For each pair of sets of coordinates, we give first the value of the sum over ions having the same sign as the migrating ion at the $(\frac{1}{2},\frac{1}{2},0)$ position, and then the value of the sum over ions of opposite sign. The S sums agree within 1% with those calculated by Guccione *et al.*[7] by the same method, with a direct summation up to $t_{ld}\simeq 4$.

Finally, the evaluation of Eq. (1) for the saddle-point configuration involves the evaluation of the dipole-dipole and dipole-quadrupole van der Waals potentials of the perfect lattice (excluding the two vacancies) at the $(\frac{1}{2},\frac{1}{2},0)$ position. The pertinent sums can be obtained from the sums A_s and C_s over points of a simple cubic and of a face-centered-cubic lattice reported by Jones and Ingham,[26] for $s=6$ and $s=8$, as $\frac{1}{6}(2^{s/2}C_s-A_s)$.

[26] J. E. Jones and A. E. Ingham, Proc. Roy. Soc. (London) **A107**, 636 (1925).

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Lattice Vibration Spectra of $GaAs_xP_{1-x}$ Single Crystals*

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The energies of the two-phonon summation bands and the reststrahlen bands have been measured in $GaAs_xP_{1-x}$ single crystals. The data were obtained by observing the transmittance and the reflectivity at 300°K in the region of 400 to 800 cm^{-1} and 220 to 500 cm^{-1}, respectively. Crystals were prepared by open-tube epitaxial vapor-growth techniques and were not subject to any free-carrier absorption in the near infrared. The alloys show absorption peaks at frequencies which are only slightly shifted from the transverse optic TO(Γ) phonons, as well as several optical and acoustical zone-boundary phonons, characteristic of both GaP and GaAs. The reststrahlen-like band spectra of these alloys are explained by a virtual-crystal model in which average parabolic potentials are given to the three species of atoms in the lattice. This model does not require the assumption of gross composition inhomogeneities, which are known to be absent in these crystals.

I. INTRODUCTION

THE determination of the vibrational spectra of disordered systems is a problem that has attracted many workers in the past few years. Dean[1] applied mathematical techniques to obtain quantitatively accurate results for the spectra of disordered diatomic chains. A complete theory of three-dimensional disordered systems is yet to be developed. The alternative approach is to study such systems by the experimental method.

Some data have already been reported for a few semiconductor binary alloy systems. Oswald[2] studied a reststrahlen band in various composition alloys of $InAs_xP_{1-x}$, which has a frequency close to that of pure InP. He found that the wavelength increased very slightly and the intensity decreased with increasing x. Since the maximum wavelength of his measurement was 35 μ, he could not study any changes associated with a pure InAs band[3] of 45 μ at large x.

The infrared spectral absorptances of thin films of $GaAs_ySb_{1-y}$ have been studied by Potter and Stierwalt.[4] They found a single peak whose frequency shifted continuously with increasing y from that of pure GaSb to that of pure GaAs. This result is qualitatively different from the type of results presented below.

Finally, the vibrational spectra of Si-Ge alloys have been studied. Braunstein[5] found infrared absorption spectra which indicated the existence of modes associated with both pure Ge and pure Si.

In contrast, Logan *et al.*[6] reported that the composition dependence of a particular phonon mode, obtained from a tunneling experiment, was continuous and single-valued in the alloy. It should be noted that first-order photon-phonon interaction cannot be observed in Si-Ge alloys because of their homopolar nature, whereas it can be observed in diatomic compounds. In addition, the interpretation of the tunneling experiments in disordered crystals is somewhat uncertain. It is clear that more experimental work is needed in this field.

In this work, the interaction of photons with phonons in $GaAs_xP_{1-x}$ single crystals was investigated over a

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[1] P. Dean, Proc. Roy. Soc. (London) **A254**, 507 (1960).

[2] F. von Oswald, Z. Naturforsch. **14a**, 374 (1959).

[3] G. Picus, E. Burnstein, B. W. Henvis, and M. Hass, J. Phys. Chem. Solids **8**, 282 (1959).

[4] R. F. Potter and D. L. Stierwalt, in *Proceedings of the International Conference on The Physics of Semiconductors, Paris, 1964* (Academic Press Inc., New York, 1965), p. 1111.

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[6] R. A. Logan, J. M. Rowell, and F. A. Trumbore, Phys. Rev. **136**, A1751 (1964).

wide spectral region in the infrared. This particular alloy system was selected for the following reasons: (a) A strong first-order photon-phonon interaction is present in addition to the higher order interaction; (b) a method has been developed for preparing macroscopically homogeneous single crystals by epitaxial vapor growth; and (c) the infrared lattice absorption spectra of both GaAs and GaP are known in considerable detail.[7,8] The main purpose of this work is twofold: (1) to determine the effect of disorder on the two-phonon absorption bands in the alloy, and (2) to investigate the behavior of the reststrahlen bands as a function of ally composition.

These studies are essential in order to obtain fundamental knowledge of phonon spectra in disordered systems.

This paper is, primarily, a presentation of the experimental results. A theoretical model is presented which explains the major changes of vibrational frequencies with composition.

II. EXPERIMENTAL PROCEDURE

A. Crystal Growth

An open-tube epitaxial vapor-growth system, similar to that reported by Finch and Mehal,[9] was employed to grow single crystals of $GaAs_xP_{1-x}$. Alloys with x ranging from 0 to 1 were successfully grown on (111)A surfaces of GaAs seeds (held at 800 to 825°C under a thermal gradient of 16°C cm^{-1} in a 1-in. i.d. reaction tube). The reactions took place in an H_2 atmosphere with Ga (at 960°C), $AsCl_3$, and PCl_3 used as source materials. The growth conditions were as follows: (1) The total flow rate of H_2 was from 120 to 150 cc/min; (2) the total feed rate of halides (vapor carried by H_2) was from 5 to 9×10^{-5} mole/min; and (3) the seed was tilted at an angle of 30 deg from the direction of gas flow to achieve an epitaxial layer of uniform thickness. The growth rate was approximately 1.2 μ/min; layers 0.5 mm in thickness were obtained during a typical run of 7 h.

