorption it is concluded that the principal mechanism for the combination bands is the anharmonic potential energy.

### I. INTRODUCTION

THE intrinsic absorption edge<sup>1</sup> of gallium phosphide at 300°K occurs at a wavelength  $\sim 0.55\mu$  (2.24 eV). The purest crystals are transparent and orange in color; less pure samples may appear dark green or opaque. The optical properties of GaP have been studied by Folberth and Oswald,<sup>1</sup> Oswald,<sup>2</sup> and Spitzer, Gershenzon, Frosch, and Gibbs.<sup>3</sup> The effect of pressure on the absorption edge has been studied by Edwards, Slykhouse and Drickamer.<sup>4</sup> The work of Oswald<sup>2</sup> revealed lattice absorption bands in the 13- to  $15\mu$  region, although the details of these bands are obscured by a background absorption increasing with wavelength which is probably due to free carriers. The fundamental infrared absorption has not been previously reported at this writing.

We have investigated the infrared properties in the region 1 to  $40\mu$  in polycrystalline samples of low carrier concentrations. This range includes a broad transmission window from 1 to  $12.5\mu$ , the lattice combination bands from  $12.5$  to  $24\mu$ , and the fundamental band at  $27.3\mu$ . The fundamental band was studied by reflection and the other bands by transmission.

It has been customary to report optical data in terms of the so-called optical constants, the index of refraction *n* and the extinction coefficient *k*, which are the real and imaginary parts of the complex index of refraction  $n - ik$ . Actually, *n* and *k* are not constants but rapidly varying functions of wavelength in the neighborhood of absorption resonances. A discussion of the problem of obtaining *n* and *k* from optical measurements, with particular application to semiconductors, has been given by Oswald and Schade<sup>5</sup> together with references to earlier published work. We have approached the problem from a different point of view

in which we attempt to fit the reflectivity exactly (within experimental error) by classical dispersion theory. This involved the trial and error adjustment of four parameters which are: the resonance frequency, resonance strength, resonance width, and high-frequency dielectric constant. Once the bulk reflectivity or the transmission of a thin film has been fitted in this way the optical constants are known as a by-product of the calculation. In a cubic crystal like GaP the optical properties are isotropic and the fundamental band is due to a single oscillator, the long-wavelength transverse optical mode vibration of the lattice. This method of analysis of the reflectivity has been successfully applied to SiC<sup>6</sup> and ZnO.<sup>7</sup>

### II. EXPERIMENTAL PROCEDURE

The material for these measurements came from polycrystalline rods prepared by Frosch by using the reaction of gallium with phosphorus at elevated temperature and a pressure of 20 atm. The material as grown was *n* type with a carrier density in the range  $10^{17}$ – $10^{18}$  cm<sup>-3</sup>. By comparing the reflectivity of two samples at the limits of this range it was determined that free carriers had no effect on the reflectivity measurements reported here. The reflectivity samples were about  $7 \times 15 \times 1$  mm in size and were ground front and back with 600-mesh abrasive powder. The front surface was polished and the reflectivity measured; the surface was then etched for 5 min in concentrated bromine and the reflectivity remeasured. It was observed that after the Br etch about 5% of the surface was pitted. The average size of the pits was about  $20\mu$ . The distribution of pits over the samples was not perfectly uniform and the maximum reflectivity,  $\sim 93\%$ , was found to vary 2% to 3% over the surface.

The measured reflectivity of an etched specimen is shown by the points in Fig. 1 while the solid curve is

<sup>1</sup> O. Folberth and F. Oswald, *Z. Naturforsch* **9a**, 1050 (1954).

<sup>2</sup> F. Oswald, quoted by H. Welker, *J. Electronics* **1**, 181 (1955).

<sup>3</sup> Spitzer, Gershenzon, Frosch, and Gibbs, *J. Phys. Chem. Solids* **11**, 339 (1959).

<sup>4</sup> Edwards, Slykhouse, and Drickamer, *J. Phys. Chem. Solids* **11**, 140 (1959).

<sup>5</sup> F. Oswald and R. Schade, *Z. Naturforsch* **9a**, 611 (1954).

<sup>6</sup> W. G. Spitzer, D. Kleinman, and D. Walsh, *Phys. Rev.* **113**, 127 (1959).

<sup>7</sup> R. J. Collins and D. Kleinman, *J. Phys. Chem. Solids* **11**, 190 (1959).

the theoretical fit to be discussed in the next section. Figure 2 shows an enlarged view of the reflection peak for three surface treatments. There is a significant difference between the polished surface and the polished and etched surface. Presumably the polished surface before etching is sufficiently damaged so that it does not give a reflectivity characteristic of the bulk material. The difference between the two samples which were polished and etched is typical of the differences over the surface of any sample and is therefore not significant. The surface treatment affects only the peak of the reflectivity. At lower reflectivity all samples agree. A similar effect of polishing and etching was also observed<sup>6</sup> for SiC.

Three transmission samples were prepared starting with *n*-type material of about  $10^{17}$  cm<sup>-3</sup> carrier density. The transmission was measured from 1 to 24.5 $\mu$ . Although there is an appreciable absorption background, due presumably to free carriers, it is possible

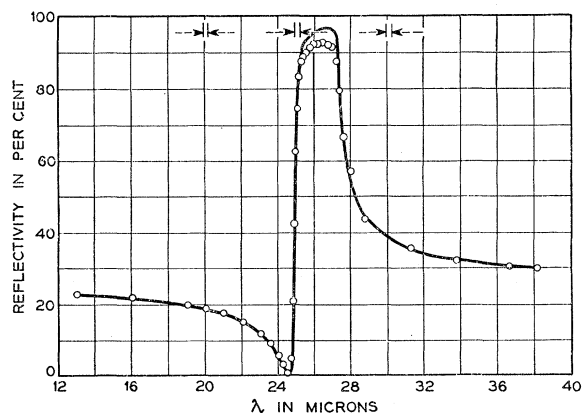


FIG. 1. Reflectivity of GaP. Data shown by points and theoretical fit by solid curve. The spectral resolution is indicated at several wavelengths.

