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Dynamics of the H-C_{As} complex in GaAs

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Infrared-absorption measurements have been made on epitaxial layers of GaAs grown by metal-organic molecular-beam epitaxy and doped with either ^{12}C or ^{13}C impurities to a concentration of 1.5×10^{19} cm^{-3}. After the introduction of either hydrogen or deuterium atoms from a radio-frequency plasma the localized vibrational modes (LVM) of H-C_{As} pairs have been observed and analyzed. Two A_1 modes and two E modes have been found for D-C_{As} pairs, and so this is the first hydrogen-passivated shallow-impurity pair for which all four LVM's are present. Admixing of the two E modes explains an apparent anomaly when the spectra of samples containing H-$^{12}C_{As}$ are compared with those containing D-$^{12}C_{As}$ pairs. There is good agreement with published *ab initio* theory, and anharmonicity of the stretch modes is discussed. No evidence has been found for the presence of the other carbon complexes, nor for the amphoteric behavior of carbon.

I. INTRODUCTION

Carbon impurity atoms which occupy arsenic lattice sites in GaAs and act as shallow acceptors, give rise to localized vibrational modes (LVM's) at 582.8 cm^{-1} ($^{12}C_{As}$) and 561.8 cm^{-1}($^{13}C_{As}$) (Table I), which can be detected by infrared- (IR) absorption spectroscopy[1] or Raman-scattering measurements.[2] The natural abundance of the heavier isotope is only 1.1% so that the strength of the associated absorption is usually too small to be detected. When atomic hydrogen is incorporated in the as-grown crystal, or is introduced after growth by plasma or heat treatments, some fraction of the carbon impurities forms close H-C_{As} pairs and the acceptor activity of these atoms is passivated.[2-10] There is now a consensus that the hydrogen atoms occupy bond-centered sites to form complexes with trigonal C_{3V} symmetry (Fig. 1). Since two light atoms are present, a H-C_{As} complex could give rise to two nondegenerate LVM's with A_1 symmetry, and two doubly degenerate LVM's with E symmetry. The A_1-hydrogen stretch modes in which the C_{As} and the hydrogen atom vibrate out of phase have been reported for the three isotopic combinations H-$^{12}C_{As}$,[3-5] D-$^{12}C_{As}$,[3-5] and H-$^{13}C_{As}$ (Ref. 4) (Table I). In the other A_1 mode, previously designated X,[5-7] the two atoms vibrate in phase and modes $^{12}X^{\rm H}$ and $^{12}X^{\rm D}$ have been found (Table I and Fig. 1). The latter assignments, made from the analysis of Raman-scattering measurements,[2] are unambiguous.

Another line[5] $^{12}Y^{\rm H}$ (now written as $^{12}Y_1^{\rm H}$ in Table I) was shown to have a strength that correlated with the strengths of the LVM lines $^{12}X^H$ and the stretch mode of H-$^{12}C_{As}$ in IR spectra and so it was assigned to one of the two E modes of the H-$^{12}C_{As}$ pair. The line has not been detected in Raman spectra, because of strong underlying two-phonon scattering, and its symmetry has not been determined. An isotopic analog $^{12}Y^{\rm D}$ was not detected in IR spectra and possible reasons for the absence, relating to anomalous line broadening, were proposed.[7] Because of the absence, it was unclear whether line $^{12}Y_1^{\rm H}$ was due to the transverse (E) mode of the paired C_{As} atom or to the hydrogen-wag (E) mode. The possibility that the line might be assigned to C_{Ga} donors was ruled out, but only as a consequence of the correlations of LVM line strengths noted above, and because it was thought inconceivable that treatments of samples in a hydrogen plasma

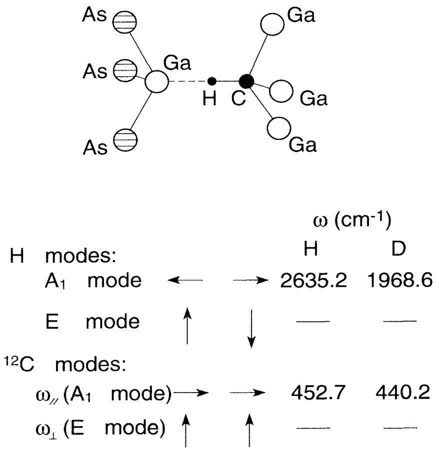

FIG. 1. Model of the H-C_{As} pair showing the carbon atom in the bond-centered position only weakly coupled to the neighboring Ga atom. The relative displacements of the two atoms are shown for the two A_1 modes and the two E modes, together with the frequencies for the A_1 LVM's of ^{12}C paired with H or D. The E modes are admixed and are discussed in the text.

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would always produce carbon donors but that treatments in the same equipment in a deuterium plasma would not. It is important to recall that isotopic fine structure[11–13] due to mixed Ga nearest neighbors (^{69}Ga is 60% abundant and ^{71}Ga is 40% abundant) is not observed for the LVM line of C_{As} in highly doped GaAs,[5,7] and so its absence provides no further information about the site occupied by the carbon atom giving line $^{12}Y_1^H$.

