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Raman Scattering from Localized Vibrational Modes in GaP

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¹⁰The possibility that the observed characteristics are due to a weak link, possibly at a contact, instead of the whisker crystal itself was eliminated by two results: The critical currents in a substantial region of temperature below the fluctuation-limited regime agree with Ginzburg-Landau prediction for thin wires. No Anderson-Dayem steps, i.e., constant-voltage steps in the presence of microwave radiation, could be produced in the resistive transitions of similar properly mounted whisker crystals although such steps were readily seen in some poor contacts just as in thin-film bridges, by W. H. Henkels, in extensive experiments in our laboratories.

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Raman Scattering from Localized Vibrational Modes in GaP[†]

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High-frequency localized vibrational modes of impurities in a III-V compound have been observed by Raman scattering. Three lines from the GaP samples closely correspond to some local modes previously reported in infrared studies, and depolarization measurements tend to confirm their proposed assignments. We describe several attractive features of this method for the study of semiconductor impurities.

It is well known¹ that a small concentration of impurities introduced into a perfect crystal will have little effect on the vibrational dispersion branches. But in some cases there may appear vibrational modes^{1,2} lying outside of the allowed frequency range of the perfect crystal. These are called localized vibrational modes, or local modes, because the mode energy is spatially concentrated near the defect site.

Following the observation of the local mode of nitrogen³ in GaP in luminescence, infrared absorption was observed for a number of impurities in several different III-V semiconductors.⁴⁻¹¹ To the best of our knowledge, this is the first report of Raman scattering from high-frequency local modes in a III-V compound. Other related

system types from which Raman scattering has been reported include mixed crystals,¹²⁻¹⁴ the *U* center in alkaline-earth halides,¹⁵ and the *F* center in alkali halides¹⁶; only the second belongs to a well-defined high-frequency localized vibrational excitation. The systems we discuss here are found to give generous signal levels with impurity concentration as low as 10^{17} cm⁻³.

The four GaP ingots used in this study were chosen from a set used in some previously reported infrared work.¹⁰ We shall continue the labeling scheme established in Ref. 10 (ingots Nos. 1, 2, 3, 4, 5, 6), and extend it with further numerals for additional samples (see Table I). They are compensated polycrystals prepared by the vertical Bridgman technique; for the de-

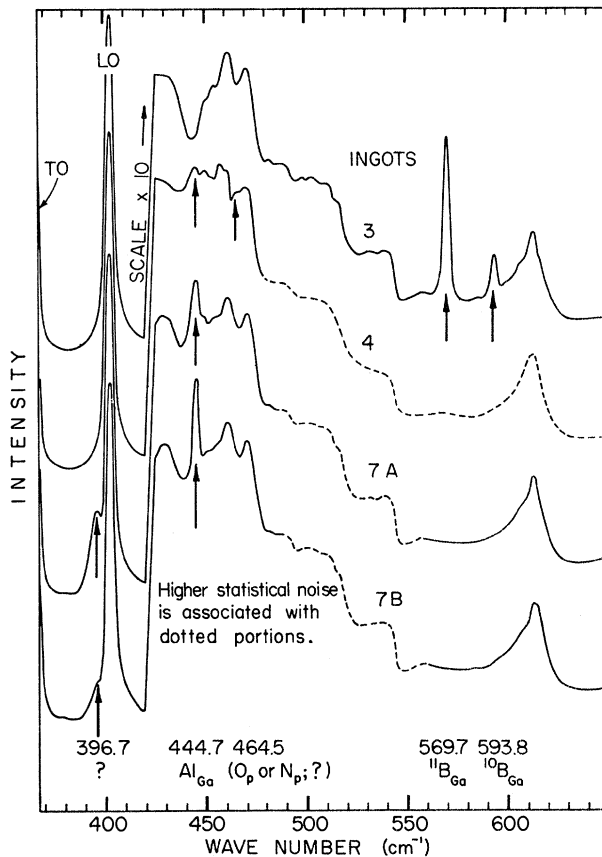


FIG. 1. Raman spectra from ingots 3, 4, 7A, and 7B, showing lines attributed to local modes in GaP, without a polarizer. All lines have essentially the same depolarization (~ 0.75). The general background and unlabeled structure common to all traces is due to second-order Raman scattering typical of pure GaP.

tails of preparation, see Ref. 10 and Blum, Chicotka, and Bischoff.¹⁷

In this experiment, the linearly polarized beam from a krypton laser ($\lambda = 5681.9 \text{ \AA}$, power $\approx 10 \text{ mW}$) was focused onto a cooled sample ($T \approx 100^\circ\text{K}$). Spectra were taken at 90° , with provision for polarization analysis. A Spex model 1400 tandem spectrometer and a liquid-nitrogen-cooled model ITT FW 130 photomultiplier were used.

While the signal-to-noise ratio was generally very favorable, the interpretation of the data has been handicapped by the background from second-order Raman scattering as well as fluorescence associated with certain impurities. Steps are being taken to alleviate these difficulties.