to identify a number of absorption bands. The transmission is shown in Fig. 3. To reduce the carrier concentration and the absorption background we acted upon a suggestion by Hrostowski. Previously Hrostowski and Fuller<sup>8</sup> had shown that background absorption in GaSb can be reduced by an order of magnitude by compensation with lithium. Hoping to achieve similar results in GaP, Fuller diffused copper into two of our samples. One of these attempts was particularly successful and the background absorption was greatly reduced. This sample of thickness 0.0419 cm yielded the transmission curve shown in Fig. 4. Careful comparison of Figs. 3 and 4 shows that the same absorption bands appear in each. The dropoff in transmission for  $\lambda > 16\mu$  is due to the fundamental absorption at 27.3 $\mu$ .

To study the temperature dependence of the lattice absorption the copper-diffused sample was measured

<sup>8</sup> H. Hrostowski and C. Fuller, J. Phys. Chem. Solids 4, 155 (1958).

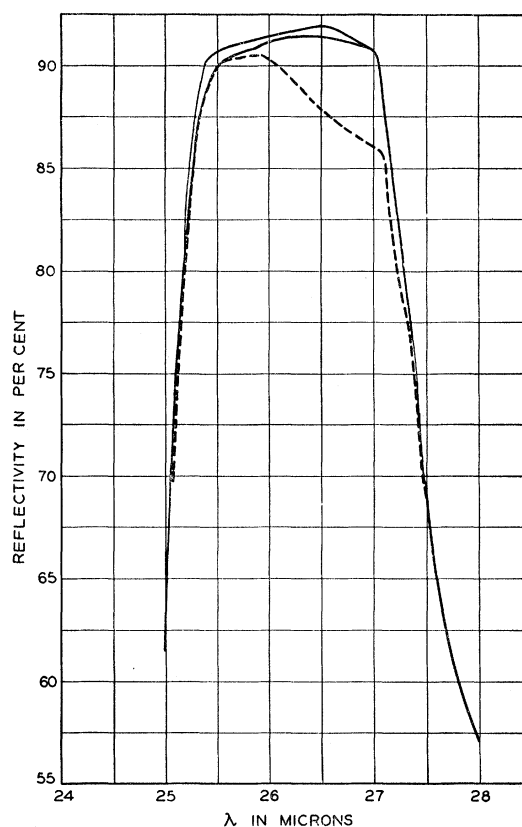


FIG. 2. Effect of surface treatment on the measured reflectivity. Polished and etched samples are given by the solid curves, polished and not etched by the dashed curve.

in transmission at 200°C. It was observed that with the sample at 200°C, the transmission decreased with time. This effect made it impossible to measure accurately the regions of high transmission. The regions of the absorption maxima could be measured, however, with fair accuracy, and this is shown in Fig. 4 by the dotted curve. The change of transmission with time suggests that copper is precipitating on grain boundaries or dislocations. The decoration of grain boundaries and

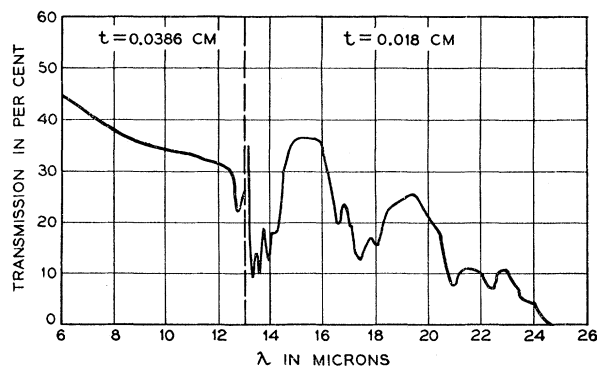


FIG. 3. Room temperature transmission of GaP samples without copper diffusion. The curve is discontinuous because two samples of different thickness were used.

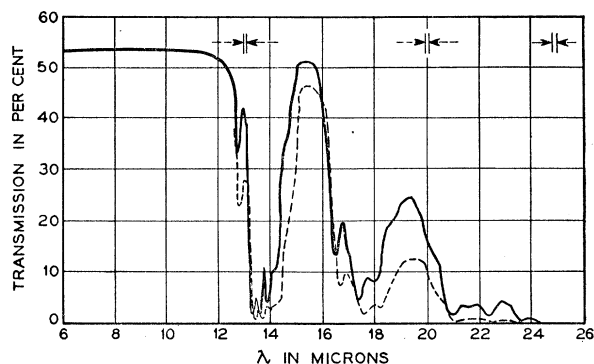


FIG. 4. Transmission of GaP after copper diffusion. Solid curve, room temperature; dashed curve, 200°C.

dislocations by impurities has been observed in ionic crystals<sup>9</sup> and in silicon.<sup>10</sup> Under microscopic examination lines of precipitation were clearly visible in the interior of the sample. Figure 5 shows a photograph of a typical decoration.

