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Dynamics of the H-C_{As} complex in GaAs determined from Raman measurements

J. Wagner and K. H. Bachem
Fraunhofer-Institut für Angwandte Festkörperphysik, Tullastrasse 72, D-71908 Freiburg, Federal Republic of Germany

B. R. Davidson and R. C. Newman
Interdisciplinary Research Centre for Semiconductor Materials, The Blackett Laboratory,
Imperial College of Science, Technology and Medicine, London SW7 2BZ, United Kingdom

T. J. Bullough and T. B. Joyce
Department of Materials Science and Engineering, P.O. Box 147, Liverpool University, Liverpool L69 3BX, United Kingdom

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The frequencies of the localized vibrational modes of H-C_{As} pairs in GaAs epitaxial layers have been measured using Raman spectroscopy for all four isotopic combinations involving ^{12}C, ^{13}C, H, and D. Good agreement has been obtained with earlier infrared-absorption measurements, but, in addition, the symmetry of the two A_1 modes and two E modes of each isotopic combination has been determined directly from the relative intensities of the scattering for different polarizations of the incident and scattered light. The hydrogenlike wag mode of H-C_{As} has been found and its frequency of 738.6 cm^{-1} is in close agreement with the predictions of modeling.

I. INTRODUCTION

The passivation of shallow acceptors resulting from the pairing with atomic hydrogen in III-V compound semiconductors is now well known.[1,2] The hydrogen may be introduced during the growth of layers by metal-organic vapor-phase epitaxy (MOVPE),[3-5] metal-organic molecular-beam epitaxy (MOMBE), or chemical-beam epitaxy (CBE),[6,7] and is derived from the decomposition of precursors such as trimethyl gallium (TMGa) and arsine (AsH_3). The hydrogen concentration may be greatly increased by exposing heated material to a radio-frequency (RF) hydrogen (deuterium) plasma[1,8] which generates atomic hydrogen. Rapidly diffusing hydrogen atoms, present in the positive charge state, are then trapped by the negatively charged acceptor impurities. The paired hydrogen atom gives rise to a high-frequency antisymmetric localized vibrational mode (LVM) with A_1^- symmetry, corresponding to stretching of the bond to its nearest-neighbor atom.[1,2] This mode is infrared (IR) and Raman active,[9] and its frequency is characteristic of the paired acceptor impurity and the host crystal. For acceptors such as Zn_{Ga} (Ref. 10) or Cd_{Ga} (Ref. 2) with a mass comparable to or greater than, the host lattice atom that is replaced, this is the only LVM that is detected.

It was recognized that additional LVM's should occur if hydrogen paired with an acceptor of low mass that gives rise to a LVM in its nonpassivated state. This was confirmed by IR and Raman measurements made on beryllium-doped GaAs, in which the $^9Be_{Ga}$ (T_d) atoms give rise to a LVM (Refs. 11–13) at 482 cm^{-1}. The passivated pair H (D)-$^9Be_{Ga}$ (C_{3v}) gives stretch modes of H (D) at 2037 cm^{-1} (1471 cm^{-1}), while another mode at 555.7 (553.6) cm^{-1} was attributed to the antisymmetric transverse E^- mode of the paired Be_{Ga} atom.[14] These results were in agreement with the expectations of *ab initio* local-density functional (LDF) theory,[15] which predicted that the hydrogen atom should be located in a bond-centered (BC) site between the Be_{Ga} atom and one of its

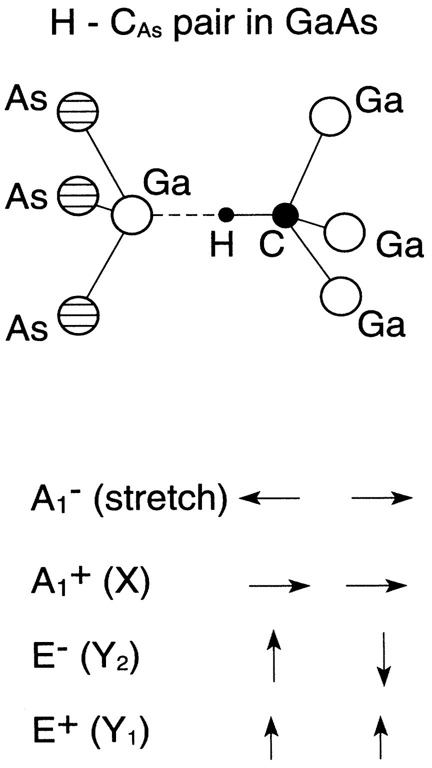

FIG. 1. Model of the H-C_{As} pair in GaAs showing the hydrogen atom in the bond-centered position only weakly coupled to the neighboring Ga atom and the associated vibrational modes.