Figure 1 shows the Raman spectra from the various samples. We have omitted ingot No. 1, which did not give any significant information because of strong fluorescence. Three lines agree with local modes observed previously by

infrared absorption. Table I compares the results from the two methods. The lines at 593.8 and 569.7 cm^{-1} are believed to be due to $^{10}\text{B}_{\text{Ga}}$ and $^{11}\text{B}_{\text{Ga}}$, respectively, where X_Y designates isotope X located on a Y site; and the one at 444.7 to Al_{Ga} . Our depolarization measurements tend to corroborate these substitutional assignments. A line at 464.5 is too weak to be certain, although the same sample did yield such a line in the infrared spectrum, where it was tentatively assigned to O_p or N_p . No gap modes have been observed in our spectra thus far. We studied two samples from ingot No. 7, which was heavily doped with Al: One was taken from a slice 6 cm from the melt, the other 1.5 cm . For each there is a strong line at 396.7 cm^{-1} on the low-frequency shoulder of the LO phonon. The identity of this line has yet to be determined, but its intensity and location between the LO and TO lines raise some interesting speculations.

Previous to this work, the assignment of the pair of lines 593.8 and 569.7 cm^{-1} to $^{10}\text{B}_{\text{Ga}}$ and $^{11}\text{B}_{\text{Ga}}$ had been somewhat inconclusive, not only because these values are substantially different from those obtained by the simple formula of Dawber and Elliott,¹⁸ but also because of the possibility of a defect pair of the type $X_{\text{Ga}}-Y_{\text{interstitial}}$. But such a defect pair would have symmetry C_{3v} (instead of T_d as for the proposed case of $^{10}\text{B}_{\text{Ga}}$ and $^{11}\text{B}_{\text{Ga}}$), and it would give rise to local modes belonging to A_1 (two modes) and E (two modes each doubly degenerate), as shown in Table II. For each of our lines the depolarization is found to be ~ 0.75 : This rules out the A_1 modes (which would give a value ≤ 0.016). The two lines could also be due to the two modes belonging to E (which would indeed give the observed depolarization); but this would require that the two A_1 modes, which are both Raman- and infrared-active by group-theory considerations, be so weak as to be absent in both spectra. Furthermore, the intensity ratio ~ 1.4 is approximately equal to that of the natural isotopic abundances of boron. The same intensity ratio was also obtained between the corresponding lines in the infrared absorption spectra reported in Refs. 10 and 11. The assignment of the lines 593.8 and 569.7 cm^{-1} to $^{10}\text{B}_{\text{Ga}}$ and $^{11}\text{B}_{\text{Ga}}$ have thus become essentially conclusive. (There is still, in principle the possibility of a boron atom in an interstitial site with symmetry T_d . But such a defect is extremely unlikely for an isoelectronic atom, by experience and by theoretical considerations. In particular, the frequencies should be much

Table I. Local mode frequencies (cm⁻¹) and relative intensities (in parentheses).

Ingot No. (See Ref. 10)								
1	Infrared		453(13)	464(20)				606(4)
	Raman	< no data due to very strong fluorescence background >						
3	Infrared					569(35)	592(8)	606(8)
	Raman					569.7(15)	593.8(4)	
4	Infrared		443		464(27)	527(22)		
	Raman		444.7(3)		464.5(1?)			< strong fluorescence >
7A ^a (6 cm from melt)	Infrared		443					
	Raman		396.7(100)	444.7(6)				
7B ^a (1.5 cm from melt)	Infrared		443					
	Raman		396.7(40)	444.7(10)				
Assignment		?	Al _{Ga}	Si _{Ga}	N _P or O _P	C _P ?	¹¹ B _{Ga}	¹⁰ B _{Ga}


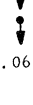






^aIngot 7, from which samples 7A and 7B were cut, was discussed in the addendum of Ref. 10 without a label assignment, 7A, ~6 cm from the melt; 7B, ~1.5 cm.

lower than those observed.)

Further effort is being made to investigate a larger variety of dopants and hosts of the III-V family, with various exciting laser frequencies, including longer wavelengths to minimize fluorescence. Attractive features of this technique include the following: (i) Spectra can conveniently

be taken in small volumes of material; (ii) one can work with uncompensated samples in which free carriers produce excessive absorption in the infrared; (iii) one can study frequency regions where the infrared method may be infeasible due to intrinsic absorption; and (iv) it provides much more definitive information on site

Table II. Localized vibrational modes for C_{3v} and T_d symmetries. All those are both infrared and Raman active.

Symmetry	C _{3v}			T _d		
	A ₁	E		F ₂		
Representation	z	y	-x	x	y	z
Infrared Active	z	y	-x	x	y	z
Raman Tensor	$\begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix}$	$\begin{bmatrix} c & 0 & 0 \\ 0 & -c & d \\ 0 & d & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -c & -d \\ -c & 0 & 0 \\ -d & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$
Modes	(a)  (b) 	(a)  (b) 				
Depolarization, ρ, (random orientation)	ρ < .06	ρ = .75		ρ = .75		

symmetry than does infrared absorption. Complementary to the EPR and infrared methods, laser Raman spectroscopy will prove to be a very useful tool in the study of impurities in semiconductors.

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