0.02% crystals at 30 GHz and 1.3°K is 7 cm, and this decreases roughly as the inverse third power of the frequency.

In conclusion, we want to emphasize that besides performing a successful experiment on a long outstanding problem, this work also demonstrates most of the features of our tunable phonon detector concept.[12] Although in this problem the phonon generator is strongly dependent on the magnetic field, there are many problems where the spins can readily be tuned without affecting the phonon distribution, and so the spins can be used to measure that distribution. As examples of this we have recently measured[13] the harmonic output of piezoelectric transducers at 10 GHz and have made preliminary measurements on the spectral distribution of phonons in crystals with thermal gradients across them.[14]

---

[1] J. H. Van Vleck, Phys. Rev. 59, 724 (1941).

[2] P. L. Scott and C. D. Jeffries, Phys. Rev. 127, 32 (1962).

[3] J. A. Giordmaine and F. R. Nash, Phys. Rev. 138, A1510 (1965).

[4] W. J. Brya and P. Wagner, Phys. Rev. Letters 14, 431 (1965).

[5] N. S. Shiren, Phys. Rev. Letters 17, 958 (1966).

[6] K. Dransfeld, Bull. Am. Phys. Soc. 3, 324 (1958).

[7] N. S. Shiren and E. B. Tucker, Phys. Rev. Letters 2, 206 (1959).

[8] B. W. Faughnan and M. W. P. Strandberg, J. Phys. Chem. Solids 19, 155 (1961).

[9] C. H. Anderson, H. A. Weakliem, and E. S. Sabisky, Phys. Rev. 143, 223 (1966).

[10] E. S. Sabisky and C. H. Anderson, to be published.

[11] The density of states was calculated using D. Gerlich's velocity of sound measurements in SrF_2, Phys. Rev. 135, A1334 (1964).

[12] C. H. Anderson and E. S. Sabisky, Phys. Rev. Letters 18, 540 (1967).

[13] E. S. Sabisky and C. H. Anderson, in Proceedings of the Fifth International Conference on Quantum Electronics, Miami, Florida, May, 1968 (to be published); also to be published.

[14] C. H. Anderson and E. S. Sabisky, Bull. Am. Phys. Soc. 13, 511 (1968).

INFRARED REFLECTION SPECTRA OF $Ga_{1-x}In_xAs$: A NEW TYPE OF MIXED-CRYSTAL BEHAVIOR

M. H. Brodsky*
Night Vision Laboratory, Ft. Belvior, Virginia

and

G. Lucovsky†
Case Western Reserve University, Cleveland, Ohio

(Received 16 May 1968)

The infrared reflection spectra of $Ga_{1-x}In_xAs$ crystals reveal a new type of mixed-crystal behavior in which two bands are seen, one near the InAs *Reststrahlen* region and one which shifts monotonically with x between the InAs and GaAs *Reststrahlen* regions. A discussion is given in terms of postulated criteria using local and gap modes.

In this paper we report and offer an interpretation of measurements of the infrared reflectivity spectra of $Ga_{1-x}In_xAs$ single crystals. The spectra, which represent a new type of mixed-crystal behavior, are characterized by the occurrence of two *Reststrahlen* bands, a strong band which is shifted down in frequency monotonically out of the GaAs *Reststrahlen* region to the edge of the InAs *Reststrahlen* region with increasing molar fraction of InAs (i.e., increasing x) and a lower frequency weak band which occurs in the InAs *Reststrahlen* region. Workers had previously distinguished two types of behavior in similar mixed polar crystals.[1] Alloy crystals such as $Na_{1-x}K_xCl$[2] and $Cd_{1-x}Zn_xS$[3] have been reported to exhibit a single *Reststrahlen* band for all values of x. The frequencies characterizing this band are observed to be intermediate to those of the end members and shift *monotonically* with composition. Mixed-crystal systems exhibiting this type of behavior have been called "one-mode" systems. In contrast to this, "two-mode" behavior occurs in crystals such as $GaAs_{1-x}P_x$[4] and $CdS_{1-x}Se_x$[5]; here two reflection bands are observed for all compositions. For each band the frequencies of the optic modes lie approximately *within* the *Reststrahlen* region of the end-member constituent compounds ($x = 0$ or 1); however, the strength of each band varies with the composition. The behavior we report here represents a third and new type of mixed-crystal *Reststrahlen* band response which is intermediate to that observed in the "one-" or "two-"mode systems discussed earlier. In an earlier publication, the authors (in collaboration with Burstein) have postulated a model[1] which sets forth criteria for the existence of "classic" "one-" or "two-"mode behavior. In this paper we extend that model to include the type of behavior reported here.