It has been suggested that carbon might be amphoteric, as it is a group-IV impurity, and that the presence of C_{Ga} donors in highly doped GaAs might account for measured values of the hole concentration being smaller than the total carbon content.[14–16] There are clearly important technological implications, relating to the fabrication of certain devices such as heterojunction bipolar transistors which incorporate highly carbon-doped layers. However, in this paper we restrict the discussion to the dynamics of the H-C_{As} pair. We present further IR measurements made on GaAs samples doped with either ^{12}C or ^{13}C. Measurements were made both on material in its as-grown state and following passivation in a radio-frequency hydrogen or deuterium plasma (13.56 MHz, 2 mbar, 40 W, $T=350\,°\mathrm{C}$).[6,7] The stretch mode of D-$^{13}C_{As}$ was detected, allowing an analysis of anharmonic effects to be made.[17] The isotopic analogs $^{13}X^H$ and $^{13}X^D$ have been observed, and show the expected frequency shifts[18] from lines $^{12}X^H$ and $^{12}X^D$. The most interesting results are the observations of lines which are interpreted as admixed E modes of the carbon transverse mode and the deuterium-wag mode of D-$^{12}C_{As}$ and D-$^{13}C_{As}$ pairs. The interpretation is supported by the results of a simple harmonic vibrational model leading to a definitive assignment of line $^{12}Y_1^H$ to the transverse E mode of H-$^{12}C_{As}$ pairs. The experimental data are also compared with the predictions of *ab initio* theory.[18]

II. EXPERIMENTAL DETAILS

The samples were grown at Liverpool University by metal-organic molecular-beam epitaxy (MOMBE) using beams of triethyl gallium [beam equivalent pressure (BEP) of 2×10^{-5} mbar] and cracked arsine (BEP$=2\times10^{-4}$ mbar). Carbon doping was introduced from a beam of $^{12}CBr_4$ or $^{13}CBr_4$ (BEP$=1\times10^{-7}$ mbar) after the growth of an undoped buffer layer, 200 Å in thickness. The substrates were (100) semi-insulating GaAs, grown by the liquid encapsulated Czochralski method, and the epitaxial growth was carried out at 540 °C. The epilayer thicknesses were 4 μm (^{12}C) and 3 μm (^{13}C) and the hole concentrations, measured by the Hall effect, were 1.2×10^{19} and 1.5×10^{19} cm^{-3}, respectively. The latter concentration agreed, within the experimental errors, with secondary-ion mass spectrography measurements which yielded $[\mathrm{C}]=1.2\times10^{19}$ cm^{-3}. IR measurements were made on wedged (substrate) samples to minimize the presence of interference fringes in recorded spectra. IR spectra were obtained using a Bruker IFS120 or a Bruker IFS 113v interferometer, operated at resolutions of 0.25 and 0.1 cm^{-1}, respectively, and with the samples at a temperature of $\sim$10 K. Spectra from the substrate material were subtracted from those of the samples to minimize the strengths of recorded intrinsic phonon features.

III. INFRARED MEASUREMENTS

The IR spectra of the as-grown samples (Fig. 2) revealed strong Fano derivative shaped profiles[5,6] due to the LVM's of $^{12}C_{As}$ and $^{13}C_{As}$ (Table I). The spectrum of the GaAs doped with natural carbon also revealed the LVM line from $^{13}C_{As}$ corresponding to 5×10^{13} atom cm^{-2}, just above the areal detection limit for such highly doped p-type material. The spectra of the GaAs ^{13}C samples showed no detectable LVM from ^{12}C in the epitaxial layer, although residual $^{12}C_{As}$ in the substrate was observed and showed the associated fine-structure features.[11–13] It was therefore inferred that the isotopic abundance of ^{13}C in our $^{13}CBr_4$ source was close to 100%. None of the as-grown samples showed detectable lines due to H-C_{As} pairs, indicating that any hydrogen incorporation was at a very low level. This conclusion is consistent with previous IR measurements made on other GaAs samples grown in the same equipment,[7] but doped with carbon from trimethyl-Ga, used as the Ga precursor.

After samples had been exposed to the hydrogen/deuterium plasma their IR spectra indicated that significant passivation had occurred since the LVM lines of the isolated C_{As} acceptors were generally more symmetrical (Fig. 3). In addition, stretch modes (Fig. 4) and lines X (Fig. 5) for all four possible isotopic combinations were observed, as well as line $^{13}Y_1^H$ (Fig. 3). Lines $^{13}X^H$, $^{13}X^D$, and $^{13}Y_1^H$ all showed the expected isotopic shifts from their ^{12}C analogs due to an increase of the carbon mass by 1 amu. The magnitude of the shift between lines $^{12}Y_1^H$ and $^{13}Y_1^H$, respectively (Table I), immediately demonstrates that they have to be assigned to

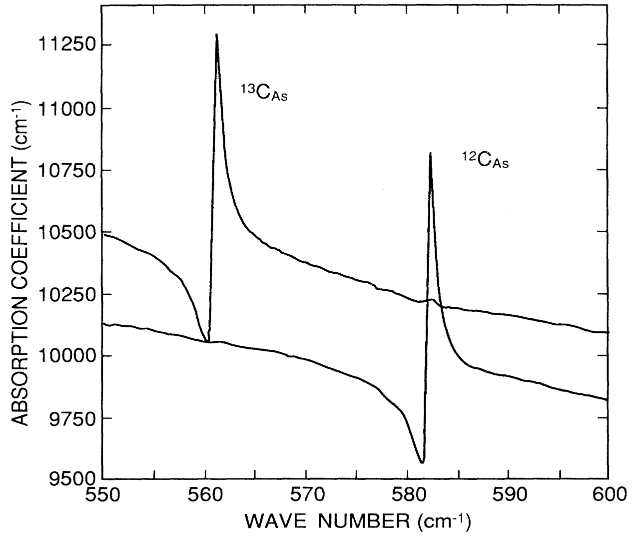


FIG. 2. The infrared absorption of (a) the $^{12}C_{As}$ and (b) the $^{13}C_{As}$ LVM's in epitaxial layers grown by MOMBE. The derivative shapes (Fano profiles) are due to interactions with the strong free-carrier absorption.