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As nearest neighbors to which it should be bonded strongly: the Be atom would then be bonded strongly only to its three remaining As neighbors. The frequencies of the symmetric longitudinal A_1^+ mode of the As-H pair, and the symmetric E^+ (H-wag) mode, were predicted to lie in the band mode region, below the maximum lattice frequency of pure GaAs, so that they could not be detected. It follow that the dynamics of the pair could not be fully characterized.

Subsequently, attention was focused on C_{As} acceptors, since they have a lower diffusion coefficient than Be_{Ga} or Zn_{Ga} acceptors, and are therefore more suitable for device fabrication.[16–20] The LVM's of isolated $^{12}C_{As}$ and $^{13}C_{As}$ (T_d) are well known[21] (Table I), and the fine structure,[22] due to mixed Ga isotope nearest neighbors observed in high-resolution spectra for samples with low [C], confirms the As site occupancy. LDF theory indicated that passivating hydrogen atoms would again occupy BC sites but would be strongly bonded to the C_{As} acceptors (Fig. 1).[23] This conclusion was consistent with the isotopic shift of the H-stretch A_1^- mode from 2635.2 to 2628.5 cm^{-1} (Table I),[24] when pairing occurred with $^{13}C_{As}$ rather than $^{12}C_{As}$ in as-grown material. Additional modes of the H (D)-$^{12}C_{As}$ pair were then found by IR (Ref. 25) and Raman[26] spectroscopy, and measurements involving different polarization conditions for the latter technique enabled a definitive assignment to be made for the longitudinal symmetric A_1^+ modes (X lines) of the pairs (Table I, Fig. 1). The assignment of further modes of H (D)-$^{12}C_{As}$ pairs observed by IR absorption remained unclear until corresponding measurements had been made on samples containing isotopically enriched (essentially 100%) $^{13}C_{As}$ acceptors.[27] Assignments have now been made for the two types of A_1 modes (eight lines) and six of the eight possible E modes expected for D-$^{12}C_{As}$ and D-$^{13}C_{As}$ pairs. However, hydrogenlike E^- modes were not observed for either H-$^{12}C_{As}$ or H-$^{13}C_{As}$ pairs, but LDF theory[23] predicted that these modes should have a low (IR) dipole moment although they should be Raman active. The IR frequencies of the E^+ and E^- modes all occurred in the range 460–640 cm^{-1} (Table I), and were analyzed using a model of two coupled oscillators leading to the prediction that the hydrogenlike E^- mode occurred at 745 (739) cm^{-1} for H-$^{12}C_{As}$ (H-$^{13}C_{As}$).[28] To test the validity of this model, it was clearly necessary to obtain experimental values for the frequencies of these two undetected modes. Highly doped samples (Sec. II) that were suitable for Raman measurements have now been studied, and these results are presented in Sec. III. The missing E^- modes have been observed, allowing comparisons to be made with *ab initio* theory and predictions of the modeling.

TABLE I. Comparison of measured LVM frequencies (cm^{-1}) with *ab initio* LDF theory and the coupled oscillator model.

Mode	IR (cm^{-1})	Raman (cm^{-1})	Model (cm^{-1})	LDF Theory (Refs. 30 and 31) (cm^{-1})
$^{12}C_{As}$ (T_d)	582.8	581.5		
$^{13}C_{As}$(T_d)	561.8	561.1		
$^{12}C_{Ga}$(T_d)	a	a		
H-$^{12}C_{As}$(A_1^-,*str*)	2635.2 (2811.2)[b]	2637.4	2635.2 (2811.2)	2950
H-$^{13}C_{As}$(A_1^-,*str*)	2628.5 (2804.5)[b]	2631.7	2628.3 (2803.9)	2942
D-$^{12}C_{As}$(A_1^-,*str*)	1968.6 (2056.6)[b]	1970.0	1927.7 (2056.6)	2154
D-$^{13}C_{As}$(A_1^-,*str*)	1958.3 (2046.3)[b]	1959.6	1917.8 (2046.0)	2144
H-$^{12}C_{As}$(A_1^+,$^{12}X^H$)	452.7	452.2	452.6	456
H-$^{13}C_{As}$(A_1^+,$^{13}X^H$)	437.8	437.0	436.0	440
D-$^{12}C_{As}$(A_1^+,$^{12}X^D$)	440.2	439.9	437.7	442
D-$^{13}C_{As}$(A_1^+,$^{13}X^D$)	426.9	426.5	422.7	428
H-$^{12}C_{As}$(E^-,$^{12}Y_2^H$)	a	738.6	740.3	888
H-$^{13}C_{As}$(E^-,$^{13}Y_2^H$)	a	≈730	733.9	883
D-$^{12}C_{As}$(E^-,$^{12}Y_2^D$)	637.2	638.6	636.1	707
D-$^{13}C_{As}$(E^-,$^{12}Y_2^D$)	616.6	618.1	615.6	693
H-$^{12}C_{As}$(E^+,$^{12}Y_1^H$)	562.6	562.5	565.1	553
H-$^{13}C_{As}$(E^+,$^{13}Y_1^H$)	547.6	a	547.5	536
D-$^{12}C_{As}$(E^+,$^{12}Y_1^D$)	466.2	≈466	465.2	495
D-$^{13}C_{As}$(E^+,$^{13}Y_1^D$)	463.8	≈463	461.9	487