The samples used in this investigation are listed in Table I. The six mixed crystals of $Ga_{1-x}In_xAs$ are single-crystal epitaxis films grown by Texas Instruments, Inc., and were prepared by evaporation of $Ga_{1-x}In_xAs$ from a single heated source.[6] The films, whose thickness varied from 12 to 102 μm, were grown on (100) faces of semi-insulating Cr-doped GaAs. The compositions were determined by x-ray diffraction and Vegard's law. The crystals were p type with sufficiently low carrier concentrations so that the plasma frequencies were much smaller than the lowest lattice frequency of interest.

The two unmixed GaAs and InAs crystals were supplied by the Monsanto Company and had carrier concentrations of 2×10^{15} cm^{-3} and 8×10^{15} cm^{-3}, respectively. Polished and etched (100) faces were used for the measurements.

All of the reflection spectra were taken at room temperature using a Perkin-Elmer Model 301 spectrophotometer with a 20-line/mm grating in first order. The spectrophotometer was operated in a single beam mode and the reflectances of the samples were compared with that of an aluminum-coated mirror with an assumed reflectance of 0.98. Some of the samples (x = 0.30, 0.40, 0.50) were quite small (about 4 mm across) and therefore intercepted only part of the infrared beam. Normalizations of these spectra were made based on measured reflectances in the short-wavelength region where adequate sensitivity was available with a smaller beam. One should note that the Kramers-Kronig analysis is unaffected by multiplying the entire reflectance spectrum by a common normalization factor.[7]

Figure 1 contains the reflectivity spectra of the $Ga_{1-x}In_xAs$ crystals studied. Included also are reflectivity spectra for both GaAs and InAs. For the mixed-crystal samples two reflectivity bands are evident. For the $x = 0.39$ and 0.72 samples additional structure is observed in the frequency domain from 265 to 320 cm^{-1}. Note that the $Ga_{1-x}In_xAs$ layer of the $x = 0.72$ sample is considerably thinner than all but one of the other epitaxic samples studied (see Table I). The structure in the 265- to 320-cm^{-1} domain is due to interference effects and is enhanced by the dispersion of the GaAs substrate in its *Restsrahlen* region. A comparison of the reflectivity spectra of two samples of approximately the same composition ($x = 0.39$ and $x = 0.40$) but of different thicknesses was made. The comparison showed interference fringes which were present in the thinner sample in the 280-cm^{-1} region but were not observed in the thicker sample.

The reflectivity spectra were analyzed using a Kramers-Kronig dispersion analysis. Prior to the analysis the interference fringes of the $x = 0.72$ were "smoothed" out. The phonon frequencies derived from the ϵ_1 and ϵ_2 curves resulting from the Kramers-Kronig analysis are shown in

Table I. Summary of results for all samples measured. The Kramers-Kronig results for the thinnest film ($x = 0.39$) are not listed because the analysis is subject to large errors due to the thinness of the film. For this case, a simple form of the Fresnel normal reflectance is no longer valid.

x = mole fraction of InAs	Film thickness (μm)	ω_{TO_2} (cm^{-1})	ω_{LO_2} (cm^{-1})	ω_{TO_1} (cm^{-1})	ω_{LO_1} (cm^{-1})
0	bulk	⋯	⋯	268	291
0.22	69	230	⋯	265	287
0.30	102	230	232	264	282
0.39	12	⋯	⋯	⋯	⋯
0.40	74	227	234	257	276
0.50	64	228	233	256	273
0.72	37	222	234	250	264
1.00	bulk	215	238	⋯	⋯