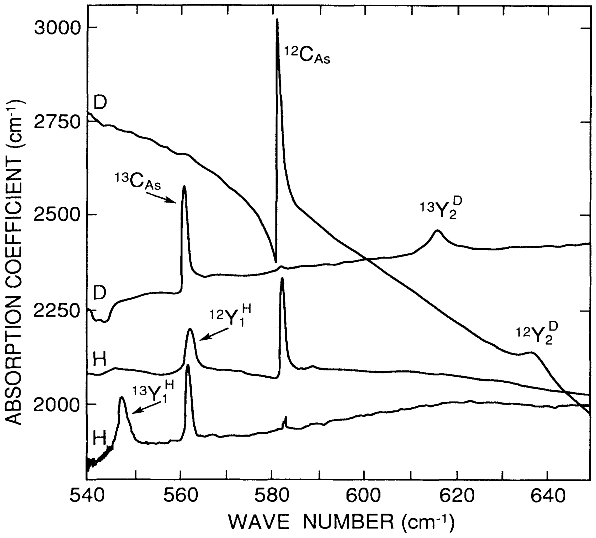


FIG. 3. Infrared-absorption spectra of samples containing either $^{12}C_{As}$ or $^{13}C_{As}$ after passivation treatments in either hydrogen or deuterium (see left-hand side). The LVM's of the C_{As} acceptors in three samples have become more symmetrical than those shown in Fig. 2 and there was a reduction in the free-carrier absorption. The important features are the new lines labeled Y_1^H due to the (carbonlike) transverse E modes of H-C_{As} and corresponding lines labeled Y_2^D from D-C_{As} pairs, respectively. For clarity the spectra have been shifted vertically from top to bottom by -1900, -190, -870, and 0 cm^{-1}.

the transverse E modes of paired carbon atoms, rather than to wag modes of hydrogen, since we show in Sec. IV B that they are indeed LVM's of H-C_{As} pairs.

Other weak lines that were detected have been labeled $^{12}Y_1^D$ and $^{13}Y_1^D$ (Fig. 5) and $^{12}Y_2^D$ and $^{13}Y_2^D$ (Fig. 3) (Table II). The frequencies of all the Y lines can be understood

TABLE I. Comparison of LVM frequencies (cm^{-1}) with *ab initio* theory. ND denotes not detected and str denotes stretch.

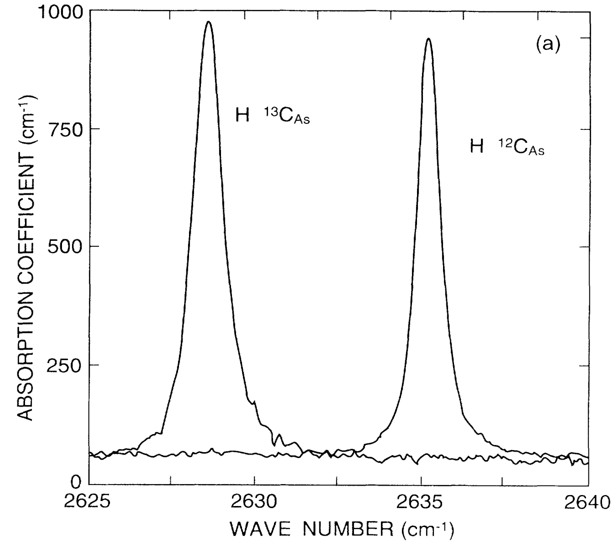
Mode	Line	Expt.	Theory[a]
$^{12}C_{As}$ (T_d)		582.8	544
$^{13}C_{As}$ (T_d)		561.8	b
$^{12}C_{Ga}$ (T_d)		ND	538
H-$^{12}C_{As}$ (str)		2635.2	2605
H-$^{13}C_{As}$ (str)		2628.5	2598
D-$^{12}C_{As}$ (str)		1968.6	1905
D-$^{13}C_{As}$ (str)		1958.3	b
H-$^{12}C_{As}$ (A_1)	$^{12}X^H$	452.7	413
H-$^{13}C_{As}$ (A_1)	$^{13}X^H$	437.8	399
D-$^{12}C_{As}$ (A_1)	$^{12}X^D$	440.2	402
D-$^{13}C_{As}$ (A_1)	$^{13}X^D$	426.9	b
H-$^{12}C_{As}$ (wag)	$^{12}Y_2^H$	ND	718
H-$^{13}C_{As}$ (wag)	$^{13}Y_2^H$	ND	716
H-$^{12}C_{As}$ (E)	$^{12}Y_1^H$	562.6	379
H-$^{13}C_{As}$ (E)	$^{13}Y_1^H$	547.6	367

[a] Jones and Öberg (Ref. 18).
[b] Not reported.

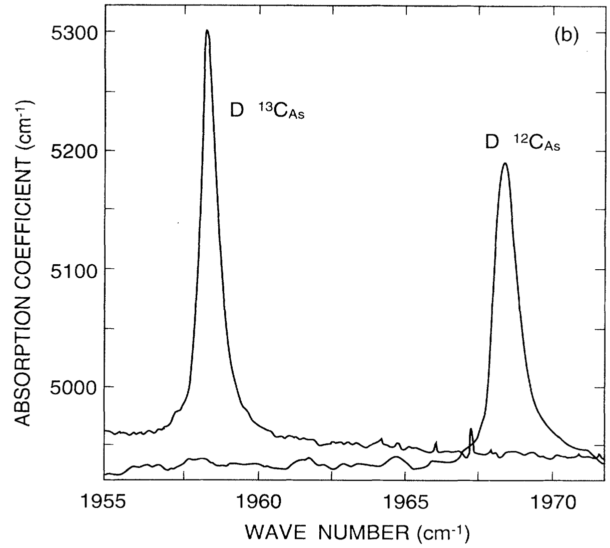
TABLE II. Vibrational E modes of H-C_{As} (cm^{-1}). ND denotes not detected.