X-ray diffraction patterns were taken on powdered samples of the alloy mixed with Si as reference material to determine the lattice constant (hence the composition according to Vegard's law[10]). The composition of the grown crystal was found to depend entirely on the mole ratio of PCl_3 to $AsCl_3$ carried into the reaction tube. The diffraction lines at high Bragg angles were as sharp as those of Si and the variation of lattice constant in a given sample was found to be within ±0.0005 Å. We were thus sure that crystals grown by this method were free of gross inhomogeneities in the distribution of the constituent atoms. This was further confirmed by band-edge absorption data on GaP-rich samples which were known to have indirect transitions. The slopes of the square root of the absorption coefficient with respect to the photon energy were as sharp as the slope of GaP,[11] as shown in Fig. 1. Electron concentrations n_0 of the undoped crystals obtained by Hall measurements[12] were found to be consistently lower than 10^{15} cm^{-3} at room temperature. No free-carrier absorption in the near infrared was detected. GaAs-rich samples grown by the same method were used to fabricate microwave oscillators[13]; the agreement between the above experiment and the pressure experiment[14] on pure GaAs further indicates that the material is free of gross inhomogeneities. Thus it is concluded that material prepared by the epitaxial method is excellent for the study of phonon spectra in disordered systems.

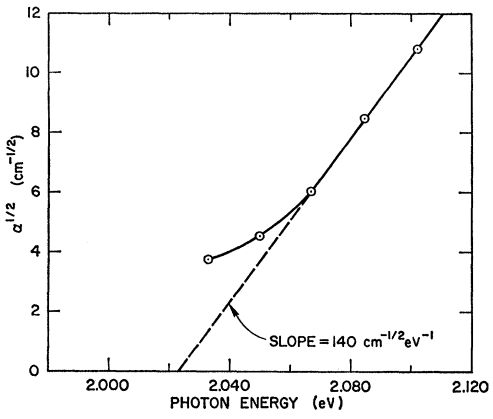

FIG. 1. Square root of the absorption coefficient versus photon energy at the band edges of $GaAs_{0.325}P_{0.675}$.

B. Sample Preparation and Apparatus

The substrates of the epitaxial layers with As content less than 0.65 were removed by etching in a solution of 1 part HF and 1 part HNO_3; those with As content greater than 0.65 were removed by lapping. The separated epitaxial layers were first lapped in abrasives of successively smaller grit sizes and then mechanically polished until mirror surfaces were obtained. The finished samples were typically $10\times10\times0.3$ mm in size.

The apparatus used for the transmittance measurements was a Beckman IR-9 infrared spectrophotometer which had a prism-grating monochromator covering a range of 2.5 to 25 μ. The double-beam mode was used and a resolution (in wave number) better than 0.5 cm^{-1}

[7] W. Cochran, S. J. Fay, F. A. Johnson, J. E. Quarrington, and N. William, J. Appl. Phys. Suppl. **32**, 2102 (1961).
[8] D. A. Kleinman and W. G. Spitzer, Phys. Rev. **118**, 110 (1960).
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[14] A. R. Hutson, A. Jayaraman, A. G. Chynoweth, A. S. Coriell, and W. L. Feldman, Phys. Rev. Letters **14**, 639 (1965).