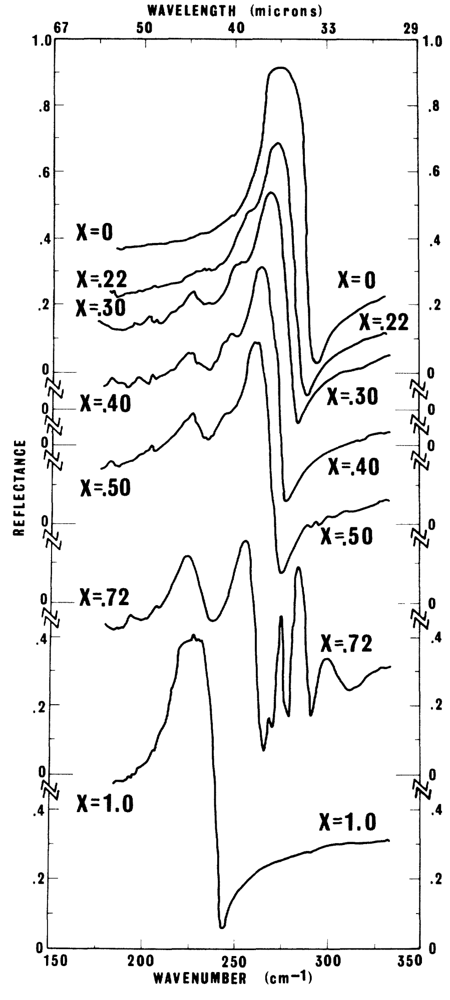

FIG. 1. The reflectances of seven samples of $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}$. The curves and their respective ordinate scales are displaced for clarity.

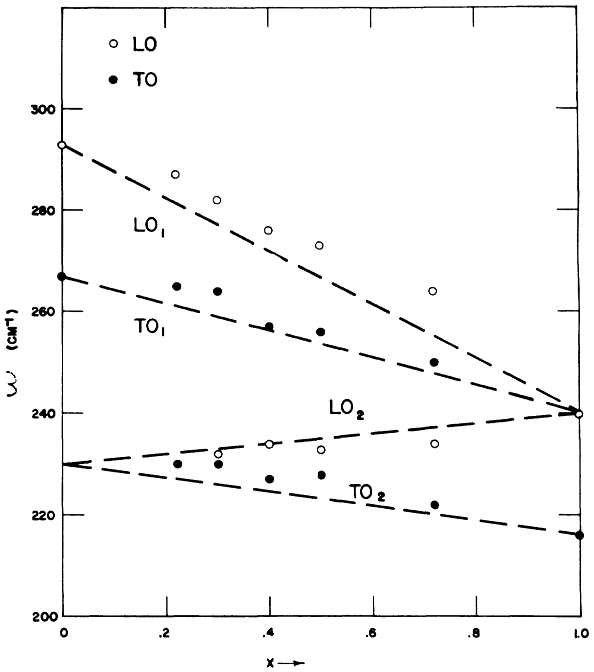

FIG. 2. The LO and TO frequencies for $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}$ deducted by a Kramers-Kronig analysis of the reflectivities. The points are derived from the data. The lines are straight lines connecting the frequencies of $x=0$ and x 1 crystals.

Table I and Fig. 2. Transverse optic (TO) mode frequencies are obtained from the maxima in ϵ_2, whereas the longitudinal optic (LO) mode frequencies are obtained from relative maxima in $\mathrm{Im}(1/\epsilon)$. One set of frequencies (TO_1 and LO_1) *shift* smoothly with composition, *decreasing*, respectively, from the GaAs TO and LO frequencies and shifting out of the GaAs *Reststrahlen* band towards the InAs LO frequency with increasing InAs content (increasing x). The second set of frequencies (TO_2 and LO_2) lies *within* the region of the InAs TO and LO for *all compositions*. This behavior of the optical-phonon modes of $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}$ is quite different from that observed in other mixed crystals, having features similar to both "one-" and "two-"mode systems. Specifically, in "two-"mode systems, e.g., $\mathrm{CdS}_{1-x}\mathrm{Se}_x$ in each branch, the LO frequency *increases* and the TO frequency *decreases* as one moves away from the respective low-concentration gap and localized modes. In contrast to this, in a typical "one-"mode system both frequencies shift in the *same sense* as the composition range is traversed. The data presented here clearly indicate a different and new type of response. Explicitly the low-frequency band behavior (TO_2 and LO_2) is "two-" modelike, whereas the high-frequency band behavior (TO_1 and LO_1) is "one-"modelike.

Two-mode behavior.—In an earlier work[1] phenomenological criteria were set forth for the occurrence of two-mode behavior. Consider a mixed-crystal system $A_{1-x}B_xC$, where the atomic mass of A is less than that of B. The criteria for two-mode behavior are those that permit a localized mode above the optical branch of BC *and* a gap mode between the acoustical and optical branches of AC to exist for small alloying concentrations.

