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LETTER TO THE EDITOR

Localized vibrational modes due to isotopes of nitrogen in gallium phosphide

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Abstract. Infrared absorption measurements on nitrogen doped gallium phosphide grown by the vapour phase epitaxial technique have revealed localized vibrational mode lines at 495.8 and 480.3 cm^{-1} due to $^{14}\text{N(P)}$ and $^{15}\text{N(P)}$ respectively. The frequencies of these lines are compared with theoretical values.

Infrared (IR) absorption lines due to the localized vibrational modes of various impurities in GaP have been reported by Spitzer *et al* (1969), Hayes *et al* (1969, 1970) and Thompson and Newman (1971). For boron, carbon and silicon in isolated tetrahedral sites, lines from more than one isotope have been detected and hence it has been possible to make unambiguous assignments. A line at 496.1 cm^{-1} was ascribed to ^{14}N (Thompson and Newman 1971) but the corresponding line for ^{15}N was not observed owing to the low natural abundance of this isotope (0.37 per cent). The frequency of the ^{14}N line is in good agreement with the value of 495 cm^{-1} determined by Thomas and Hopfield (1966) from the separation of sharp vibrational sidebands associated with zero phonon transitions of excitons bound to pairs of nitrogen atoms. By isotopic substitution of ^{15}N for ^{14}N these authors obtained a corresponding frequency of 481 cm^{-1} for the former isotope. In this letter we report IR measurements on GaP samples containing both ^{14}N and ^{15}N impurity atoms and, to the authors' knowledge, give the first direct observation of local mode lines from more than one isotope of an isoelectronic impurity on a group V site in any of the III-V compounds. A comparison is then made between the observed frequencies of these lines and theoretically predicted values.

Epitaxial gallium phosphide layers were grown by a process similar to that described by Tietjen and Amick (1966), using phosphine as the source of phosphorus and hydrogen chloride gas to transport the gallium. The material was deposited to a thickness of about $50\text{ }\mu\text{m}$ on the (111)A faces of compensated GaP substrates cut from crystals grown by the liquid encapsulation Czochralski method (Bass and Oliver 1968). Nitrogen doping up to a level of about $5 \times 10^{19}\text{ cm}^{-3}$ was achieved by the addition to the vapour stream of ammonia produced from ammonium sulphate which contained ^{14}N and ^{15}N in equal abundance.

The infrared absorption spectra from these samples were similar to those obtained previously (see figure 1 of Thompson and Newman 1971) except that there was an additional line at 480.3 cm^{-1} with a strength equal to that of the line at 495.8 cm^{-1} . The latter line was ascribed to the localized vibrations of ^{14}N on a phosphorus site and the

former line is therefore undoubtedly due to $^{15}\text{N}(\text{P})$. The widths of these IR lines were about 4 cm^{-1} in samples containing the maximum concentration of nitrogen, but no resolved satellites due to $[\text{N}-\text{N}]$ pairs were observed although their presence was established by exciton absorption measurements near the band edge. These observations are similar to those reported and discussed previously (Thompson and Newman 1971) and imply that the vibrational modes of isoelectronic impurities are highly localized and essentially involve displacements of only the impurity and its four nearest neighbour atoms. This *must* be the reason why there is such good agreement between the frequencies reported here for ^{14}N and ^{15}N and those given by Thomas and Hopfield (1966) for nitrogen pairs.

The observed local mode frequencies of 495.8 and 480.3 cm^{-1} may be compared with the calculated values of 525 and 509 cm^{-1} for $^{14}\text{N}(\text{P})$ and $^{15}\text{N}(\text{P})$ respectively (Gaur *et al* 1971). The discrepancies between these frequencies is undoubtedly due to the mass defect approximation used in the theory and indicates that there is a reduction in the local force constant of about 12 per cent which is a reasonable result (see Hayes 1968). Calculated values of 484 cm^{-1} [ω (^{14}N)] and 470 cm^{-1} [ω (^{15}N)] have also been obtained by Allen (1970) using the equation:

$$\omega_{\text{L}}^2 = A \left(\frac{1}{m_{\text{i}}} + \frac{1}{\alpha m_{\text{nn}}} \right) \quad (1)$$

where ω_{L} is the local mode frequency, m_{i} is the mass of the impurity atom, m_{nn} is the mass of a nearest neighbour atom, α is a parameter and A is a constant related to the frequency of the transverse optic mode of the pure lattice at the Γ point. Good agreement is again obtained with the observed frequencies. The use of this formula implies that only the impurity and its nearest neighbours have significant displacements in the local mode and hence the above agreement is not surprising in view of the high degree of localization inferred from the experimental observations. The choice of the value of α in equation 1 would appear to be somewhat arbitrary. Thomas and Hopfield (1966), who first used this equation to estimate the isotopic shift in the frequencies ω (^{14}N) and ω (^{15}N), assumed that α was equal to four. This would require that a displacement of the impurity atom results in antiparallel displacements of the four nearest neighbour atoms, but this is not necessarily so. Subsequently, Allen (1970) assumed that α had a value of the order of unity. Since local mode frequencies for the two isotopes of nitrogen have now been measured it is possible to *calculate* a value of α (see table 1). For comparison corresponding values of this parameter are also included for other impurities in gallium phosphide, gallium arsenide and silicon. It will be noticed that values of α have been included for

Table 1. Values of the parameter α for various impurities in gallium phosphide, gallium arsenide and silicon

Impurity	GaP	GaAs	Si
B	1.58 (Ga) ^a	1.75 (Ga) ^d	1.22 (Si) ^f
C	2.65 (P) ^b	2.17 (As) ^d	1.46 (Si) ^f
	5.98 (Ga) ^b	2.02 (Ga) ^d	
N	2.41 (P) ^c	—	—
Si	1.16 (Ga) ^a	1.33 (Ga) ^e	—

Atom in parentheses has been replaced by the impurity atom.

a Thompson and Newman (1971)

b Hayes *et al* (1970)

c present results

d Newman *et al* (1972)

e Thompson and Newman (1972)

f Newman (1969)

carbon on group III or V sites in both GaP and GaAs for the reasons now to be discussed.

In GaP, electrical measurements indicate that carbon impurities act as acceptor centres (Bortfeld *et al* 1972) implying that they occupy phosphorus sites. From the IR measurements it is not possible to determine the site as pointed out by Hayes *et al* (1970) and hence there is some doubt as to whether the observed local mode lines should be ascribed to C(P) or C(Ga). It is seen that the value of a (table 1) for the former centre is in good agreement with the values obtained for all the other impurities which lie in the range 1.16 to 2.65 irrespective of whether the impurity is isoelectronic or a donor or acceptor. On the other hand the value for C(Ga) is 5.98 and appears to be anomalously high. This result strongly suggests that the local mode lines are definitely due to C(P) and that no appreciable fraction of the carbon content of the sample is located on gallium sites, since only one line per isotope has been reported. Unfortunately, this procedure gives no further information about the site occupied by carbon in GaAs because the masses of the two constituent host lattice atoms are very similar. However, electrical measurements show that carbon impurities give rise to an acceptor level 0.019 eV above the valence band (Sze and Irvin 1968) and therefore they presumably occupy arsenic sites.

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