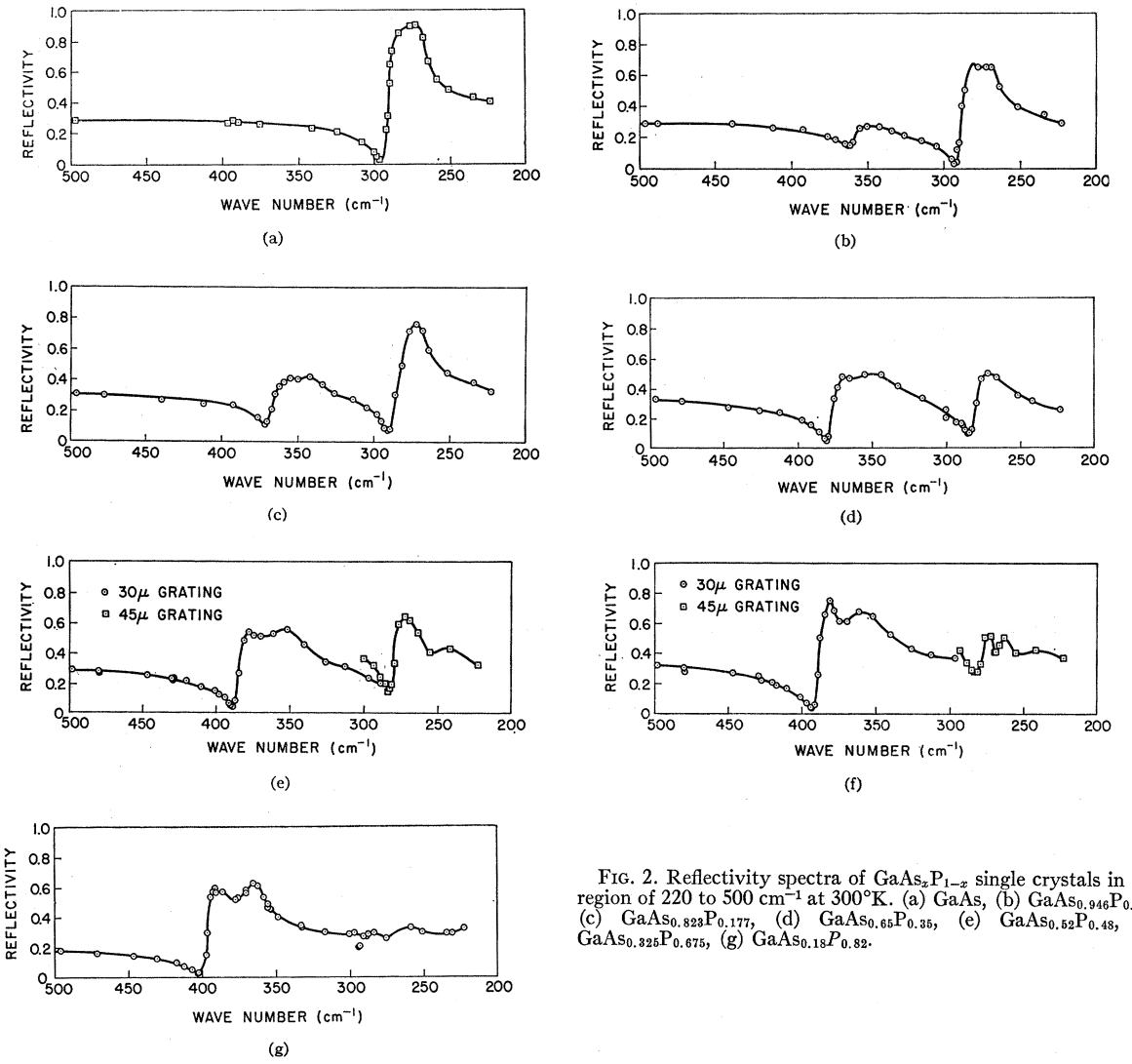

FIG. 2. Reflectivity spectra of $GaAs_xP_{1-x}$ single crystals in the region of 220 to 500 cm^{-1} at 300°K. (a) GaAs, (b) $GaAs_{0.946}P_{0.054}$, (c) $GaAs_{0.823}P_{0.177}$, (d) $GaAs_{0.65}P_{0.35}$, (e) $GaAs_{0.52}P_{0.48}$, (f) $GaAs_{0.325}P_{0.675}$, (g) $GaAs_{0.18}P_{0.82}$.

was achieved. The system was purged with dry N_2 during operation to reduce the effect of background absorption. The transmittance data were taken at 300°K in the region of 400 to 800 cm^{-1} (25 to 12.5 μ).

The apparatus used for the reflectivity measurements was an infrared spectrometer. A Perkin-Elmer model 210 filter-grating monochromator was used which covered the range of 7 to 45 μ with four interchangeable gratings whose first-order blaze wavelengths were 7.5, 22.5, 30, and 45 μ. Multilayer long-wavelength pass filters were used to confine the operation of the gratings to the first order. The incidence angle on the sample was 9.5° away from normal. Water-vapor absorption was reduced by a dry N_2 purge. Reflectivity data were taken at 300°K from 220 to 500 cm^{-1} using the sample-in and sample-out method. The accuracy of wave-number reading was better than 0.5 cm^{-1}; the resolution was better than 1 cm^{-1}.

III. RESTSTRAHLEN BANDS

A. Spectra

The reflectivity value R is plotted against the wave numbers in Figs. 2a to 2g for samples of various compositions. All but the 82% P and pure GaAs samples were grown at Stanford by the epitaxial method. The 82% P sample was from Merck and Company ($n_0=1.69\times10^{15}$ cm^{-3}), and the GaAs was from Monsanto Chemical Company ($n_0=5\times10^{15}$ cm^{-3}). Samples of 48% and 67.5% P consisted of several small pieces of crystals. The discontinuities in the reflectivity spectra of these two samples near 280 cm^{-1} were due to a change in gratings at this point. It is seen that the shape of the reflectivity spectrum of GaAs in Fig. 2(a) is comparable to the data reported by Iwasa *et al.*,[15] and thus the

[15] S. Iwasa, I. Balslev, and E. Burnstein, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Academic Press Inc., New York, 1965), p. 1077.

TABLE I. Measured reststrahlen energies of $GaAs_xP_{1-x}$.

Composition (%P)	ω_{TO}[a] of GaP (cm^{-1})	ω_{TO}[a] of GaAs (cm^{-1})	Sum of ω_{TO}[a] (cm^{-1})
0	...	268	...
5.4	341	268	609
17.7	342	269	611
35	345	270	615
48	349	271	620
67.5	355	...	...
82	360	...	...
100	366[b]		

[a] For convenience, assignments appropriate to a perfectly periodic lattice are used for the solid solutions. See text.
[b] From Ref. 8.

method of surface preparation used here is satisfactory.

The major feature of these data is that two reflectivity maxima were observed in the $GaAs_xP_{1-x}$ alloys: one close to the reststrahlen band of pure GaP,[8] and the other close to that of pure GaAs. The values of these two resonant frequencies are given in Table I. When the shapes of the maxima are square-topped the frequencies were chosen at the points where the reflectivity maxima began to decrease on the smaller wave number side. They were chosen at the maximum values when the shapes were peaked. Both GaP-like and GaAs-like bands appear throughout the entire alloy system. As the mole fraction of P decreases, the GaP band shifts slightly towards smaller wave number and decreases in strength. The shift with composition of the GaAs-like band is considerably smaller. In addition, the strength decreases much more rapidly with decreasing As concentration.