[a] Not detected.

[b] Estimated stretch mode frequency that would have been measured in the absence of an anharmonic down shift.

A subsequent study of H (D)-$^{12}C_{As}$ ($^{13}C_{As}$) pairs in AlAs then showed that the H (D)-stretch A_1^- modes had lower frequencies than the corresponding modes in GaAs, whereas *ab initio* LDF calculations predicted H (D)-stretch frequencies greater than those for GaAs.[29] This unexpected result was attributed to the use of an updated theoretical procedure used to analyze the H-C_{As}:AlAs system, for which a larger basis set was used compared with that that had been used to analyze the structure and modes of H-C_{As}:GaAs. The updated theory was later applied to GaAs,[30,31] and led to the removal of this "discrepancy" and also to changes of the predicted frequencies for the other H-C_{As} modes. A comparison of the relative vibrational displacements of the C_{As} and H atoms obtained from numerical modeling with those obtained from the mode eigenvectors determined from the updated theory[32] is given in Sec. IV. A brief discussion and conclusions are given in Sec. V.

II. EXPERIMENTAL DETAILS

Chemical-beam epitaxy (CBE) was used to grow samples at Liverpool University using beams of triethyl gallium (TEGa) [beam equivalent pressure (BEP) of 2×10^{-5} mbar] and cracked arsine (AsH_3) (BEP$=2\times10^{-4}$ mbar) after the growth of an undoped buffer layer, 200 Å in thickness (Table II). The substrates were (100) semi-insulating GaAs, grown by the liquid-encapsulated Czochralski method, and the epitaxial growth was carried out at 540 °C. Carbon doping was effected by introducing a beam of $^{12}CBr_4$ or $^{13}CBr_4$ (BEP$=1\times10^{-7}$ mbar). Epilayers were grown with thicknesses of 4 μm (^{12}C) [sample (a)] and 3 μm (^{13}C) [sample (b)] and hole concentrations, measured by the Hall effect, of 1.2×10^{19} and 1.5×10^{19} cm^{-3}, respectively. The hole concentrations agreed, within the experimental errors, with secondary-ion-mass spectrometry (SIMS) measurements which yielded $[C]=1.2\times10^{19}$ cm^{-3} for both layers. Another epilayer [sample (c)], 100 nm in thickness, was codoped with ^{12}C and ^{13}C each in a concentration of $\sim1\times10^{20}$ cm^{-3}, as measured by SIMS: this layer had a hole concentration of 2.6×10^{20} cm^{-3}, (Hall effect). After growth certain samples were exposed to a RF hydrogen or deuterium plasma (13.56 MHz, 2 mbar, 40 W, $T=350$ °C, $t=15$ min–6h).

MOVPE growth of carbon-doped GaAs layers was performed at the Fraunhofer-Institut für Angewandte Festkörperphysik using trimethyl gallium (TMGa) and trimethyl arsenic (TMAs).[33] With this group-V precursor, carbon concentrations in the range of 10^{20} cm^{-3} can be achieved.[33] As no separate carbon doping source is used, the GaAs growth and the carbon doping are simultaneously controlled by the choice of the MOVPE growth parameters. The sample for which data will be given [sample (d)] was grown at a substrate temperature of 540 °C at a pressure in the reactor of 100 mbar. The free-hole concentration (Hall effect) was 1.2×10^{20} cm^{-3} while the total carbon concentration measured by SIMS was 1.8×10^{20} cm^{-3}. The incomplete activation of the carbon acceptor was due in large part to unintentional incorporation of hydrogen during the growth, leading to the passivation of some fraction of the carbon acceptors via the formation of H-C_{As} complexes.[26] No post-growth passivation treatment was given to this sample.

TABLE II. Sample characteristics. The free hole concentration was measured by the Hall effect. SIMS data give the total carbon concentration.