A transmission measurement of the compensated

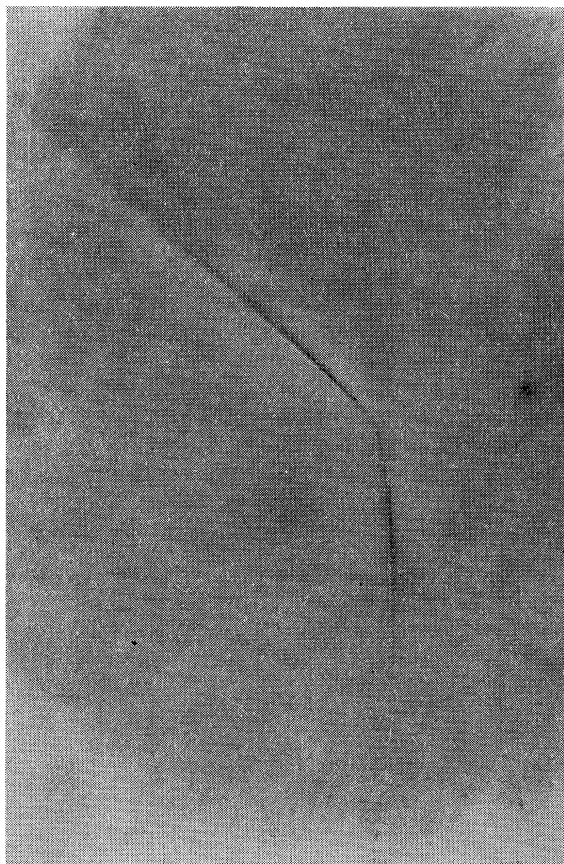


FIG. 5. Copper precipitation at 200°C in GaP X1000.

<sup>9</sup> S. Amelinchx, *Dislocations and Mechanical Properties of Crystals*, edited by Fisher, Johnston, Thomson, and Vreeland (John Wiley & Sons, Inc., New York, 1956).

<sup>10</sup> W. C. Dash, reference 9.

sample was made at room temperature at higher resolution. Except for the region near 16.5 $\mu$ , the absorption and shape of the bands remained unchanged. The transmission between 16 and 19 $\mu$  is shown in Fig. 6. It will be observed that the band at 16.55 $\mu$  appears much sharper than the other bands, which are essentially the same as in Fig. 4.

It was considered possible that some of the absorption bands in the 12- to 24- $\mu$  region may be due to the molecular vibrations of an impurity. Absorption bands have been observed in silicon which are characteristic of atomically dispersed oxygen<sup>11</sup> and precipitated Si<sub>3</sub>N<sub>4</sub>.<sup>12</sup> Oxygen, if present, might be in the combinations PO<sub>4</sub>(---) or Ga<sub>2</sub>O<sub>3</sub>. We have measured the transmission of a pellet of Ga<sub>2</sub>O<sub>3</sub> powder in KBr and the result is shown in Fig. 7. It will be observed that Ga<sub>2</sub>O<sub>3</sub> is

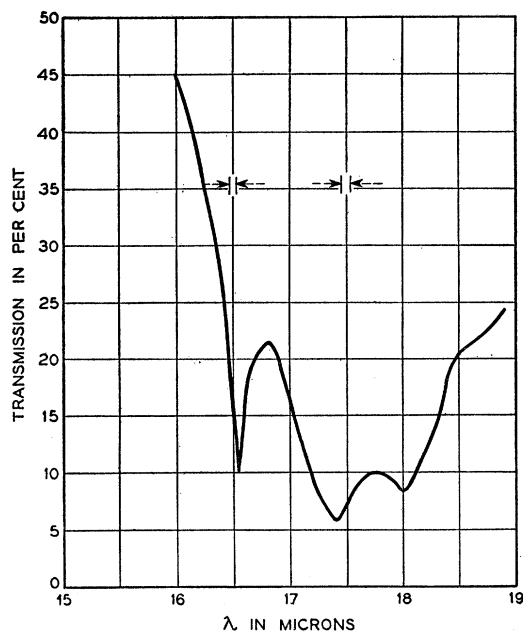


FIG. 6. Transmission of copper-diffused sample with higher resolution.

characterized by two sharp bands at 9.7 and 10.3 $\mu$ , neither of which is observed in our GaP samples. From a consideration of a large number of inorganic phosphates<sup>13</sup> one would expect PO<sub>4</sub>(---) to produce a sharp band near 10 $\mu$  and another near 6.8 $\mu$ , neither of which is observed in our samples of GaP.

### III. ANALYSIS OF THE REFLECTIVITY

The reflectivity from 13 to 42 $\mu$  shown in Fig. 1, has been fitted within experimental error by classical dispersion theory. The method is the same as described

<sup>11</sup> W. Kaiser, P. H. Keck, and C. F. Lange, *Phys. Rev.* **101**, 1264 (1956).

<sup>12</sup> W. Kaiser and C. Thurmond, *J. Appl. Phys.* **30**, 427 (1959).

<sup>13</sup> H. H. Landolt and R. Börnstein, *Zahlenwerte und Funktionen aus Physik Chemie Astronomie Geophysik und Technik* (Springer-Verlag, Berlin, 1955), Vol. 4, Part 1, p. 464.

in reference 6 except that the IBM-704 computer was used and the program has been enlarged<sup>14</sup> to accommodate 10 resonances. Only a single resonance was needed in the present case, the transverse optical vibration for zero wave vector which will be called the fundamental resonance. The fit gives the following values:

$$\begin{aligned} \lambda_0 &= (27.3 \pm 0.05)\mu, \\ \nu_0 &= (1.098 \pm 0.002) \times 10^{13} \text{ sec}^{-1}, \\ 4\pi\rho &= 1.725 \pm 0.01, \\ \gamma_0 &= 0.003 \pm 0.0005, \\ \epsilon_0 &= 8.457 \pm 0.2, \end{aligned} \quad (1)$$

where  $\lambda_0$  is the resonance wavelength,  $\nu_0 = c/\lambda_0$ ,  $4\pi\rho$  is the resonance strength,  $\gamma$  is the width, and  $\epsilon_0$  is the high-frequency dielectric constant. The definitions of  $\gamma$  and  $\rho$  are the same as given in reference 6. The origin of  $\epsilon_0$  is primarily the polarization of the valence band which becomes anomalous in the region of the intrinsic