The reststrahlen bands in ordered crystals of zinc blende structure are due to the excitation of one TO(Γ) phonon (transverse-optical phonons of zero wave vector) of frequency ω_{TO} through the absorption of a photon of the same frequency. The mechanism for this interaction is due to the first-order electric moment in the crystal arising from the difference in charge of the two atoms in the unit cell. The existence of well-defined reflection maxima at frequencies which vary smoothly and slowly with composition, and which terminate at the $\omega_{TO}(\Gamma)$ frequencies of the pure crystals, indicates that modes which are quite closely related to the TO(Γ) phonons of GaAs and GaP exist simultaneously in their alloys.

In the limit of either very small As or very small P concentrations, we would expect localized modes to be there because of vibrations of isolated impurities. Consider the situation where the P concentration is very small. Since the mass of P is small compared to those of Ga and As, a localized mode is expected to rise out of the GaAs optical bands. Similarly, small concentrations of As in GaP may lead to either a localized mode in the gap between the acoustical and optical branches, if an appropriate gap exists, or a resonance mode if no such gap is present in the spectrum. At the concentrations considered here these modes will broaden into bands. Since the theory of this broadening is not sufficiently well developed, we shall describe the observed modes as $\omega_{TO}(\Gamma)$-like and present a theory which deals with the high concentration effects in the simplest possible manner. A more complete theory, which deals with the splittings and the two-phonon processes, will be presented elsewhere.

B. Random-Element–Isodisplacement Model

The reststrahlen frequencies of $GaAs_xP_{1-x}$ alloys summarized in Table I, can be explained over the entire composition range by a surprisingly simple model with only one adjustable constant. The model being proposed can be regarded as a random-element–isodisplacement model (or REI model): The fundamental assumption is that the As and P ions are randomly distributed on the anion sublattice and that anions of like species vibrate in phase and with identical amplitudes against the cations which also vibrate together as a rigid unit.

The assumption of isodisplacement is exactly true for the reststrahlen frequency in an ordered diatomic crystal. For that case the energy (hence the frequency) of the TO(Γ) phonon is determined by the resonant vibration of the cations against anions; its k vector is zero because there is no phase shift from unit cell to unit cell in the lattice. The only change introduced by the random assumption is that each atom is subjected to forces produced by a statistical average of its neighbors and that no effects of order are actually present.

Our simple model extends the isodisplacement feature for each element to obtain the resonant frequencies in the reflectivity spectra of a given $GaAs_xP_{1-x}$ single crystal. These frequencies, we conclude from the calculations described below, are actually, in the first-order approximation, the vibrational modes of randomly distributed P and As atoms against the ordered Ga atoms in the lattice.

The quantitative aspects of the random isodisplacement model averages out the fluctuations in neighbors by using x, the fraction of anion sites occupied by As. Accordingly, each Ga is regarded as surrounded by exactly $4x$ ions of As and $4(1-x)$ ions of P. Furthermore, both As and P ions are assumed to have exactly $12x$ next-nearest neighbors of As and $12(1-x)$ next-nearest neighbors of P. For the REI mode, relative motions occur only between atoms of different species. Applying Newton's second law on a per atom basis, the forces on the 3 elements are:

Gallium

$$m_g\ddot{u}_g = -xF_a(u_g-u_a)-(1-x)F_p(u_g-u_p), \quad (1)$$

Arsenic (fraction x)

$$m_a\ddot{u}_a = -F_a(u_a-u_g)-(1-x)F_s(u_a-u_p), \quad (2)$$

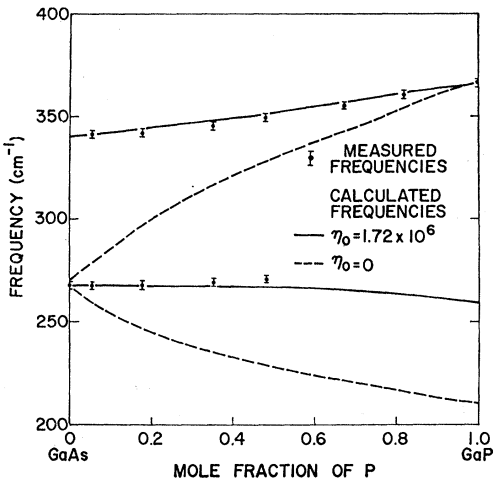

FIG. 3. Reststrahlen frequencies in $GaAs_xP_{1-x}$, showing measured points and theoretical curves with and without next-nearest-neighbor interaction.

Phosphorous (fraction $1-x$)

$$m_p\ddot{u}_p=-F_p(u_p-u_g)-xF_s(u_p-u_a), \tag{3}$$

where u_g, u_a, and u_p are the isodisplacements of all the atoms of Ga, As, and P; m_g, m_a, and m_p are the atomic masses and F_a is the force constant between a Ga ion and four surrounding As ions, so that, for composition x, the restoring force on a Ga ion due to the relative displacement of the As ions is $-xF_a(u_g-u_a)$. Similarly, $-(1-x)F_p(u_g-u_p)$ applies to force on Ga due to the P ions. There are no next-nearest-neighbor relative displacements for Ga ions, since for the REI model, they all have equal displacements. Newton's action-reaction law then leads to the F_a and F_p terms for the As and P motions.

The remaining force terms that need to be explained contain the factor $-F_s(u_a-u_p)$. This force is the next-nearest-neighbor restoring force that would be exerted on one As ion due to relative displacement u_a-u_p in respect to 12 next-nearest-neighboring P atoms. For the general composition x, only the fraction $(1-x)$ of the next-nearest neighbors are P so that the force on the As ion becomes $-(1-x)F_s(u_a-u_p)$.