Mode	$^{12}Y_1^H$	$^{13}Y_1^H$	$^{12}Y_2^H$	$^{13}Y_2^H$
Expt.	562.6	547.6	ND	ND
Model	564.1[a]	546.4[a]	745.2	739.0
Mode	$^{12}Y_1^D$	$^{13}Y_1^D$	$^{12}Y_2^D$	$^{13}Y_2^D$
Expt.	466.2	463.8	637.2	616.6
Model	467.0	463.4	636.9	616.6

[a] The frequencies 564 and 546 cm^{-1} are increased to 594 and 571 cm^{-1}, respectively, as the mass of the paired H tends to zero (amu) in the model calculation.



HYDROGEN STRETCH A_1 MODES



DEUTERIUM STRETCH A_1 MODES

FIG. 4. Absorption spectra showing (a) the hydrogen (A_1) stretch modes of H-$^{12}C_{As}$ and H-$^{13}C_{As}$ pairs, and (b) the deuterium stretch modes of D-$^{12}C_{As}$ and D-$^{13}C_{As}$ pairs in samples after plasma treatments.

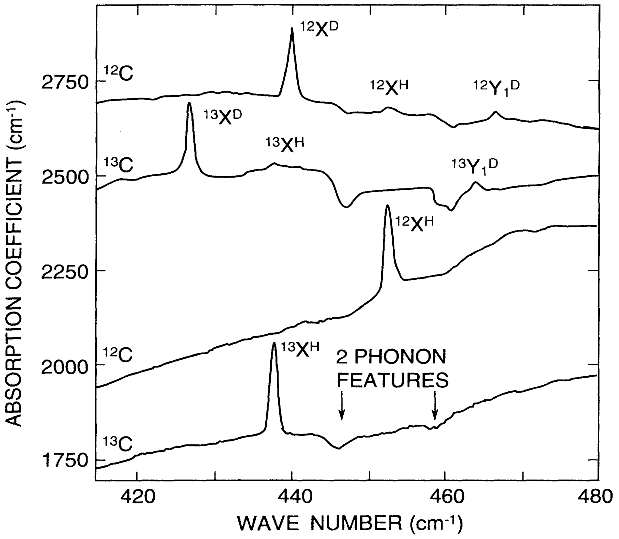


FIG. 5. Infrared-absorption spectra of plasma-treated samples showing the symmetric A_1 modes of H-^{12}C, H-^{13}C, D-^{12}C, and D-^{13}C pairs labeled X. Also shown are the E modes of the deuterium waglike LVM's of D-$^{12}C_{As}$ and D-$^{13}C_{As}$, labeled $^{12}Y_1^D$ and $^{13}Y_1^D$, respectively. Other features are due to incomplete matching of the two-phonon absorption of the samples and the undoped reference GaAs. For clarity the spectra have been shifted vertically from top to bottom by -2300, $+50$, -700, and 0 cm^{-1}.

if there is a near degeneracy of the deuterium-wag mode of the D-C_{As} pair with the transverse E mode of the paired carbon atom. Since the modes have the same symmetry, they would exhibit an anticrossing on an energy-level diagram if the mass of the hydrogen atom were regarded as the independent variable (Sec. IV B). It then follows that the wag mode of paired hydrogen atoms would have to lie at a significantly higher frequency, by a factor of $\sim 2^{1/2}$, than that of $^{12}Y_1^H$ or $^{13}Y_1^H$.

IV. ANALYSIS OF MEASUREMENTS

A. Anharmonicity of the stretch modes

Because of anharmonicity, the observed frequencies ω (cm^{-1}) of the A_1-stretch modes will be smaller than the harmonic frequency ν (cm^{-1}), according to the relationship $\omega = \nu - B/M$.[17] The parameter B is a measure of the anharmonicity, arising from both cubic and quartic terms in the potential, and M is the mass (amu) of the paired H or D atom. The frequency ν_H is expected to be given by the expression

$$\nu_H^2 = k(1/M_H + 1/\chi M_C) , \tag{1}$$

where k is the stretch force constant and χ is a parameter to be determined (see, for example, Ref. 19). The requirement for the inclusion of anharmonicity is evident if measured values of $r = (\omega_H/\omega_D)$ are inserted into Eq. (1), since this leads to values of $\chi = 0.64$ for $M_c = 12$ amu and $\chi = 0.59$ for $M_c = 13$ amu, respectively. The conclusion that the hydrogen atom is bonded to another atom with a mass significantly smaller than that of carbon is clearly untenable. There is therefore a requirement to find values of $\nu > \omega$, as discussed above. Now the difference between the two ratios $R(\omega,\text{H}) = [\omega(\text{H-}^{12}\text{C})/\omega(\text{H-}^{13}\text{C})]^2$ and $R(\nu,\text{H}) = [\nu(\text{H-}^{12}\text{C})/\nu(\text{H-}^{13}\text{C})]^2$ should be small since the former ratio would be independent of anharmonic corrections to first order: we then calculate a value of $\chi = 1.16$. Likewise, we should have $R(\omega,\text{D}) = [\omega(\text{D-}^{12}\text{C})/\omega(\text{D-}^{13}\text{C})]^2 \sim R(\nu,\text{D}) = [\nu(\text{D-}^{12}\text{C})/\nu(\text{D-}^{13}\text{C})]^2$, leading to a calculated value of $\chi = 1.06$. Both values are greater than unity, as is required, because displacements of the paired carbon atom along the [111] axis are opposed by the bending force constants of its three remaining Ga neighbors (Fig. 1). χ is therefore set equal to the average value of 1.1, allowing the ratios $r' = (\nu^H/\nu^D)$ to be calculated from Eq. (1): we obtain $r' = 1.367$ and 1.370 for H(D)-^{12}C and H(D)-^{13}C, respectively. It has been shown[17] that the parameter B is given by