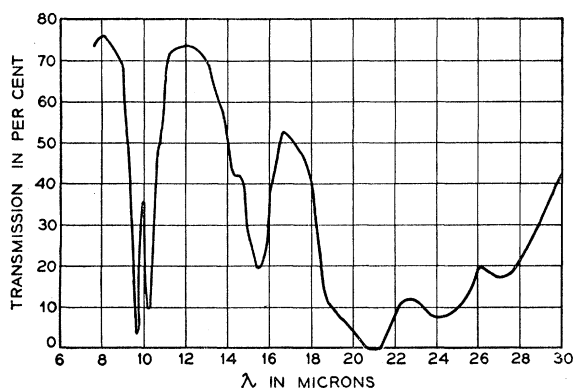


FIG. 7. Transmission of  $\text{Ga}_2\text{O}_3\text{-KBr}$  pellet.

absorption edge  $\sim 0.55\mu$ . Therefore the dielectric constant for  $\lambda \ll \lambda_0$  is not strictly constant, and the variation may contribute to the error indicated for  $\epsilon_0$  in (1). A number of the values are given to more figures than errors would warrant because these are the values actually used to calculate the theoretical curve shown in Fig. 1.

Figure 8 shows the optical constants,  $n$  and  $k$ , as obtained from the reflectivity calculation.

The estimates of error given in (1) were obtained in the following manner. The error in  $\lambda_0$  arises from the resolution of the measurements. The error in  $4\pi\rho$  is estimated on the basis of the sensitivity of the theoretical fit to variations in this quantity. Two methods for estimating the error in  $\epsilon_0$  have been used. The first is to relate it to the experimental error,  $\Delta R$ , in the measured reflectivity at short wavelength ( $\sim 13\mu$ ); this leads to the relation  $\Delta\epsilon_0 \sim 44\Delta R$ . The second way concerns the position of the reflectivity minimum.

<sup>14</sup> We are indebted to Dr. J. Hopfield for use of a subroutine which was incorporated in the program.

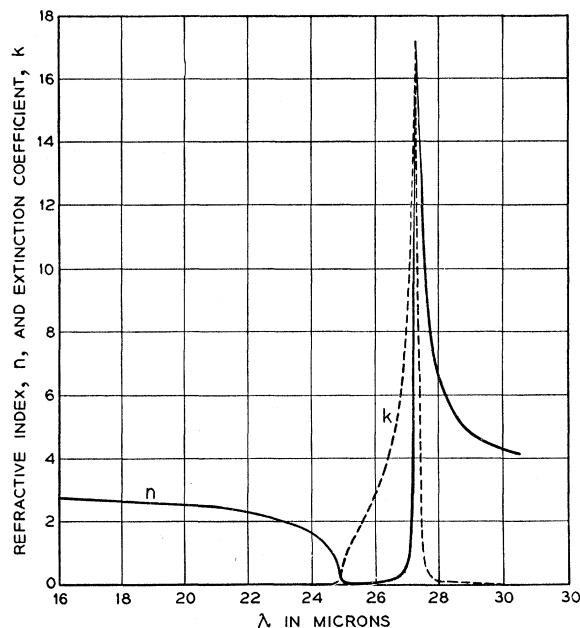


FIG. 8. Optical constants,  $n$  and  $k$ , as functions of wavelength.

The minimum is quite sharp so we assume its position,  $24.6\mu$ , is exactly known; the various errors are then related by the formula  $\Delta\epsilon_0 - 5\Delta(4\pi\rho) + 83(\Delta\lambda_0/\lambda_0) = 0$ . Both methods give  $\Delta\epsilon_0 \sim 0.2$  which is indicated in (1). The analysis shows that, within the indicated error,  $\epsilon_0$  is constant between 13 and  $24.6\mu$ .

The width  $\gamma$  requires more discussion since the fit is relatively insensitive to  $\gamma$  except near the top of the reflectivity peak. It will be seen in Fig. 1 that, right at the top, the theoretical curve does not fit the experimental points. There is, in fact, no value of  $\gamma$  which fits the measurements exactly in this region. It will be recalled from the experimental details of the previous section that the peak reflectivity varied by 2% to 3% from place to place due to the presence of etch pits. This suggests that the true reflectivity is higher than any of our measured points in the peak region. We have adopted two criteria which serve to define  $\gamma$  to the extent indicated in (1). The first is that  $\gamma$  should be chosen to give the best fit of the left (short wavelength) side of the peak subject to the restriction that the theoretical  $R$  must never fall below the measured  $R$ . This narrows  $\gamma$  to the range 0.003 to 0.004. The second criterion, which concerns the transmission in the 12- to  $24\text{-}\mu$  region, is that the transmission for the fundamental absorption alone must not be less than the observed transmission. This criterion is satisfied by  $\gamma = 0.003$  and not by  $\gamma > 0.0035$ . On this basis we adopt  $\gamma = 0.003 \pm 0.0005$  as our final value.

An explanation may be given for the polishing-etching effect shown in Fig. 2. We assume that polishing produces a thin damaged layer in which the resonance width  $\gamma$  is very much larger than in the bulk material.

As long as the penetration depth of the radiation is much larger than the thickness of the damaged layer, the layer has little effect. But very near the resonance wavelength the penetration depth would be small and the large  $\gamma$  of the damaged layer would cause the reflectivity to be much reduced. We can estimate the thickness of the layer by assuming that at the wavelength ( $25.7\mu$ ) where the reflectivity of the polished sample first begins to drop below that of the etched sample, the penetration depth equals the layer thickness. The depth of penetration at this wavelength can be obtained from the calculated extinction coefficient  $k$ . In this manner the thickness of the damaged layer is estimated to be  $\sim 0.9\mu$ .

