responsible for the reduction in radiative efficiencies observed at much lower GaP compositions than expected. The behavior of the threshold current near the point where the different band edges are equal in energy lends support to our choice of the values for b, $b\rho$, and A given in Fig. 5. The evidence further suggests that the lower limit for the generation of coherent oscillations at 77°K in Ga(As_{1-x} P_x) will probably be close to 6400 Å.

ACKNOWLEDGMENTS

We would like to acknowledge fruitful discussions with F. S. Ham and R. N. Hall. We also appreciate the technical assistance of G. J. Charney, H. W. Demkowski, and R. S. Ehle. The diodes were kindly supplied by N. Holonyak, R. Grubel, and T. J. Soltys, in part from material prepared by F. K. Heumann. We also benefited from results of diode studies conducted by R. O. Carlson.

PHYSICAL REVIEW

VOLUME 137, NUMBER 3A

1 FEBRUARY 1965

Infrared Spectral Emittance of InAs

D. L. STIERWALT AND R. F. POTTER Infrared Division, Research Department, U. S. Naval Ordnance Laboratory, Corona, California (Received 17 August 1964)

The infrared absorption spectra for a p-type InAs sample were determined by measuring the spectral emittance at 77, 203, and 373°K. The spectra contained features which are identified with optical edge transitions, free-carrier absorption, intervalence-band transitions, multiphonon absorption and the reststrahlen band. The two-phonon spectra are analyzed in detail. Using selection rules, assignments at the critical points Γ , L, and \overline{X} are given for the optical and acoustical modes. It is found that the "sum rule" for lattice modes is in good agreement with the assignments.

INTRODUCTION

ULTIPLE phonon combination absorption bands observed in the infrared spectra of diamond and zincblende lattices can provide detailed information concerning the lattice dispersion. Johnson¹ and Loudon and Johnson² have demonstrated and discussed this for several such crystals. Mitra³ has also discussed dispersion relations and their connection with infrared absorption. Johnson has also emphasized that optical data (infrared and Raman scattering) will probably be the main sources of such information for crystals of the indium compounds of the III-V zincblende type because they are not suitable for neutron scattering experiments. Previously, we have reported the infrared emittance results for InP.⁴ This is a report on the compound InAs.

EXPERIMENTAL

The infrared absorption spectra at temperatures of 77, 203, and 373°K were determined by measuring the spectral emittances of the InAs sample at those temperatures. The essential descriptions of the experimental technique have been given elsewhere.^{5,6}

The InAs sample was ground and mechanically polished to a parallel sided slab 0.4 mm thick. It is fitted into a tight spring-loaded sample holder so that the contact to the thermal bath is along the sample sides. The sample chamber, for the low-temperature runs, is evacuated by an ion pump to 10^{-6} Torr or better.

RESULTS

In Fig. 1 are shown the principal features of the spectra for 2.5 $\mu < \lambda < 44 \mu$. (Fine detail in the multiphonon bands is not shown.) The advantages of an emit tance spectrum are demonstrated here; for one sample, optical properties are measured from the opaque region of the optical edge, through the partially transparent



FIG. 1. Emittance spectra for the wavelength region 2.5 to 44 μ . Temperatures are shown. Fine detail in the region from 15 to 40 μ is not shown.

national Conference on Physics of Semiconductors, Exeter, July 1962 (Institute of Physics and Physical Society, London, 1962).

¹ F. A. Johnson, Progress in Semiconductors (to be published). ² R. Loudon and F. A. Johnson, Proceedings of the International

 ^a S. S. Mitra, Physics of Semiconductors (to be published).
^a S. S. Mitra, Phys. Rev. 132, 986 (1963).
^d D. L. Stierwalt and R. F. Potter, Proceedings of the International Conference on the Physics of Semiconductors (to be

⁶ D. L. Stierwalt, J. Bernstein, and D. Kirk, J. Appl. Opt. 2, 1169 (1963).

⁶ D. L. Stierwalt and R. F. Potter, Proceedings of the Inter-



FIG. 2. Detailed emittance spectrum 77 to 203° K. Spectral region 15 to 40 μ .

interband and free-carrier absorbing region, to the multiphonon region and finally the opaque region of the reststrahlen band.

The intrinsic optical edge is at 4.2 μ . Lack of energy prohibited a study of the temperature shift of the optical edge but indications are that the shift is positive and in agreement with previous results concerning the edge.⁷

The 373°K curve exhibits the intervalence band transition at 0.19 eV.^{7,8} These transitions between the light and heavy hole bands, are also seen at slightly shorter wavelengths in the 203°K curve. An interesting feature in this region is the closeness of the 203°K emittance to the 77°K emittance; in fact, in places it is lower. This p-type absorption has been discussed by Dixon⁷ and Matossi and Stern.⁸ The absorption is such that the excess hole concentration is estimated to be $\sim 10^{16}$ /cm³.

The region from 39 μ to 44 μ is opaque and the emittance is a measure of 1-R (R is the front surface reflectance). This has also been measured by Hass and Henvis⁹ using reflectance techniques and the present results are in good agreement with theirs.

The emittance from 16 to $39 \,\mu$ exhibits strong absorption features. The detailed emittance spectra for the temperature 203 and 77°K are shown in Fig. 2. The 203°K curve is slightly lower initially because of the hole absorption; however, it is higher at the longer wavelengths as would be expected for lattice absorption.