$$B \sim 2\omega_D(r' - r)/(2 - r') , \tag{2}$$

leading to $B = 176$ cm^{-1}, using the values for H(D)-^{12}C. Thus, $\nu(\text{H-}^{12}\text{C}) = (\omega + 176)$ cm^{-1} $= 2811.2$ cm^{-1}, $\nu(\text{D-}^{12}\text{C}) = (\omega + 88)$ cm^{-1} $= 2056.6$ cm^{-1}, $\nu(\text{H-}^{13}\text{C}) = 2804.5$ cm^{-1}, and $\nu(\text{D-}^{13}\text{C}) = 2046.3$ cm^{-1}. There is then overall consistency for all the frequency ratios calculated from Eq. (1). For example, $R(\omega,\text{H}) = 1.0051$ and $R(\nu,\text{H}) = 1.0048$, giving a difference of 0.032%: the corresponding difference between $R(\omega,\text{D})$ and $R(\nu,\text{D})$ is 0.016%.

An important point that emerges is that the hydrogen atom must be strongly bonded to the carbon atom, so that the pairs H-^{12}C and D-^{12}C would have "effective" masses close to 13 and 14 amu, respectively, in their symmetric A_1 (X) modes. It follows that the mode for H-^{13}C should have almost the same frequency as that of D-^{12}C. The measured frequencies of 437.8 and 440.2 cm^{-1}, respectively, support this prediction. The anharmonic parameter $B = 176$ cm^{-1} is almost a factor of 2 greater than that found for H-C vibrations in a molecule such as H-C-N, where the hydrogen stretch mode occurs at 3312 cm^{-1} and the measured anharmonic reduction is 103 cm^{-1},[20] determined from measurements of the frequency of the second harmonic. We have not so far detected second-harmonic absorption in our samples.

B. Modeling of the E modes

The frequencies of the H-C_{As} E modes (Y lines) have been modeled by assuming that the two atoms experience restoring forces proportional to their displacements x_2 and x_1 perpendicular to their equilibrium positions on a $\langle 111 \rangle$ bond axis. The carbon atom experiences a force $-k_1x_1$ due to the stretching and bending of the bonds to its three remaining Ga neighbors: the H atom experiences a force $-k_2x_2$ due to a weak bond-bending interaction with its axial Ga neighbor: there is a force $-k_3(x_1 - x_2)$ acting on the carbon atom and $-k_3(x_2 - x_1)$ acting on the hydrogen atom due to their relative displacement which causes bending of the H-C_{As} bond. A choice of $k_1 = 243.4$ N/m, $k_2 = 9.2$ N/m, and

$k_3 = 20.5$ N/m leads to the frequencies given in Table II. If the mass of the hydrogen atom is regarded as a continuous independent variable we obtain the frequencies given in Fig. 6. This diagram is informative as it shows that the interactions between the two modes are quite small for hydrogen-carbon pairs since an extrapolation of the frequencies of modes ${}^{12}Y_1^{\mathrm{H}}$ and ${}^{13}Y_1^{\mathrm{H}}$ as the mass of the hydrogen atom tends to zero yields values only ~ 25 cm^{-1} greater than those observed. However, the admixing for D-$\mathrm{C_{As}}$ pairs is strong and there is an effective interchange of the nature of the two modes, as revealed by the magnitudes of the isotopic splittings from ^{12}C and ^{13}C. The force constants used were chosen to give the best least-squares fit to the experimentally determined frequencies (Table II). The maximum discrepancy for any line is 1.5 cm^{-1}, suggesting that the simple model provides a reasonable representation of the dynamics of the E modes. It should be noted that anharmonicity has not been taken into account in the analysis.

We next examine the magnitudes of the force constants to find whether they are physically reasonable. Previously, we used a simplified Keating model with bond-stretching and bond-bending force constants $\alpha = 35$ N/m and $\beta = 5$ N/m, respectively, to represent the phonon frequencies of GaAs.[21] When a carbon impurity was substituted for an As atom it was necessary to choose a modified nearest-neighbor stretch force constant $\alpha' = 40.9$ N/m and a modified $\beta' = 23.4$ N/m (at the apex of the carbon atom) to obtain the correct LVM frequency and the observed overall width of the Ga-isotopic fine structure. The isotropic force constant for carbon in a static well[19] would then be given by

$$k = 4\alpha' + 2\beta' + 3\beta \ , \tag{3}$$

leading to $k = 225$ N/m. In any reasonable model of the H-$\mathrm{C_{As}}$ pair, the force constant for transverse displacements of the paired carbon atom would have to be close to this value, since the measured frequency of the carbon E mode (562.6 cm^{-1}) is only 20 cm^{-1} lower than that of the LVM of isolated $\mathrm{C_{As}}$ impurities (582.8 cm^{-1}), while the extrapolated frequency of the E mode as $M_{\mathrm{H}} \rightarrow 0$ is 594 cm^{-1}. Thus, the value of our parameter $k_1 = 243.4$ N/m is in good agreement with the requirement. In general, bending force constants are only some 10% of those of stretching constants so that the low values of $k_2 = 9.2$ N/m and $k_3 = 20.5$ N/m are consistent with this expectation. For example, the bend constant of H-C in the linear molecule HCN is ~ 20 N/m.[22] The overall conclusion is therefore that the force constants derived from the simple model are satisfactory and the model is physically meaningful. The model then leads to the prediction that the hydrogen-wag modes for H-${}^{12}\mathrm{C_{As}}$ and H-${}^{13}\mathrm{C_{As}}$ lie close to 745 and 739 cm^{-1}, respectively. So far these lines have not been detected in IR spectra.