The static or long-wavelength dielectric constant has the value

$$\epsilon_{\infty} = \epsilon_0 + 4\pi\rho = 10.182 \pm 0.2. \quad (2)$$

At the present time no other measurement of  $\epsilon_{\infty}$  has been reported. The measurement of  $\epsilon_{\infty}$  by microwave techniques would be very difficult on the high-conductivity samples that have been available up to the present time. It may be hoped, however, that compensation by copper diffusion may make microwave measurements possible.

The pronounced fundamental reflection band shows that GaP is an ionic crystal in the sense that a charge resides on the atoms of Ga and P in the lattice. It is presumably not an ionic crystal in the sense that the Madelung energy is the major part of the cohesive energy. A value may be obtained for the ionic charge  $e^*$  from the dispersion parameters on the basis of the theory of Szigeti<sup>15</sup>

$$\frac{e^*}{e} = \left[ \frac{4\pi^2\rho m\nu_0^2}{Ne^2} \right]^{\frac{1}{2}} \frac{3}{\epsilon_0 + 2}, \quad (3)$$

where  $m$  is the reduced mass of the ion pair and  $N$  is the concentration of ion pairs. The appropriate values for GaP are  $N = 2.49 \times 10^{22} \text{ cm}^{-3}$ ,<sup>16</sup>  $m = 3.56 \times 10^{-28} \text{ g}$ ,  $4\pi\rho = 1.725$ ,  $\nu_0 = 1.098 \times 10^{13} \text{ sec}^{-1}$ , and  $\epsilon_0 = 8.457$ , which give

$$e^*/e = 0.58. \quad (4)$$

The effective charges of a number of other III-V compounds have been discussed by Picus, Burstein, Hennis, and Hass<sup>17</sup> on the basis of measured reflectivities and a simplified dispersion analysis. According to a suggestion made by Slater and Koster<sup>18</sup> one might expect the effective charge in III-V compounds to be small compared to unity. This idea has been used by Folberth and Welker<sup>19</sup> to account for the energy gaps

<sup>15</sup> B. Szigeti, *Trans. Faraday Soc.* **45**, 155 (1949).

<sup>16</sup>  $a = 5.4505 \text{ \AA}$ , G. Geisecke and H. Pfister, *Acta. Cryst.* **11**, 369 (1958).

<sup>17</sup> G. Picus, E. Burstein, B. W. Hennis, and M. Hass, *J. Phys. Chem. Solids* **8**, 282 (1959).

<sup>18</sup> J. Slater and G. Koster, *Phys. Rev.* **94**, 1498 (1954).

<sup>19</sup> O. Folberth and H. Welker, *J. Phys. Chem. Solids* **8**, 14 (1959).

and binding energies of isoelectronic sequences of III-V compounds. The effective charges reported<sup>17</sup> have varied from 0.34 for InSb to 0.60 for InP.

#### IV. ANALYSIS OF THE COMBINATION BANDS

##### A. Determination of Absorption Coefficient

Woodbury and Tyler<sup>20</sup> have shown that copper in germanium has three acceptor levels, one of which is only 0.04 eV above the valence band. The present interpretation of these levels is that they are associated with the tetrahedral bonding of substitutional copper in the lattice. This is consistent with the observations<sup>20</sup> that gold also has three acceptor levels while zinc, iron, nickel, cobalt, and manganese have two levels. Therefore, we expect that substitutional copper should give three acceptor levels in GaP, one of which is close to the valence band. It has not yet been established that copper enters GaP substitutionally, but the present work shows that copper introduces at least one acceptor level. Any level lying higher than the lowest copper level will be unoccupied in the compensated sample. On the other hand, any level lying lower than the Fermi level in the as-grown  $n$ -type samples will be occupied. Therefore, there should be a great difference between the uncompensated and compensated samples as regards the occupation of impurity levels in the energy gap. The probability of the ionization of impurity levels and of transitions between impurity levels should be a sensitive function of the occupations of the levels. It was observed, however, that the same bands in the 12- to 24- $\mu$  region are observed in the compensated and uncompensated samples indicating that these bands are due to absorption by the lattice. The possibility of observing bands in this region due to the molecular vibrations of impurities has not been ruled out. We believe that the bands are not due to oxygen, since we would expect to observe bands characteristic of  $\text{PO}_4^{(---)}$  or  $\text{Ga}_2\text{O}_3$  in that case. We can say nothing at present about the optical effects of nitrogen, carbon, or silicon. The conclusion that the observed bands (with one exception, see Sec. IV C) are due to the lattice is supported by the following analysis and by the observed temperature dependence.

The transmission  $T$  is given by

$$T = \frac{(1-R)^2 e^{-\alpha x}}{1 - R^2 e^{-2\alpha x}}, \quad (5)$$

where  $R$  is the reflectivity,  $\alpha$  the absorption coefficient, and  $x$  the thickness of the sample. From this expression the absorption coefficient  $\alpha$  can be calculated and is plotted in Fig. 9. It is assumed that  $\alpha$  is the sum of two absorption coefficients,  $\alpha_f$  representing the fundamental infrared lattice absorption, and  $\alpha_c$  representing the combination bands of the lattice. The absorption by

<sup>20</sup> H. Woodbury and W. Tyler, *Phys. Rev.* **105**, 84 (1957).

the fundamental resonance is given by

$$\alpha_f = 8\pi^2 \rho \gamma \frac{1}{n} \frac{\lambda_0 \lambda^2}{(\lambda_0^2 - \lambda^2)^2} \quad (6)$$

The requirement that  $\alpha_f \leq \alpha$  for all  $\lambda$  has already entered into the choice for the value of  $\gamma$ . A plot of  $\alpha_f$  is also shown in Fig. 9. Subtracting the two curves gives  $\alpha_c$ , the absorption coefficient for combination bands which is also given in Fig. 9.