The expression for αd (absorption coefficient and thickness d) can be written

$$lpha(\lambda)d = \ln\left\{1 + \left(\frac{\epsilon(\lambda)}{1 - \epsilon(\lambda)/\epsilon_{\infty}(\lambda)}\right)\right\},$$
 (1)

where $\epsilon_{\infty}(\lambda)$ is the emittance for an opaque sample, i.e., $1-r^2$ where $r^2 = ((n-1)/(n+1))^2$, and $\alpha = 4\pi k/\lambda$;

TABLE I. Two-phonon combinations for InAs. $\stackrel{(1/\lambda)}{(cm^{-1})}$ $(1/\lambda)$ (cm^{-1}) Feature^a Assignment λ(μ) 20.2 $2LO(\Gamma)$ pk 492 492 21.3 ŝh 467 $LO(\hat{\Gamma}) + TO(\Gamma)$ 467 22.6 442 $2T\dot{O}(\Gamma)$ 442 pk 23.2 pk 431 2TO(L)432 23.6 ŝh 424 2TO(X)424 24.5 $^{\rm sh}$ 408 TO(L) + LO(L)410 25.7389 2LO(L)388 \mathbf{pk} 26.6 TO(X) + LO(X)sh376 376 27.5 28.0 364 357 TO(L) + LA(L)pk 364 TO(X) + LA(X)sh-pk 357 339 29.5LO(L) + LA(L)pk 342 31.0 sh-pk TO(X) + TA(X)LO(X) + LA(X)322 323 314 31.8 309 pk 33.9 $\widetilde{\frac{2LA(L)}{TO(L)}} + TA(L)$ $\mathbf{sh} ext{-pk}$ 295 296 35.0 286 289 pk 36.2 276 LO(X) + TA(X)275 37.2 269 267 LO(L) + TA(L)39.3 254 LA(X) + TA(X)256 222 $2T\dot{A}(\dot{X})$ TA(L) + LA(L)221 A(L)146

* pk = peak; sh = shoulder; pk-sh = indeterminate.

the use of (1) assumes $k/n \ll 1$ where n is the real part of the refractive index and k the imaginary part (see Ref. 6).

It is evident from (1) that the absorption coefficient as determined from emittance measurements is not sensitive to the refractive index until $\epsilon(\lambda) \rightarrow \epsilon_{\infty}(\lambda)$. ϵ_{∞} was taken as being 0.67 and constant in order to calculate the α values, shown in Fig. 3.



FIG. 3. Absorption coefficient based on the spectra of Fig. 2. A refractive index 3.7 was assumed for reducing the data

⁷ J. R. Dixon, Proceedings of the International Conference at Prague (Academic Press Inc., New York, 1960). ⁸ F. Matossi and F. Stern, Phys. Rev. 111, 472 (1958). ⁹ M. Hass and B. Henvis, Phys. Chem. Solids 23, 1099 (1962).



FIG. 4. Schematic outline of the lattice dispersion of InAs. Small-q acoustic curves are based on room temperature elastic constants.

When the curves of Fig. 3 are compared with those of Fig. 2 the similarity is most striking. One can use the emittance spectra directly for selecting structural features of interest without having to reduce the data. Thus when the data are taken as a continuous run more reliance can be given to the direct observations.

The features of Figs. 2 and 3 which are attributed to two phonon absorption processes are given in Table I. The second column describes them as a peak (pk), as a shoulder (sh), or indeterminate (pk-sh). The features short of 20.0 μ appear to be due to three or more phonon processes. The final three features given in Table I are taken from Fig. 2.

DISCUSSION

The critical points corresponding to the density of states maxima at the L, X, and Γ points of the Brillouin zone are used along with the two-phonon selection rules of Birman¹⁰ to assign the spectral features observed. Johnson¹ and Loudon and Johnson² have discussed the critical point analysis in detail. While they use a dynamical lattice model in order to refine the selection, our approach is empirical, and will lack some sensitivity.

TABLE II. Phonon frequencies for InAs (in cm⁻¹).

	Г	L	X
LO	246	194	164
ТО	221	216	212
LA		148	145
TA		73	111
Sum rule (cm ⁻²) \times 10 ⁻⁴	15.90	16.40	16.24

Nevertheless the assignments can be made with reasonable confidence, especially for the optical modes.

The twenty-one allowed double-phonon dipole optical transitions for Γ , L, and X are listed in Table I. We make the first and third assignments consistent with the given reststrahlen frequencies.⁹ Also the first eight features are assigned to combinations of optical modes alone.

The resulting frequencies at the critical points are given in Table II. They are also schematically represented in Fig. 4. It is seen that the dispersion curve for InAs is similar to other III-V compounds as given by Johnson. The small q values for the acoustical modes are based on the values of the elastic constants given by Gerlich.¹¹

Another test of the assignments can be made by applying the "sum rule." Rosenstock¹² has shown that an interaction of either an electrostatic nature or between unlike atoms has a q-independent trace. He ascribes "trace variable" forces principally to interaction between second neighbors. Most III-V semiconductors appear to follow the "trace constant" law to a large degree, i.e., the sum rule is given as

$$\sum_{i}^{n} \omega_{i}^{2}(\mathbf{q}) = \text{constant.}$$
 (2)

The consistent applicability of the sum rule to the zincblende-type crystal has been pointed out by Mitra and coworkers.³ The bottom row of Table II gives the sum rule for the present assignments. The fact that the rule is followed so closely lends support to the assignments. This also indicates that the second neighbor forces are not very strong.

ACKNOWLEDGMENTS

We would like to thank F. A. Johnson for furnishing us with preprints as well as enlightening discussions. Significant contributions were made by J. Bernstein and D. Kirk to the experimental portions of this work.

¹⁰ J. L. Birman, Phys. Rev. 131, 1489 (1963).

¹¹ D. Gerlich, Bull. Am. Phys. Soc. 8, 472 (1963).

¹² H. B. Rosenstock, Phys. Rev. 129, 1959 (1963).