All three constants F_g, F_a, and F_p are actually functions of the lattice constant. This functional dependence is assumed to be linear and is taken to have the form

$$F_a/F_{a0}=F_p/F_{p0}=F_s/F_{s0}=1-\theta x, \tag{4}$$

where the constant θ is calculated independently on the basis of the Gruneisen relationship,[16] as shown later in this section. F_{a0}, F_{p0}, F_{s0} represent the limits approached by the F's as x approach zero.

From the above, it is seen that the REI model employs the following 7 constants, which are evaluated below as indicated by the parentheses:

m_g, m_a, m_p (known mass constants)
θ (determined from thermal expansion, compressibility, etc., but not infrared frequencies.)
F_{p0} (determined from reststrahlen frequency in GaP.)
F_{a0} (determined from reststrahlen frequency in GaAs and θ.)
F_{s0} (this is the one adjustable constant chosen to give the best fit of theory and experiment in Fig. 3.)

The necessary relationships to fit theory to experiment require solving the REI-model equations (1) to (4).

The center of gravity of the entire system remains stationary; this is indicated by the sum of atomic motions in the equation

$$m_g\ddot{u}_g+xm_a\ddot{u}_a+(1-x)m_p\ddot{u}_p=0. \tag{5}$$

In the case of sinusoidal vibration, the frequency ω is determined by the following equation:

$$\begin{vmatrix} m_p\omega^2-F_p-xF_s & xF_s & F_p \\ (1-x)F_s & m_a\omega^2-F_a-(1-x)F_s & F_a \\ (-x)F_p & xF_a & m_g\omega^2-(1-x)F_p-xF_a \end{vmatrix}=0. \tag{6}$$

One trivial solution is $\omega^2=0$, which is equivalent to constant-velocity motion of the center of gravity given by Eq. (5). The remaining part of Eq. (6) is a quadratic equation in ω^2. The following solutions are obtained for limiting cases in the limits of $x=0$ (GaP) and $x=1$ (GaAs):

$$x=0,\quad \omega^2=\frac{F_{p0}}{m_p}\left(1+\frac{m_p}{m_g}\right)=\omega_{TO}(\Gamma)(\text{GaP}), \tag{7a}$$

$$=\frac{F_{a0}+F_{s0}}{m_a}=\omega_{as}; \tag{7b}$$

$$x=1,\quad \omega^2=\frac{F_{p0}+F_{s0}}{m_p}(1-\theta)=\omega_P, \tag{8a}$$

$$=\frac{F_{a0}}{m_a}\left(1+\frac{m_a}{m_g}\right)(1-\theta)=\omega_{TO}(\Gamma)(\text{GaAs}), \tag{8b}$$

where $\omega_{TO}(\Gamma)$'s are self-explanatory, while ω_{as} and ω_P represent the localized vibration frequencies for the limiting cases of vanishing concentrations of As and P in GaP and GaAs, respectively.

[16] C. Kittell, *Introduction to Solid State Physics*, 2nd ed., (John Wiley & Sons, Inc., New York, 1961), Chap. 6, p. 154.