### B. Nature of Combination Bands

Combination bands are so called because they are due to processes in which two or more phonons combine to interact with the radiation field. The mechanism of the interaction has usually been assumed<sup>21,22</sup> to be the anharmonic part of the crystal potential. In this case the combination bands are part of the fundamental resonance absorption. The interaction with the field arises from the dipole moment of the fundamental resonance, in the sense that the interaction of the

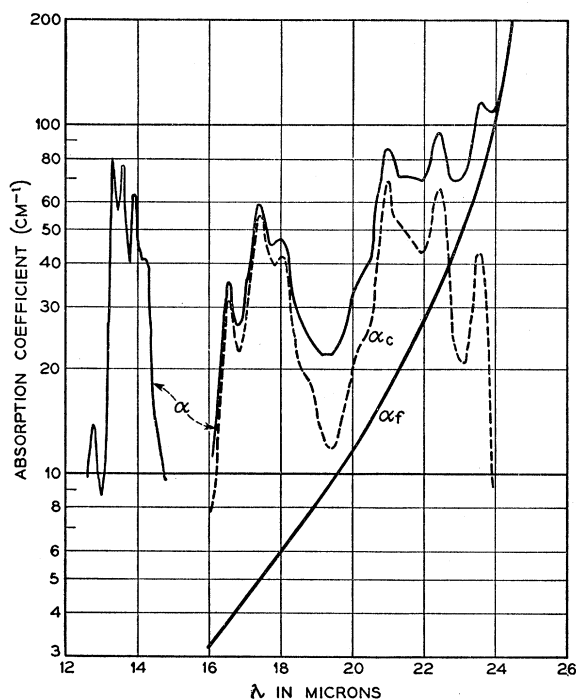


FIG. 9. The experimental absorption coefficient  $\alpha$ , the absorption coefficient for the fundamental resonance  $\alpha_f$ , and the absorption coefficient for the combination bands  $\alpha_c = \alpha - \alpha_f$ .

<sup>21</sup> M. Born and M. Blackman, *Z. Physik* **82**, 551 (1933); M. Blackman, *Z. Physik* **86**, 421 (1933); *Trans. Roy. Soc. (London)* **A226**, 102 (1936); L. L. Barnes, R. R. Brattain, and F. Seitz, *Phys. Rev.* **48**, 582 (1935).

<sup>22</sup> It should be mentioned that the possibility of one-phonon absorption bands arising from a breakdown of periodic boundary conditions has been considered by H. Rosenstock, *J. Chem. Phys.* **23**, 2415 (1955). The bands considered here, which extend to about twice the fundamental frequency, cannot be explained in this way.

crystal with the radiation takes place through the dipole moment of the fundamental oscillations. The absorption may be regarded as a second order process in which a photon is absorbed and two phonons are created through an intermediate state in which the fundamental oscillation is excited. Neither of the two phonons ultimately produced is a fundamental phonon. This mechanism evidently could not operate in homopolar crystals such as silicon in which the fundamental resonance has no dipole moment. To explain the observed absorption in such cases it has been suggested<sup>23</sup> that two phonons can interact directly with the radiation field through terms in the electric moment of second order in the atomic displacements.

The mechanism of the second order electric moment may be important in crystals of the zincblende structure such as GaP and in ionic crystals as well as in homopolar crystals. Lax and Burstein<sup>23</sup> point out that in the sequence MgO, LiF, NaF, NaCl, and KCl, the ratio of the main reflection side band to the main reflection peak follows the same trend as the strain polarizability and the deviation from the Cauchy relation. From this they conclude that charge deformation, which implies the existence of second and higher order moments, may be an important absorption mechanism.

Recently Johnson<sup>24</sup> has analyzed the lattice absorption in silicon. He has obtained a reasonably good fit to the locations of eleven absorption maxima and to their temperature dependence on the basis of only four frequencies. These frequencies he designates in a conventional way as longitudinal optical (LO), transverse optical (TO), longitudinal acoustic (LA), and transverse acoustic (TA). Actually, the combination bands are a continuous absorption, but singularities<sup>25</sup> in the phonon frequency distribution give rise to absorption peaks. These singularities arise from critical points<sup>26</sup> in the phonon Brillouin zone where the frequency as a function of wave vector is flat. We expect such points to occur at or near the edge of the Brillouin zone. The circumstance that a whole branch can be represented by a single frequency such as (LA) is probably fortuitous for silicon and not to be expected generally. In general each branch might have several important critical points.

According to the theory<sup>23</sup> for the second order moment mechanism a selection rule forbids combination bands in which both phonons belong to the same branch. Johnson<sup>24</sup> obeyed this selection rule in his assignment of two-phonon processes. This selection rule holds only in homopolar crystals and would not hold in GaP. The anharmonic mechanism also has no such selection rule for GaP. Thus, we may assign the

<sup>23</sup> M. Lax and E. Burstein, *Phys. Rev.* **97**, 39 (1955).

<sup>24</sup> F. Johnson, *Proc. Phys. Soc. (London)* **73**, 265 (1959). Also see B. Brockhouse and P. Iyengar, *Phys. Rev.* **111**, 747 (1958).

<sup>25</sup> E. Montroll, *J. Chem. Phys.* **15**, 575 (1947). L. Van Hove, *Phys. Rev.* **89**, 1189 (1953).

<sup>26</sup> J. Phillips, *Phys. Rev.* **104**, 1263 (1956).

TABLE I. Summary of combination bands in GaP.  $\lambda(\mu)$  and  $\bar{\nu}(\text{cm}^{-1})$  are the wavelength and wave number of the observed absorption bands. The third column gives the assignments of the bands. The  $\bar{\nu}_{\text{expected}}$  is determined from the assignment and the phonon values given at the bottom of the table.  $f_{\text{exp}}$  is the ratio of  $\alpha_c(200^\circ\text{C})$  to  $\alpha_c(25^\circ\text{C})$ , and  $f_{\text{theor}}$  is the ratio of  $f(T)$  at the same two temperatures.  $f(T)$  is defined in Eq. (7).