One requirement of these criteria is that the phonon dispersion of AC is such that a gap does exist between its acoustical and optical branches, or less severely, that the density of phonon states is very low between the acoustical and optical branches. In general the existence or nonexistence of such a gap is known only from extensive knowledge of the dispersion curves such as are obtainable from inelastic-neutron-scattering measurements or from theoretical calculations. GaAs does not have such a gap[8] and it therefore follows that any alloy of GaAs with a crystal having a larger atomic mass (e.g., InAs) cannot exhibit the conventional two-mode behavior. On the other hand, the growth of the second mode from a localized or gap mode is nicely illustrated in recent Raman and infrared measurements of the two-mode systems $\mathrm{ZnS}_{1-x}\mathrm{Se}_x$[9] and $\mathrm{CdS}_{1-x}\mathrm{Se}_x$.[10] A second feature of the two-mode criteria is that the *Reststrahlen* bands must be separated in frequency space. In the limit of small concentrations, the LO and TO frequencies (which define the limits of the *Reststrahlen* band) are degenerate[9,10] at the local- or gap-mode frequency. If this frequency is not distinct from the *Reststrahlen* band of the host crystal, then the second mode does not form.

One-mode behavior.—From the above discussion we can set the criterion for one-mode behavior, namely that *neither* a gap *nor* a localized mode exists in small concentrations; therefore the formation of a second mode is precluded. A special case of this is the occurrence of overlapping *Reststrahlen* bands.

Intermediate case.—In crystals such as $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}$, the criteria are not satisfied for either behavior and therefore a third type of behavior is observed. Two-mode behavior is not permitted as InAs is admixed to GaAs because of the lack of a frequency gap in the phonon distribution spectrum of GaAs. However, strict one-mode behavior is excluded because of the separation of the *Reststrahlen* bands and therefore the possibility of a local mode developing as Ga is added to InAs.

Presumably strong interactions due to overlapping of modes in frequency space between this localized mode and the InAs lattice branch shift it down in frequency toward the InAs *Reststrahlen* region. Therefore we observe two-mode behavior at the InAs-rich end of the alloy system, one-mode behavior near the GaAs-rich end, and a smooth transition between the two at intermediate frequencies. The conditions necessary for this type of intermediate- or "mixed-"mode behavior are (1) the absence of an energy gap in the phonon spectrum of the lighter compound and (2) the occurrence of nonoverlapping *Reststrahlen* bands. On the basis of the criteria set forth above we would expect similar behavior to that which we report for $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}$ to occur in the alloy system $\mathrm{GaAs}_{1-x}\mathrm{Sb}_x$. Initial measurements on thin films reported a single *Reststrahlen* band that shifted smoothly from the GaSb *Reststrahlen* to the GaAs *Reststrahlen* with increasing GaAs content[11]; however, recent measurements indicate the possible presence of a weak, second low-frequency band.[12]

The authors thank Dr. L. G. Bailey of Texas Instruments, Inc., for the loan of his samples, Dr. J. R. Dixon of the Naval Ordnance Laboratory (White Oak) for the use of his spectrometer, and M. L. Slade of Xerox Corporation for aiding in the computer analysis.

---

[*] Present address: IBM Thomas J. Watson Research Center, Yorktown Heights, N. Y.

[†] Present address: Xerox Research Laboratories, Webster, N. Y.

[1] G. Lucovsky, M. H. Brodsky, and E. Burstein in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum Press, Inc., New York, 1968), p. 592.

[2] F. Krueger, O. Reinkobar, and A. E. Koch-Holm, Ann. Physik *85*, 110 (1928).

[3] G. Lucovsky, E. Lind, and E. A. Davis, in *Proceedings of the International Conference on II-VI Semiconducting Compounds, Providence, Rhode Island, 1967* (W. A. Benjamin, Inc., New York, 1968).

[4] H. W. Verleur and A. S. Barker, Jr., Phys. Rev. *149*, 715 (1966).

[5] H. W. Verleur and A. S. Barker, Jr., Phys. Rev. *155*, 750 (1967).

[6] R. W. Conrad, P. L. Hoyt, and D. D. Martin, J. Electrochem. Soc. *114*, 164 (1967).

[7] M. H. Brodsky and E. Burstein, J. Phys. Chem. Solids *28*, 1655 (1967).

[8] G. Dolling and J. L. T. Waugh, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, New York, 1965), p. 19.

[9] O. Brafman, I. F. Chang, G. Lengyel, S. S. Mitra, and E. Carnell, Jr., Phys. Rev. Letters *19*, 1120 (1967).

[10] J. F. Parrish, C. H. Perry, O. Brafman, I. F. Chang, and S. S. Mitra, in *Proceedings of the International Conference on II-VI Semiconducting Compounds, Providence, Rhode Island, 1967* (W. A. Benjamin, Inc., New York, 1968).

[11] R. F. Potter and D. L. Stierwalt, in *Proceedings of the International Conference on Physics of Semiconductors, Paris, 1964* (Dunod, Paris, 1964), p. 1111.

[12] R. F. Potter and D. L. Stierwalt, private communication.