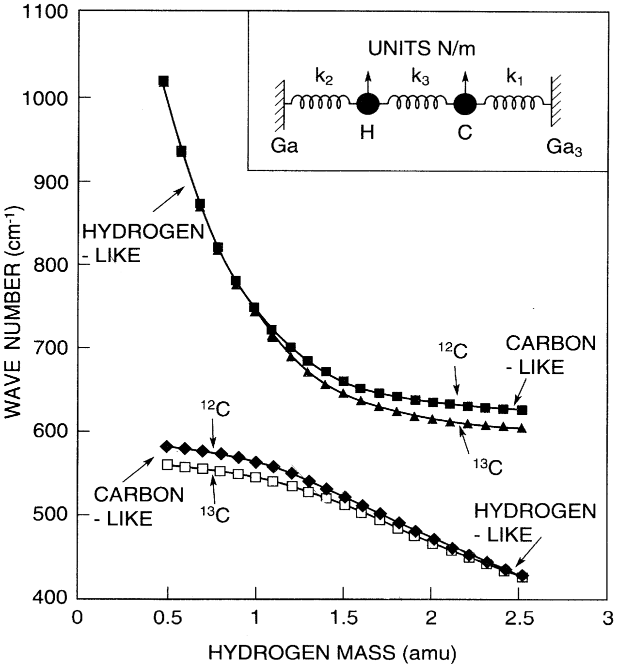


FIG. 6. Vibrational transverse E modes of the coupled masses shown in the inset, used as a simple model to represent the H-$\mathrm{C_{As}}$ pair. The observed LVM frequencies are reproduced by the choice of spring constants, given in the text. The carbon-like modes are observed for H-${}^{12}\mathrm{C_{As}}$ and H-${}^{13}\mathrm{C_{As}}$ pairs, while all four modes are detected for D-${}^{12}\mathrm{C_{As}}$ and D-${}^{13}\mathrm{C_{As}}$ pairs (Table II). The important feature is the strong anticrossing of the modes which changes their effective identities for H-$\mathrm{C_{As}}$, compared with D-$\mathrm{C_{As}}$.

C. Modeling of the A_1 modes

The harmonic analysis for the coupled E modes of the H-$\mathrm{C_{As}}$ pair clearly demonstrates that a deviation of a ratio $\omega_{\mathrm{H}}/\omega_{\mathrm{D}}$ from its expected value need not be due to anharmonicity. As a consequence, we have also modeled the A_1 modes of the pair defect to check that the essence of the analysis given in Sec. IV A is valid. Thus, the spring constant for longitudinal displacements of the $\mathrm{C_{As}}$ atom relative to its three Ga neighbors was designated k_1', the longitudinal constant for displacements of the H atom relative to its Ga neighbor k_2', and the H-$\mathrm{C_{As}}$ stretch constant k_3'. Values of k_1', k_2', and k_3' were then determined by fitting to the *measured* vibrational frequencies of the H-${}^{12}\mathrm{C_{As}}$ stretch mode and the symmetric A_1 mode of the same isotopic center. As there was insufficient information to obtain a unique solution, the calculations were made for a range of values of $k_2' = 0-100$ N/m. As k_2' was increased it was necessary to reduce the value of k_1' from 158 to 77 N/m and the value of k_3' from 379 to 293 N/m for the same range. For each choice of the force constants, the frequencies of the two modes for all the isotopic combinations were determined. The ratios $r = \omega(\mathrm{H}\text{-}{}^{12}\mathrm{C})/\omega(\mathrm{D}\text{-}{}^{12}\mathrm{C})$, plotted as a function of k_2' for the range 1.357 ($k_2' = 0$) to 1.380 ($k_2' = 100$ N/m), are all significantly greater than the experimental value of $r = 1.3386$ (Fig. 7). It was then noted that the results of *ab initio* harmonic calculations, presented in the following section, predict a ratio $r = 1.367$. This value is again too large in comparison

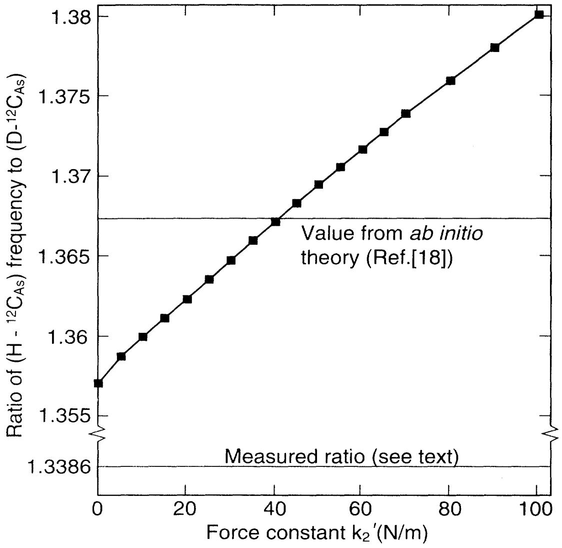


FIG. 7. The ratio of the calculated frequencies of the stretch modes of H-$^{12}C_{As}$ to D-$^{12}C_{As}$ as a function of the force constant k_2' (see text). Also shown are the corresponding ratios for the measured frequencies and that calculated from *ab initio* methods (Ref. 18).

with experiment but suggests a correspondence to our model with a value of $k_2' \sim 40$ N/m.