$\lambda(\mu)$	$\bar{\nu}(\text{cm}^{-1})$	Assignment <sup>a</sup>	$\bar{\nu}_{\text{expected}}$	$f_{\text{exp}}$	$f_{\text{theor}}$
12.75	784	3-phonon			
13.25	755	LO+LO	756	1.3	1.4
13.55	738	LO+TO	739	1.4	1.4
13.85	722	TO+TO	722	1.3	1.4
(14.15)	707				
16.55	604			1.5	
17.40	575	LO+LA	575	1.5	1.5
17.90	559	TO+LA	558	1.6	1.5
(18.60)	538				
(20.3)	493	LO+TA <sub>1</sub>	493	1.8	1.5
20.95	477	TO+TA <sub>1</sub>	476	1.6	1.5
22.40	446	LO+TA <sub>2</sub>	444	1.6	1.6
23.50	426	TO+TA <sub>2</sub>	427	~1.5	1.6

<sup>a</sup> LO=378, TO=361, LA=197, TA<sub>1</sub>=115, TA<sub>2</sub>=66.

process LO+LO. Even in silicon the assignment TO+TO is allowable since there are two transverse branches.

### C. Assignment of Bands

From the absorption curve  $\alpha_c$  in Fig. 9 we have selected thirteen combination bands, the wavelength of which are listed in the first column of Table I. Some of those we have selected are only shoulders on the curve are therefore doubtful; these are indicated by parentheses. The second column in the table gives the wave numbers of the bands. The bands 755, 738, 722  $\text{cm}^{-1}$  have a uniform spacing of 16 or 17  $\text{cm}^{-1}$  which suggests the assignments 2 LO, LO+TO, and 2 TO, respectively. The values would then be TO=361, LO=378  $\text{cm}^{-1}$ . The bands 575, 559 also have the spacing 16  $\text{cm}^{-1}$  which suggests the assignments LO+LA, TO+LA, respectively and the value LA=197  $\text{cm}^{-1}$ . To fit the last four bands it is necessary to use two more frequencies TA<sub>1</sub>=115, TA<sub>2</sub>=66  $\text{cm}^{-1}$ . A summary of the assignments is given in the third column. The wave numbers at which the assigned bands would be expected are listed in the fourth column. A comparison with the second column shows that the assignments are within 1  $\text{cm}^{-1}$  of the measured bands except for the 22.40- $\mu$  band which is off by 2  $\text{cm}^{-1}$ . This must be considered very good agreement. The assignment scheme is successful in that a large number (nine) of the bands are accounted for, all the bands that would be predicted are observed, and the locations of the bands are accurately given.

The theory of two-phonon combination bands by the mechanism of the anharmonic potential is considered in a separate paper.<sup>27</sup> It is found that the temperature dependence is the same for the anharmonic and second

order moment mechanisms, and, for processes where phonons of frequencies  $\nu_1, \nu_2$  are created, is given by

$$f(T) = 1 + F(h\nu_1/kT) + F(h\nu_2/kT), \quad (7)$$

with

$$F(x) = (e^x - 1)^{-1}.$$

The measured temperature dependences obtained from Fig. 4 are listed in the fifth column of Table I, where  $f_{\text{exp}}$  is the ratio of  $f(T)$  at 200°C to its value at room temperature. The corresponding theoretical quantity is listed in the sixth column. In obtaining the experimental values it was assumed that the absorption of the fundamental resonance did not change in going to 200°C. The error of this assumption only affects the last four bands, and is not expected to be larger than other errors in the measurement. The agreement between columns five and six is generally satisfactory.

It may also be noted that the combination bands shift to longer wavelength with increasing temperature (see Fig. 4). Within experimental error the frequency shift for all the bands is given by

$$(1/\nu)(\Delta\nu/\Delta T) \sim -5 \times 10^{-5} \text{C}^{-1}. \quad (8)$$

This effect will be discussed in more detail in a following paper.<sup>27</sup>

Four of the bands listed in Table I do not fit in with the proposed assignment scheme. The band at 12.73 $\mu$  is weaker than the others, as may be seen in Fig. 9, and is higher in frequency, so we assign it to some unspecified three-phonon process. The bands at 14.15 and 18.60 $\mu$  are doubtful, and therefore perhaps need no explanation. They are not quite as prominent as the doubtful band at 20.3 $\mu$  which is part of the assignment scheme. The only real problem is the prominent band at 16.55 $\mu$ . We submit that this band is not due to two-phonon processes on the ground that any scheme sufficiently enlarged to account for this band would predict many bands that are not observed, or else fail to explain other bands that are observed. It cannot be a three-phonon process because of its temperature dependence (see Table I). A three-phonon process would be expected to have a temperature dependence  $f = (1+F_1)(1+F_2) \times (1+F_3) - F_1F_2F_3$  which would give a ratio of about 2.5 for a temperature rise of 200°C from room temperature. Also on the grounds of its strength we would rule out explanation as a three-phonon process. As explained in Sec. II it is probably not due to oxygen impurity. In Fig. 6 we see that this band is much narrower than the other bands, and therefore it seems reasonable to suggest that it is not a lattice combination band. The most plausible explanation is that it is due to molecular vibrations of an unidentified impurity which is not oxygen.