Sample	Growth technique	Dopant	Hole concentration (10^{19} cm^{-3})	SIMS concentration (10^{19} cm^{-3})
(a)	MOMBE	^{12}C	1.2	1.2
(b)	MOMBE	^{13}C	1.5	1.2
(c)	MOMBE	^{12}C/^{13}C	26	$\simeq$10 each
(d)	MOVPE	^{12}C	12	18

IR spectra were obtained from samples at a temperature of $\sim$10 K using a Bruker IFS-120 or a Bruker IFS 113v interferometer, operated at resolutions of 0.25 or 0.1 cm^{-1}. Spectra from the substrate material were substracted from the composite spectra of the samples to minimize the strengths of recorded intrinsic phonon features.

Raman measurements were performed in the backscattering geometry from the (100) growth surface. The spectra were excited with either the 3.00-eV line of a Kr-ion laser or with the 2.71-eV line of an Ar-ion laser. The laser light, with a power of about 150 mW, was focused on a spot $\sim$70 μm in diameter at the surface of the samples, which were cooled to 77 K. For crystalline GaAs, the probing depth $1/(2\alpha)$ (where α denotes the absorption coefficient), is 10 and 20 nm for the higher and lower photon energies, respectively.[34] The scattered light was dispersed by a triple monochromator and detected with a liquid-nitrogen-cooled silicon charge-coupled detector (CCD) array. The spectral resolution was $\simeq$2.5 cm^{-1}.

III. LVM MEASUREMENTS

A. IR absorption

The IR spectra of the as-grown samples (Fig. 2) revealed strong Fano-derivative-shaped profiles[35] due to the LVM's of $^{12}C_{As}$ and $^{13}C_{As}$ (Table I). For the sample codoped with ^{12}C and ^{13}C the two LVM were clearly resolved. The fine structure on the high-energy side of the ^{12}C peak, due to carbon in the substrate, acts as a marker to show that the peak position for the highly doped epilayer is shifted down in frequency. No other peaks in this spectral region were detected for the CBE-grown samples. The spectrum for the sample grown by MOVPE showed a peak at 563 cm^{-1}, labeled $^{12}Y_1^H$, due to the formation of H-C_{As} pairs during growth.

None of the CBE samples showed detectable lines due to H-C_{As} pairs in their as-grown state, in agreement with recent results for GaAs doped using CBr_4.[36] After these samples had been exposed to a hydrogen/deuterium plasma, IR spectra indicated that significant passivation had occurred.[28] The measured frequencies of the eight possible A_1 modes and six of the possible eight E modes (Y) of H-C_{As} pairs with the four different isotropic combina-

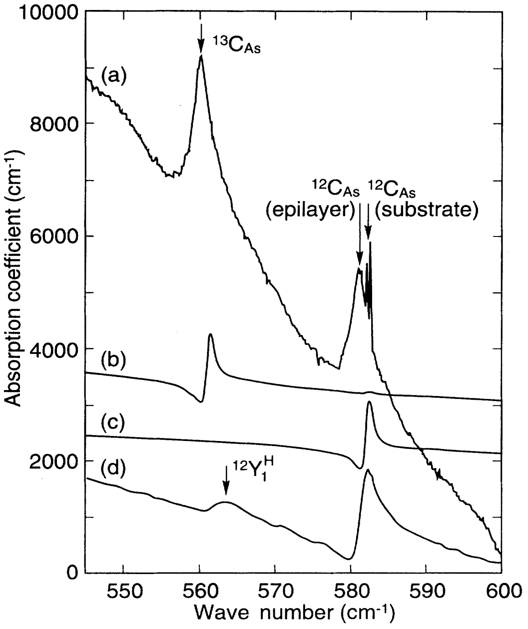

FIG. 2. IR absorption spectra of (a) ^{12}C/^{13}C doubly doped as-grown CBE GaAs [sample (c)], (b) ^{13}C-doped as-grown CBE GaAs [sample (b)], (c) ^{12}C-doped as-grown CBE GaAs [sample (a)] and (d) GaAs:^{12}C grown by MOVPE [sample (d)]. For clarity the spectra have been shifted vertically by $-134\,000$, -7000, -7700, and $-20\,000$ cm^{-1}, respectively.

tions are given in Table I for samples (a) and (b). The frequencies of the stretch modes measured for the more highly doped samples (c) and (d) were shifted up by 1–1.5 cm^{-1} due to the increased strain[36] in these epilayers. The antisymmetric E^- mode of H-C_{As} (Y_2^{H}) was not detected for either C isotope, possibly because of a weak associated dipole moment as predicted by LDF theory.[23]