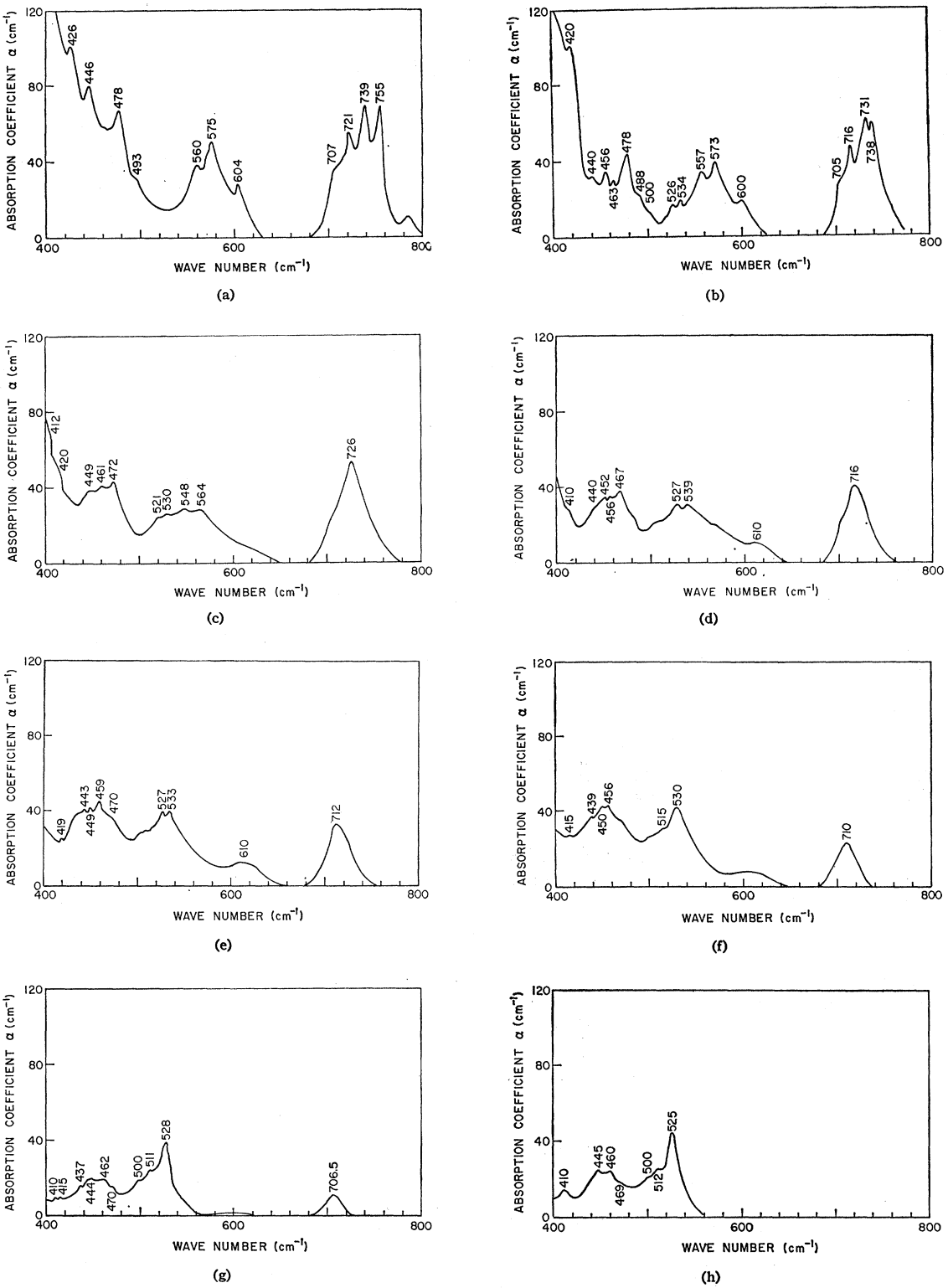

FIG. 4. Lattice absorption spectra of $GaAs_xP_{1-x}$ single crystals in the region of 400 to 800 cm^{-1} at 300°K. (a) GaP, (b) $GaAs_{0.15}P_{0.85}$, (c) $GaAs_{0.325}P_{0.675}$, (d) $GaAs_{0.52}P_{0.48}$, (e) $GaAs_{0.65}P_{0.35}$, (f) $GaAs_{0.823}P_{0.177}$, (g) $GaAs_{0.946}P_{0.054}$, (h) GaAs.

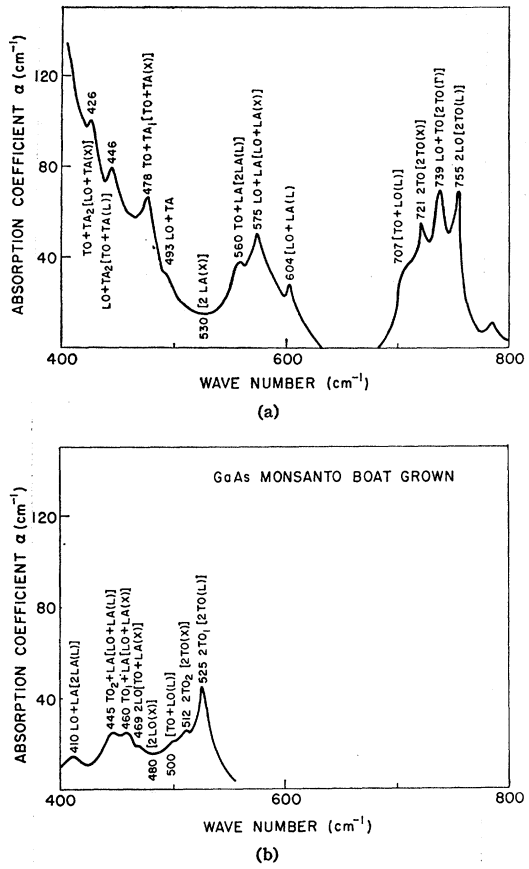

FIG. 5. Lattice absorption spectra of GaP and GaAs with the phonon-assignment schemes of Kleinman and Spitzer for GaP, and with that of Cochran for GaAs, as well as those of Johnson (in brackets) for both GaP and GaAs. (a) GaP (b) GaAs.

The value of θ is found to be 0.216 through Gruneisen's relation.[16] The derivation is shown as follows: The Gruneisen's relation leads to

$$\alpha_v = \gamma_{Gr} K C_v / V, \tag{9}$$

where γ_{Gr} is the Gruneisen constant, α_v is the volume expansion coefficient, K is the compressibility, V is the volume of one gram atom, and C_v is the specific heat per gram atom at constant volume. For GaP,[17,18] $\alpha_v = 15.9 \times 10^{-6}$ deg^{-1}, $V = 4.13^{-1}$ cm^{3}g^{-1}, $C_v = 0.124$ cal g^{-1} deg^{-1}, and $K = 0.77 \times 10^{-12}$ dyn cm^2. These values lead to $\gamma_{Gr} = 0.97$ in Eq. (9).

The relevance of γ_{Gr} to our problem is that the Gruneisen theory is based on the approximation that with change in lattice constant all phonon frequencies depend on lattice constant, or interatomic separation as

$$\frac{\Delta\omega}{\omega} = \gamma_{Gr}\frac{\Delta V}{V} = 0.97\frac{\Delta V}{V} = 2.91\frac{\Delta a}{a}. \tag{10}$$

[17] G. L. Pearson and F. Vogel, Progr. Semicond. 6, 1 (1962).
[18] M. Gershenzon and R. M. Mikulyak, J. Appl. Phys. 35, 2132 (1964).

We interpret this relationship to imply for our model that each force constant varies proportionately to ω^2 so that changes ΔF in the force constant from the F_0 values are given by

$$\Delta F/F_0 = 2\Delta\omega/\omega_0 = 5.82\Delta a/a_0,$$

where, as discussed, the subzero values correspond to $x=0$ in $GaAs_xP_{1-x}$. Since by Vegard's law (Sec. 2A) for $x=1$ we have

$$\Delta a/a_0 = (5.663-5.450)/5.450 = 0.0372,$$

it follows that $\Delta a/a_0 = 0.0372x$ and

$$\Delta F/F_0 = 0.216x = \theta x, \tag{11}$$

where the identification of 0.216 with θ follows at once from Eq. (4). It is thus seen that θ is independently determined and is not adjusted to fit the infrared data of Fig. 3.