### D. Integrated Absorption

The shape of the combination bands is determined by the shape of the frequency distribution of the

<sup>27</sup> D. A. Kleinman, following paper [Phys. Rev. 118, 118 (1960)].

phonons. The integrated intensity, however, is relatively insensitive to the frequency distribution. From Fig. 9 we can obtain an integrated intensity for the three optical branch processes LO+LO, LO+TO, and TO+TO which give absorption peaks well separated from the other processes. For GaP the dimensionless quantity  $\int \alpha d\lambda$  has the value

$$\int \alpha d\lambda \sim 7 \times 10^{-3}. \quad (9)$$

If we now consider Johnson's silicon data<sup>24</sup> for the corresponding processes we find that the integrated intensity is about  $3 \times 10^{-4}$ . (In diamond and germanium<sup>28,29</sup> the level of absorption is similar to that of silicon so that this value may be taken as representative of the homopolar crystals.) We must remember, however, that a selection rule is operating in silicon which allows only three of the six possible kinds of transition between the three optical branches. Supplying a factor of two gives  $6 \times 10^{-4}$ ; this is about what one would expect the integrated intensity to be in GaP if the same mechanism operated as in silicon. Since this is an order of magnitude lower than what we observe, we conclude that the principal mechanism for the combination bands in GaP is the anharmonic potential. In SiC<sup>6</sup> the integrated intensity for optical branches is  $2 \times 10^{-2}$ . In this case it is particularly difficult to see how the integrated absorption in SiC could be  $\sim 60$  times larger than in either silicon or diamond. In a separate paper<sup>27</sup> it is shown that the anharmonic mechanism is consistent with the observed integrated absorption.

### E. Sum Rule for Frequencies

Recently Brout<sup>30</sup> has given the sum rule

$$\sum_{i=1}^6 \omega_i(\mathbf{q})^2 = \frac{1}{\beta} \frac{18}{m} r_0, \quad (10)$$

<sup>28</sup> R. J. Collins and H. Y. Fan, Phys. Rev. **93**, 674 (1954).

<sup>29</sup> W. Kaiser and W. L. Bond, Phys. Rev. **115**, 857 (1959).

<sup>30</sup> R. Brout, Phys. Rev. **113**, 43 (1959).

where  $\beta$  is the compressibility,  $m$  the reduced mass,  $r_0$  the interionic distance, and  $\omega = 2\pi\nu$ . This relation is derived on the basis of Coulomb attractive forces and nearest neighbor repulsive forces.

At the center of the Brillouin zone the frequency of the transverse optical branches is given by (1). According to the Lyddane-Sachs-Teller<sup>31</sup> relation the longitudinal branch has a frequency  $\nu_e = (\epsilon_\infty/\epsilon_0)^{1/2} \nu_0 = 1.207 \times 10^{13} \text{ sec}^{-1}$ . Therefore we can evaluate the left side of (10) at  $\mathbf{q} = 0$ ,

$$\omega_e^2 + 2\omega_0^2 = 1.52 \times 10^{28} \text{ sec}^{-2}. \quad (11)$$

From the frequencies LO, TO, LA, TA<sub>1</sub>, TA<sub>2</sub> of Table I we can also calculate this quantity for some  $\mathbf{q}$  near or at the boundary of the Brillouin zone,

$$\omega_{\text{LO}}^2 + 2\omega_{\text{TO}}^2 + \omega_{\text{LA}}^2 + \omega_{\text{TA}_1}^2 + \omega_{\text{TA}_2}^2 = 1.63 \times 10^{28} \text{ sec}^{-2}. \quad (12)$$

At the present time the compressibility  $\beta$  of GaP is not known. If we assume that (10) holds at  $\mathbf{q} = 0$ , we calculate the compressibility to be

$$\beta \approx 7.8 \times 10^{-13} \text{ cgs}. \quad (13)$$

This value is probably a little small in view of the compressibility<sup>32</sup> of silicon,  $1 \times 10^{-12}$ , and of germanium,  $1.3 \times 10^{-12}$  cgs. We see from (11) and (12) that the constancy of  $\sum \omega_i^2$  required by (10) holds only approximately. The discrepancy is outside of the experimental error. On the other hand, the assumptions underlying (10) probably do not apply very well to GaP which is primarily a valence crystal.

### V. ACKNOWLEDGMENT

We wish to express our appreciation to M. Gershenson and C. J. Frosch for supplying the GaP crystals and C. S. Fuller for the copper diffusion work. G. D. Sorin and L. E. Howarth were of considerable aid during the infrared measurements. We also wish to thank J. J. Hopfield for a number of helpful discussions.

<sup>31</sup> R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. **59**, 673 (1941).

<sup>32</sup> H. Y. Fan, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1.



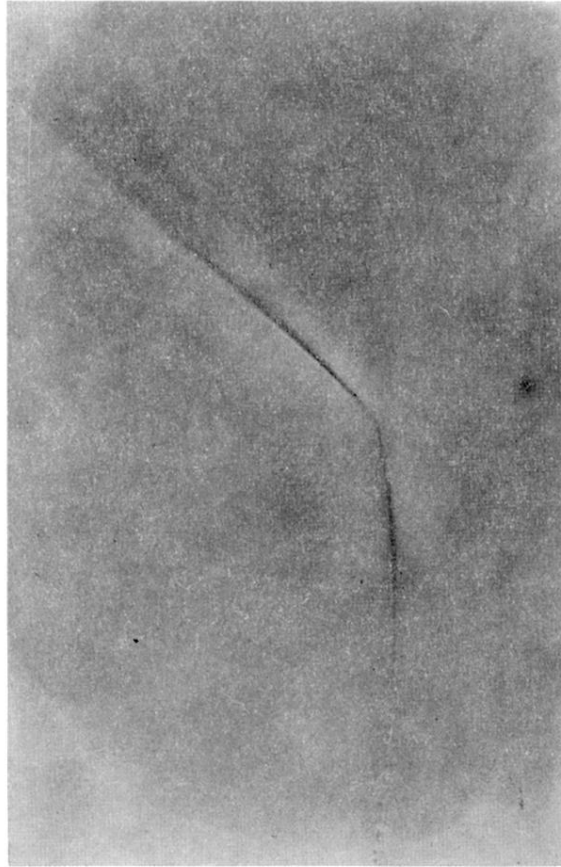


FIG. 5. Copper precipitation at 200°C in GaP X1000.