B. Raman scattering

The low-temperature (77 K) Raman spectra of (1) ^{12}C and (b) ^{13}C-doped CBE GaAs in the as-grown state are shown in Fig. 3. The spectra were excited at 2.71 eV, which is below the E_1-band gap of GaAs.[37] The LVM's of $^{12}C_{As}$ and $^{13}C_{As}$ are well resolved at frequencies of 581.5 and 561.1 cm^{-1} (Table I). The Raman spectrum of an as-grown CBE sample, doubly doped with ^{12}C and ^{13}C in about equal concentrations, is displayed in Fig. 3(c). The spectrum recorded for crossed polarizations $[x(y,z)\bar{x}]$ was excited at 3.00 eV in resonance with the GaAs E_1-band gap.[37] For this scattering configuration the LVM's of both $^{12}C_{As}$ and $^{13}C_{As}$ were well resolved, whereas for parallel polarizations ($[x(z,z)\bar{x}]$ configuration, not shown) these signals were completely suppressed. The observed polarization selection rules are consistent with the assignment of these LVM's to F_2 modes of centers with T_d symmetry.[38] Resonantly enhanced 2LO-phonon scattering, which masks the resonant excitation of the $^{12}C_{As}$ LVM in less heavily doped samples (see later Fig. 5 and Ref. 26), is almost completely suppressed in the present sample. The suppression of this 2LO-phonon signal is most probably due to the high doping level[39] which modifies the spectrum of interband electronic transitions and thus broadens and lowers the resonance profile for intrinsic Fröhlich-induced 2LO-phonon scattering.[40]

Raman spectra excited at 3.00 eV, in resonance with the E_1-band gap,[37] from as-grown MOVPE GaAs:C containing H-$^{12}C_{As}$ centers are displayed in Figs. 4 and 5 for the frequency range where the symmetric A_1^+ modes (X^{H}) are known to occur and the E^- modes (Y^{H}) were expected. The $^{12}X^{H}$ mode was significantly stronger when the polarizations of the incident and scattered light were parallel to each other, i.e., for $[x(z,z)\bar{x}]$ and $[x(z',z')\bar{x}]$ (Fig. 4) than for crossed polarizations $[x(y,z)\bar{x}]$ and $[x(y',z')\bar{x}]$, where x, y, and z denote $\langle 100\rangle$ crystallographic directions and y' and $z'\langle 110\rangle$ directions. This dependence of the scattered intensity on the polarizations is consistent with the selection rules for an A_1 mode of a defect center with C_{3v} symmetry.[38] In the frequency range from 500 to 800 cm^{-1} (Fig. 5), two modes of the H-$^{12}C_{As}$ center are resolved at 562.5 and 738.6 cm^{-1}, labeled $^{12}Y_1^{H}$ and $^{12}Y_2^{H}$, while the LVM of isolated $^{12}C_{As}$ overlaps resonantly enhanced scattering by two longitudinal-optical (2LO) phonons. The two Y^{H} lines are observed for both parallel $[x(z,z)\bar{x}]$ and $(x(z',z')\bar{x}]$ and crossed $[x(y,z)\bar{x}]$ and $[x(y',z')\bar{x}]$ polar-

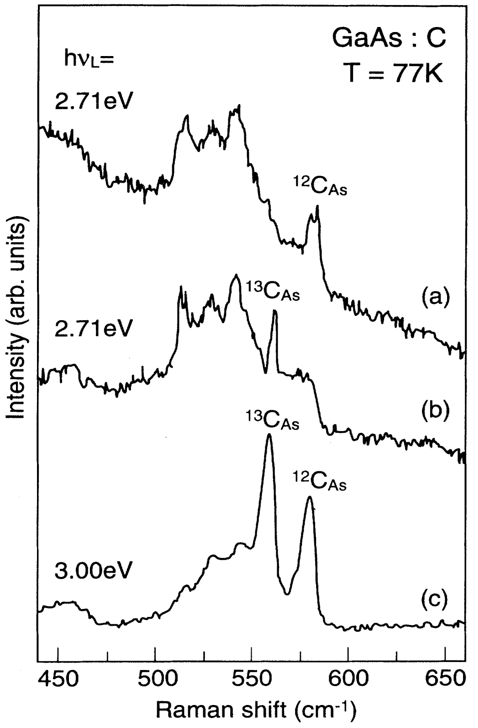

FIG. 3. Low-temperature Raman spectra of (a) ^{12}C-doped, (b) ^{13}C-doped and (c) ^{12}C/^{13}C doubly doped as-grown CBE GaAs [sample (a), (b), and (c)]. Spectra (a) and (b) were excited at 2.71 eV, while spectrum (c) was excited at 3.00 eV.