We then repeated our model calculations but used the value of ν for the H-^{12}C stretch mode, corrected for anharmonicity, rather than ω(H-^{12}C) to obtain a fit. To obtain exact agreement with the value of $r' = \nu^H/\nu^D = 1.367$ it was necessary to choose $k_1' = 117.1$ N/m, $k_2' = 42.0$ N/m, and $k_3' = 396.3$ N/m. The calculated frequencies of the A_1 modes of all the isotopic combinations are shown in Table III, together with the measured frequencies of lines X (Table I) and the stretch modes corrected for anharmonicity. There is overall agreement when anharmonic corrections have been made, but not otherwise. Changing the value of k_2' over the range 30–50 N/m, and correspondingly the values of k_1' and k_3', leads to changes in the frequencies of line $^{12}X^D$ by -0.7 and $+0.6$ cm^{-1}, $^{13}X^D$ by -0.6 and $+0.5$ cm^{-1}, the D-^{12}C stretch by $+3.7$ and -3.3 cm^{-1}, the H-^{13}C by -0.6 and $+0.4$ cm^{-1}, and D-^{13}C by $+3.1$ and -2.8 cm^{-1}. It is therefore apparent that the ratio r' is the parameter which is most sensitive to the choice of the force constant k_2'. Effects due to the admixing of the LVM's with A_1 symmetry do not appear to be important because of the large separations between the two frequencies.

Finally, the magnitude of the force constants should be examined. The value of $k_2' = 42$ N/m is small, as was expected, because the hydrogen atom is bonded primarily to the carbon impurity. The H-C_{As} stretch constant $k_3' = 396.3$ N/m is large but should be compared with the correspondingly high value of 582 N/m for H-C-N.[22] The value of $k_1' = 117.1$ N/m is about 50% of that for transverse displacements of the carbon atom (Sec. IV B). An even smaller value of 60 N/m (~25% of that for k for a tetrahedral impurity) would have been expected for an impurity with a small-angle bending constant ($\beta \sim 5$ N/m), but for carbon $\beta' = 23.4$ N/m is much larger due to the rigidity of the tetrahedral bonding and hence the larger value of k_1' is plausible. Thus the values of k_1', k_2', and k_3' are all physically sensible and are in general accordance with expectations.

D. Comparison with *ab initio* theory

The LVM frequencies of the H-C_{As} complexes have been calculated by Jones and Öberg,[18] and their numerical data are included in Table I. Their calculated frequency of 544 cm^{-1} for isolated $^{12}C_{As}$ acceptors is lower than the measured value by 7% (data were not given for $^{13}C_{As}$), which is considered to be good agreement. There appears to be better agreement to within 30 cm^{-1}, for the frequencies of the hydrogen stretch modes of H-^{12}C and H-^{13}C, but for D-^{12}C pairs the agreement is at first sight slightly less good, with a discrepancy of 60 cm^{-1}. However the dynamical calculations are carried out in a quasiharmonic approximation and the calculated frequencies of the H-C_{As} modes should also be compared with values of ν which are greater than the measured values of ω (see Sec. IV A) due to anharmonicity. When the calculated frequency for H-$^{12}C_{As}$ of 2605 cm^{-1} is compared with ν(H-$^{12}C_{As}$)=2811.2 cm^{-1} (Table III), the theoretical value is found to be 8% too low: this is also true for the H-^{13}C and D-^{12}C modes. The agreement with the symmetric A_1 modes is also remarkable, although all the calculated modes have frequencies about 9% lower than those measured. The hydrogen-wag modes, calculated to lie at 718 and 716 cm^{-1} for H-^{12}C and H-^{13}C respectively, are also only slightly lower than the positions estimated here (Table II). It would seem that almost perfect agreement with experiment would be achieved if the various calculated frequencies were increased by about 8%. Unfortunately, the calculated fre-

TABLE III. Vibrational A_1 modes of H-C_{As} (cm^{-1}). Model (a) fitted to experimental frequencies (ω) of A_1 modes of H-$^{12}C_{As}$, without anharmonic correction. Model parameters are $k_1' = 120.0$ N/m, $k_2' = 39.0$ N/m, and $k_3' = 346.3$ N/m, giving a ratio of the H-^{12}C stretch frequency to that of D-^{12}C of 1.367. Model (b) fitted to experimental frequencies (ν) of A_1 modes of H-$^{12}C_{As}$, after correcting for anharmonicity. Model parameters are $k_1' = 117.1$ N/m, $k_2' = 42.0$ N/m, and $k_3' = 396.3$ N/m, giving a ratio of the H-^{12}C stretch frequency to that of D-^{12}C of 1.367.

Stretch modes	H-^{12}C	D-^{12}C	H-^{13}C	D-^{13}C
Expt. (ω)	2635.2	1968.6	2628.5	1958.3
Model (a)	2635.2	1927.7	2628.3	1917.8
Expt. (ν)	2811.2	2056.6	2804.5	2046.3
Model (b)	2811.2	2056.6	2803.9	2046.0
X Modes	$^{12}X^H$	$^{12}X^D$	$^{13}X^H$	$^{13}X^D$
Expt. (ω)	452.7	440.2	437.8	426.9
Model (a)	452.7	437.8	436.0	422.8
Model (b)	452.7	437.7	436.0	422.7

quencies of the transverse modes of the paired carbon (^{12}C) atoms (379 cm^{-1}) are significantly too low by some 180 cm^{-1}. Consequently, the strong admixing with the D-wag mode (534 cm^{-1}) was not apparent, even though the calculations took such coupling into account. Notwithstanding this shortcoming, the overall agreement of theory with experiment is excellent.