Knowing θ, $\omega_{TO}(\Gamma)$'s, and the masses, F_{p0} and F_{a0} can be calculated from Eqs. (7a) and (8b). We found that $F_{p0} = 2.86 \times 10^6$, and $F_{a0} = 3.32 \times 10^6$. The units used here are mole grams for the masses and cm^{-1} for the frequency. The best fit is achieved by assigning a value of $F_{s0} = 1.72 \times 10^6$. This is shown in Fig. 3. Also shown in Fig. 3 are the dotted curves for the case of $F_{s0} = 0$, where second-nearest neighbor between As and P are completely neglected. It is readily seen that the fit is extremely poor with $F_{s0} = 0$. Therefore the introduction of the adjustable constant F_{s0} plays a vital role in explaining our experimental results. Such a significant interaction between As and P atoms is a natural result by randomly mixing the As and P atoms among the group V sites in the lattice.

It is believed that the REI displacement model proposed here should be equally applicable to other binary alloys of III–V compounds. Also this model explains the existence of a localized mode of P in GaAs-rich crystals (and vice versa).

In short, the model proposed here is physically realistic in that it takes into account the effect of a change in the lattice constant on the binding forces between nuclei, as well as the interactions of As and P atoms regarded as second-nearest neighbors, so that the reststrahlen frequencies over the entire composition range of $GaAs_xP_{1-x}$ can be explained by only one adjustable constant.

IV. ABSORPTION SPECTRA OF TWO-PHONON SUMMATION BANDS

The transmittance T, for normal incidence, obeys the relation

$$T = \frac{(1-R)^2 \exp(-\alpha l)}{1-R^2 \exp(-2\alpha l)}, \tag{12}$$

where α is the absorption coefficient, and l is the thickness of the sample. The coefficient α can be calculated

by means of Eq. (12) from the experimental data on T, R, and l. Absorption spectra of $GaAs_xP_{1-x}$ were obtained and are given in Figs. 4a to 4h. All but the GaAs sample (from Monsanto Company, $n=5\times10^{15}$ cm^{-3}) were grown by the epitaxial method.

The data for pure GaAs and GaP are in good agreement with the results of Cochran *et al.*[7] on GaAs and Kleinman and Spitzer[8] on GaP. These authors have given phonon-assignment schemes to the spectra with five phonon energies in each case. Johnson[19] gave alternative assignment schemes to these spectra from a critical point analysis based on the space group symmetry. The assignment schemes of GaAs and GaP are indicated in Fig. 5 [those by Johnson are presented in brackets], where TA and LA are the transverse- and longitudinal-acoustical phonons, TO and LO are the transverse- and longitudinal-optical phonons, and Γ, X, W, and L are the (0,0,0), (1,0,0), (1,$\frac{1}{2}$,0), and ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$) points in the Brillouin zone of zinc-blende crystals. As can be seen, the agreement between different assignments on a given material is poor; however, it is believed that Johnson's assignments are sounder since they have taken the physical properties of crystal symmetry into account.

The major feature of the absorption spectra of $GaAs_xP_{1-x}$ is that it is possible to trace the energies of the two-phonon bands of both GaAs and GaP in the alloy as a function of composition; this is shown in Fig. 6. Some of the two-phonon bands cannot be traced from the spectra of the alloy; this is particularly true for the bands of GaAs since the intensity of the GaP bands is inherently stronger than that of the GaAs bands. On the other hand, a number of the GaP bands appear in a spectral region in which GaAs is completely transparent and therefore are easily traced.

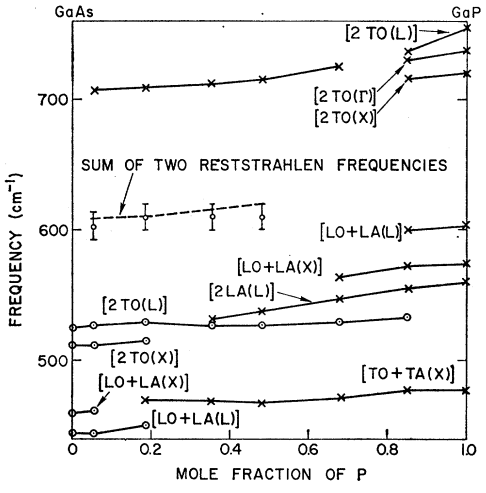

FIG. 6. Two-phonon bands of $GaAs_xP_{1-x}$ as a function of composition. Johnson's assignment schemes for GaAs and GaP are given.

[19] F. A. Johnson, Progr. Semicond. 9, 179 (1965).

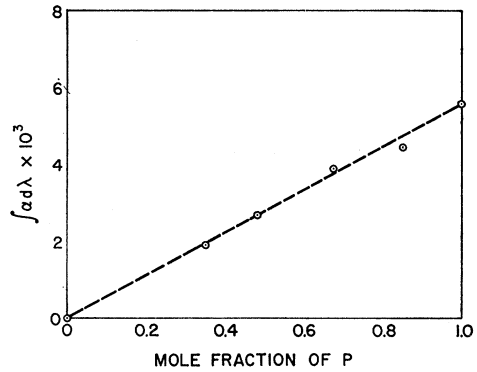

FIG. 7. Integrated intensity $\int \alpha d\lambda$ (over the region of 660 to 800 cm^{-1}) versus composition of $GaAs_xP_{1-x}$.