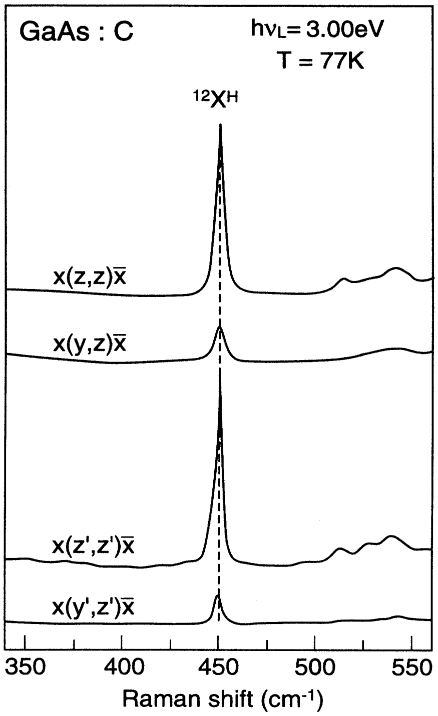

FIG. 4. Low-temperature Raman spectra of GaAs:^{12}C grown by MOVPE [sample (d)] covering the frequency range of the X^H line. The spectra excited at 3.00 eV were recorded for the different scattering configurations indicated in the figure.

izations, which allows us to assign these lines to scattering by E modes.[38] The $^{12}Y_1^H$ mode has been observed in IR absorption,[27,28] whereas the hydrogenlike E^- mode (Y_2^H) was not detected. The present Raman measurement is therefore of primary importance in relation to previous modeling.

Figure 6 shows the $X^{H(D)}$ A_1^+ mode for samples grown by CBE that were either ^{12}C or ^{13}C doped and which had been passivated with either hydrogen or deuterium. The hydrogen-passivated samples showed scattering by only the $^{12}X^H$ (or $^{13}X^H$) mode. In the deuterium-passivated material both the $^{12}X^D$ (or $^{13}X^D$) modes and weaker $^{12}X^H$ (or $^{13}X^H$) mode were resolved, indicating that the deuterium treatment also led to the incorporation of hydrogen. The observed mode frequencies (Table I) are in reasonable agreement with those measured by IR absorption.

Raman spectra covering the frequency ranges of the $X^{H(D)}$ and $Y^{H(D)}$ models are plotted in Figs. 7 and 8 for ^{12}C/^{13}C doubly doped samples passivated with hydrogen or deuterium. The $X^{H(D)}$ modes corresponding to the various isotopic combinations are well resolved (Fig. 7), even though the individual linewidths are slightly larger than those observed in less heavily doped samples (see Fig. 6). However, the $^{12}Y_1^D$ and $^{13}Y_1^D$ modes (E^+ symmetry) are hardly resolved on the high-frequency side of the

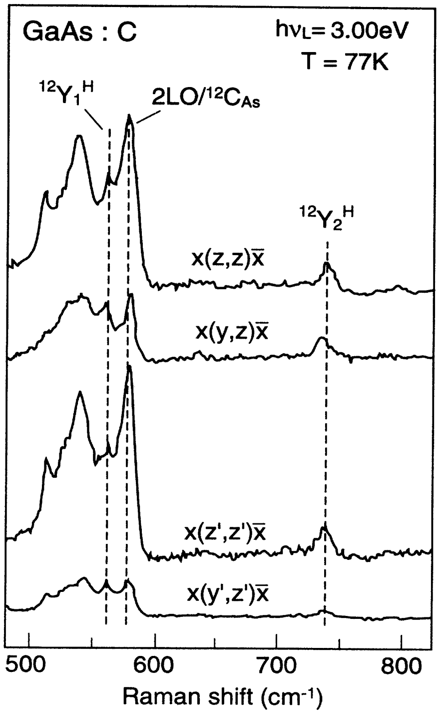

FIG. 5. Low-temperature Raman spectra of GaAs:^{12}C grown by MOVPE [sample (d)] covering the frequency range of the Y^H lines. The spectra excited at 3.00 eV where recorded for the different scattering configurations indicated in the figure.

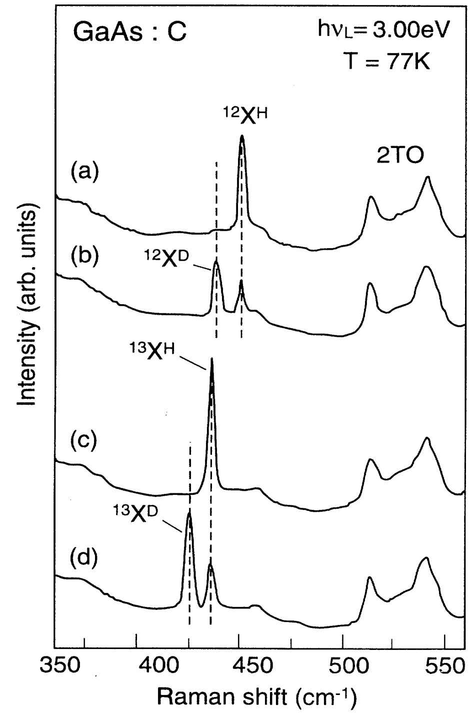

FIG. 6. Low-temperature Raman spectra of (a) hydrogen-passivated ^{12}C-doped, (b) deuterium-passivated ^{12}C-doped, (c) hydrogen-passivated ^{13}C-doped, and (d) deuterium-passivated ^{13}C-doped CBE GaAs [samples (a) and (b)]. The spectra were excited at 3.00 eV.