A further prediction from theory was that the dipole moment of the H-wag mode is very small. This may explain why this LVM has not been detected to data. However, when this mode (from deuterium) is admixed with the carbon transverse mode, the absorption associated with the latter line is shared between the two lines and they are both detected. It was found experimentally that the sum of the absorptions was still quite small, explaining the failure to detect lines $^{12}Y_1^{\mathrm{D}}$, and $^{12}Y_2^{\mathrm{D}}$ (Table II) in the less highly doped samples examined by us previously.[7]

V. DISCUSSION AND CONCLUSIONS

An examination of GaAs doped with ^{12}C or ^{13}C to a level of $\sim 1.5 \times 10^{19}$ cm^{-3} has revealed LVM lines from $\mathrm{C_{As}}$ acceptors and H-$\mathrm{C_{As}}$ pairs following exposure of samples to a hydrogen plasma. Assignments of LVM lines to the two A_1 modes and the two E modes of the pair complex have now been made, although hydrogen-wag modes, predicted to lie at ~ 745 cm^{-1}, have not yet been detected. It is clear that our earlier failure to detect an isotopic analog of line $^{12}Y_1^{\mathrm{H}}$ from D-$^{12}\mathrm{C_{As}}$ pairs was not due to anomalous line broadening effects[7] but to large line shifts due to the admixing of the E modes of the pair. This interpretation was greatly facilitated by the examination of samples containing ^{13}C rather than ^{12}C and has led to the unambiguous conclusion that lines $^{12}Y_1^{\mathrm{H}}$ and $^{13}Y_1^{\mathrm{H}}$ cannot be assigned to $\mathrm{C_{Ga}}$ donors. This result also removes another previous uncertainty relating to GaAs:C samples which showed line $^{12}Y_1^{\mathrm{H}}$ to be present after a heat treatment in arsine gas at 950 °C for 12 s, followed by a quench to room temperature.[5] Hydrogen diffused into these samples to form H-$\mathrm{C_{As}}$ pairs, as revealed by the presence of the H-$^{12}\mathrm{C_{As}}$ stretch and symmetric (X) A_1 modes, and so line $^{12}Y_1^{\mathrm{H}}$ would automatically be expected to be present.

The measurements are of interest in their own right in several ways since we believe this to be the first hydrogen-shallow acceptor (or donor) pair for which all four LVM's have been detected. Usually, when the hydrogen atom occupies a bond-centered site, the wag mode has not been observed and it has been assumed to have a low frequency so that it falls into the continuum of lattice modes. This interpretation is reasonable since the transverse modes of paired $^{9}\mathrm{Be_{Ga}}$ acceptors occur at 555.7 cm^{-1} for H-$^{9}\mathrm{Be_{Ga}}$ and at only a slightly lower energy of 553.6 cm^{-1} for D-$^{9}\mathrm{Be_{Ga}}$ pairs,[23] implying that admixing of the two E modes is negligible for both hydrogen and deuterium pairs. In this complex, the hydrogen is bonded more strongly to its arsenic neighbor than to the Be atom.[24] Likewise, the A_1 symmetric mode has not been observed and it also has been assumed to have a very low frequency. This is again reasonable if the mode is predominantly due to the longitudinal vibrations of a H-As pair, rather than a H-^{9}Be pair. However, by analogy with the present results for the H-$\mathrm{C_{As}}$ pair, it might have been expected that as well as a H-stretch mode, a hydrogen-wag mode and silicon transverse E mode would have been observed from H-$\mathrm{Si_{As}}$ pairs in hydrogenated p-type Si-doped GaAs grown by liquid phase epitaxy. Although assignments were made of H-$\mathrm{Si_{As}}$ and D-$\mathrm{Si_{As}}$ stretch modes, the origin of other lines with frequencies which would be consistent with wag modes of H and D, respectively, is unclear.[25] There must have been reservations relating to such an interpretation as these lines were not mentioned in a more recent publication.[26] We have also examined such material but failed to detect either the H-wag mode or the $\mathrm{Si_{As}}$ transverse E mode.[27] It would be important to have this more complete information for comparison with the data for H-$\mathrm{C_{As}}$ pairs.

We have now examined a large number of samples supplied from several leading laboratories and never found additional LVM lines from carbon complexes, other than H-$\mathrm{C_{As}}$, except in a few cases where modified H-stretch modes were found from centers that may involve two adjacent $\mathrm{C_{As}}$ atoms.[28] These samples were either in their as-grown state with [C] up to 10^{21} cm^{-3}, or they had received various heat treatments at high temperatures up to 900 °C. There is therefore, no information from LVM IR spectroscopy to explain why the carrier concentration may be lower than the total carbon content, except when hydrogen passivation occurs. There may be a loss of carriers due to the presence of As vacancies which could only be revealed by LVM spectroscopy as $\mathrm{C_{As}}$-$\mathrm{V_{As}}$ second-neighbor pairs (cf. data for $\mathrm{Si_{Ga}}$-$\mathrm{V_{Ga}}$ pairs[29]). We have found no evidence for the presence of $\mathrm{C_{Ga}}$ donors and are unaware of any direct evidence for the amphoteric behavior of carbon in GaAs.

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