It is important, in this context, to note that the labels used to designate specific points in the Brillouin zone lose their meaning for the disordered alloy which lacks periodicity. Nevertheless, they remain a convenient means for characterizing the spectra and are retained in this paper.

The apparent superposition of GaAs and GaP bands in the alloy is most clearly indicated by the two-phonon bands of GaP near 700 cm^{-1}. These are the two-phonon summation bands of various optical phonons as indicated in Fig. 5. This group of bands continues to exist throughout the entire composition range shifting toward smaller wave number as the phosphorus content decreases. The structure of the bands is maintained in the sample of 85% P; however, when the phosphorus content in the alloy is below 67.5%, the structure loses detail and assumes the form of a broad band. It is noticed that a band at 706.5 cm^{-1} is distinctly detectable in the sample of only 5.4% P. The integrated absorption $\int \alpha d\lambda$ of these optical modes as a function of the mole fraction of P in the alloy is a straight line through the origin, as given in Fig. 7. This means that the photon-phonon interaction in this spectral region is contributed solely by the GaP-like phonons.

The assignment scheme of Kleinman and Spitzer no longer holds in the 85% P sample because the energy shifts of these bands in the alloy from the pure GaP values are such that the middle peak, TO+LO (731 cm^{-1}), no longer bisects the outer two peaks, LO and TO (738 and 716 cm^{-1}), on the wave-number scale. On the other hand, Johnson's assignment still holds in the alloy, since the bands are designated as 2TO(L) (738 cm^{-1}), 2TO(Γ) (731 cm^{-1}), and 2TO(X) (716 cm^{-1}).

The sums of the two reststrahlen frequencies are also given in Table I. These appear near 610 cm^{-1} for $x>0.50$. It is believed that radiation may interact with the crystal in such a manner that a photon at this frequency is absorbed and the two reststrahlen modes are excited simultaneously. Momentum conservation of such an interaction is automatically satisfied since it is satisfied in each separate mode. There is no obvious

TABLE II. Phonon energies of $GaAs_xP_{1-x}$ obtained from the absorption spectra.

Phonon[a]		Phonon energies (cm^{-1}) Composition (%P) 100 (GaP)	85	67.5	48	35	17.7	5.4	0 (GaAs)
	TO	377.5	369	363[b]	358[b]	356[b]	355	353.3[b]	
	LO	329.5	321.5						
L	LA	280	278.5	274	269.5	266.5	265		
	TA	68.5	71	77	82	84	84	84	
	TO	360.5	358						
	LO	309	300						
X	LA	265	273						
	TA	117.5	120						
	TO		267	265	263.5	263.5	265	264	262.5
L	LO							238	237.5
	LA							206	206.5
	TO						257.5	255.5	256
X	LO							240	240
	LA							222	220

[a] For convenience, assignments appropriate to a perfectly periodic lattice are used for the solid solutions. See text.
[b] At these concentrations, the peak labelled TO(L) may have strong Γ character.

reason why the matrix element for such a transition should be zero. The strength of this matrix element should be in the order of that of a two-phonon absorption process and should decrease as the mole fraction of phosphorous decreases if the density of states of the localized modes is proportional to the number of the minority atoms present. It is thus expected that such a transition may be present as an absorption band in the two-phonon absorption spectra, and that its presence should be interpreted as a result of the random distribution of As and P atoms in one of the two face-centered-cubic (fcc) sublattices (the other one is occupied by Ga atoms) of the alloy crystal (zinc-blende structure). Such an absorption band was indeed observed in the spectra shown in Figs. 4(d) to 4(g).

A band at 604 cm^{-1} was observed by Kleinman and Spitzer in GaP which was grown by the reaction of Ga with P at an elevated temperature under a pressure of 20 atm. This band was not included in their phonon assignment scheme and was attributed to the molecular vibrations of an unidentified impurity. The same band was observed by us in an epitaxially grown sample. In addition, a similar band was found at 600 cm^{-1} in the sample of 85% P. It is possible that the band at 604 cm^{-1} is intrinsic to GaP and is indeed one of the two-phonon summation bands. Johnson's assignment has included this band as the [LO+LA(L)] mode. Such an assignment is therefore appropriate and is used to calculate several phonon energies from the spectra. These phonon energies are given in Table II.

The sample of 5.4% P was subjected to an annealing at 1170°C for 72 h. The purpose of this experiment was to investigate the effect of the diffusion of As and P atoms within the lattice at an elevated temperature on the two-phonon absorption spectra. The experiment was carried out in a sealed evacuated ampoule with added As and P to prevent the dissociation of the sample. No change in the spectra was observed. In particular, the shape and the position of the absorption peak at 706.5 cm^{-1} were unaffected by the annealing treatment. It is thus believed that the crystals grown at 800°C by the epitaxial method do not contain gross inhomogeneities in the distribution of As and P atoms in the lattice.

V. CONCLUSION

The most important contribution of this paper is a complete study of the one- and two-phonon infrared spectra of GaAs-GaP alloys over a wide composition range. A particularly striking feature of these spectra is that vibrational modes characteristic of both pure GaAs and pure GaP appear to persist in their alloys.

A simple model is presented to explain the appearance and frequencies of these two modes in the one-phonon spectrum. The model assumes that there are Γ-like optical modes in which all atoms of the same species have the same displacement. In addition, it is found necessary to include a significant interaction between next-nearest neighbors. It was not necessary, however, to bring in the assumption of gross inhomogeneities in the distribution of these atoms in the lattice. Such an assumption is not correct for the binary alloy system studied here as has been proven by measurements of x-ray diffraction, band-edge absorption, and microwave oscillations in the alloy crystals.

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