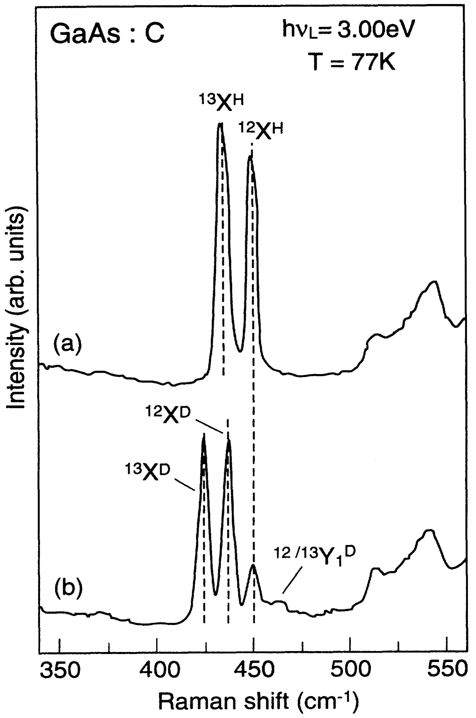

FIG. 7. Low-temperature Raman spectra of (a) hydrogen-passivated and (b) deuterium-passivated $^{12}\mathrm{C}/^{13}\mathrm{C}$ doubly doped CBE GaAs [sample (c)]. The spectra excited at 3.00 eV cover the frequency range of the $X^{\mathrm{H(D)}}$ lines.

$^{12}X^{\mathrm{H}}$ line (Fig. 7). The $^{12}Y_1^{\mathrm{H}}$ mode almost coincides in frequency with the LVM from isolated $^{13}\mathrm{C_{As}}$ and thus only the superposition of these two modes is observed [Fig. 8(a)]. At higher frequencies there are two well-resolved peaks in the deuterium-passivated sample corresponding to the $^{12}Y_2^{\mathrm{D}}$ and $^{13}Y_2^{\mathrm{D}}$ modes (E^- symmetry) [Fig. 8(b)]. In the spectrum of the hydrogen-passivated sample there is just one broadened peak in the frequency range expected for the hydrogenlike E^- mode. The peak is assigned to the superposition of the previously undetected $^{12}Y_2^{\mathrm{H}}$ and $^{13}Y_2^{\mathrm{H}}$ modes [Fig. 8(a)].

The scattering strength of the X^{H} (A_1^+) mode is strongly enhanced for optical excitation with photon energies of about 3 eV.[41] However, a strong resonant enhancement does not occur for scattering by the Y^{H} (E) modes, as is evident from the comparison of the mode intensities in Figs. 4 and 5, where the strength of the intrinsic second-order phonon band at $\simeq 540\ \mathrm{cm}^{-1}$ serves as a reference. The scattering strengths per defect center of these E modes, as well as that of the high-frequency antisymmetric A_1^- stretch modes (see below), are comparable to or even weaker than, those for scattering by centers with T_d symmetry, such as the isolated $\mathrm{C_{As}}$ acceptor,[26] $\mathrm{Be_{Ga}}$,[13] and $\mathrm{Si_{As}}$ (Ref. 42) acceptors. The reason for the extraordinarily strong resonant enhancement of the scattering by the X^{H} mode of H-$\mathrm{C_{As}}$ pairs is still unclear.

Raman spectra of the H (D)-$\mathrm{C_{As}}$ stretch modes in the $^{12/13}\mathrm{C}$ doubly doped sample are shown in Fig. 9. For both the H-$\mathrm{C_{As}}$ and the D-$\mathrm{C_{As}}$ stretch modes the $^{12}\mathrm{C}/^{13}\mathrm{C}$ isotopic splitting is resolved. The somewhat larger split-

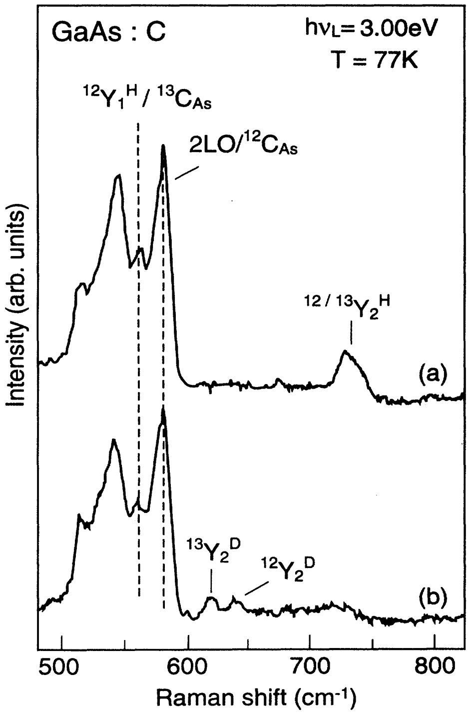

FIG. 8. Low-temperature Raman spectra of (a) hydrogen-passivated and (b) deuterium-passivated $^{12}\mathrm{C}/^{13}\mathrm{C}$ doubly doped CBE GaAs [sample (c)]. The spectra excited at 3.00 eV cover the frequency range of the $Y^{\mathrm{H(D)}}$ lines.

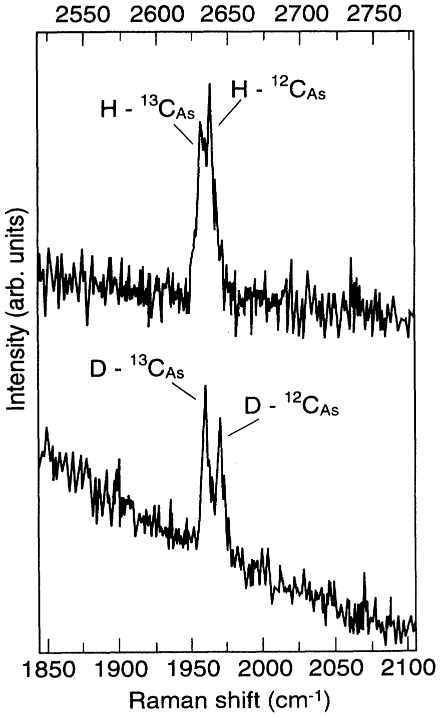

FIG. 9. Low-temperature Raman spectra of hydrogen- (top) and deuterium-passivated (bottom) $^{12}\mathrm{C}/^{13}\mathrm{C}$ doubly doped CBE GaAs [sample (c)]. The spectra were excited at 3.00 eV.

ting for the D-C_{As} mode than for the H-C_{As} mode, is consistent with Fourier transform infrared (FTIR) absorption data (Table I), although the absolute Raman mode frequencies are about 1.5 to 3 cm^{-1} higher than the IR frequencies. This shift is due to the combination of the greater lattice contraction[36] in the more highly doped samples used for the Raman measurements and the higher sample temperature during these measurements.[43]

In summary, the Raman measurements have confirmed all the assignments of the mode symmetries, and also led to the observation of the hydrogenlike wag modes of H-^{12}C and H-^{13}C pairs. We next made comparisons with the coupled oscillator model and the results of updated LDF theory.[30–32]

IV. MODELING OF MODES

The H-C_{As} pair has been modeled as a H atom and a C atom coupled together by a spring with force constant $k_{H\text{-}C}$ and springs with force constants K_H and k_C connecting the individual masses to rigid walls (see Fig. 10). This coupled oscillator model was found to give reasonable agreement with the frequencies of the various modes measured by IR-absorption spectroscopy by choice of appropriate (different) force constants for the transverse (E modes) and longitudinal (A_1 modes) displacements of the atoms relative to the pair axis.[28] The force constants required to fit to the transverse (T) E mode frequencies were $k_C^T=243.4$ N/m, $k_H^T=9.2$ N/m, and $k_{H\text{-}C}^T=20.5$ N/m. This fit predicted that the then-undetected hydrogen wag mode (E^-, $^{12}Y_2^H$) should have a frequency of 745 cm^{-1}, only 7 cm^{-1} above the frequency of 738.6 cm^{-1} now detected by Raman spectroscopy on the MOVPE-grown sample. By including this frequency in the fitting procedure, the force constants are changed by a small amount to $k_C^T=244.6$ N/m, $k_H^T=9.2$ N/m and $k_{H\text{-}C}^T=20.0$ N/m, which reproduces all the E-mode frequencies with a maximum difference of ~ 2 cm^{-1} (see Table I). Line $^{13}Y_2^H$ was not included in this fit, since this Raman peak was rather broad and was not resolved from line $^{12}Y_2^H$ for the highly codoped sample. This line was not detected for the sample doped only with ^{13}C due to the lower concentration of H-$^{13}C_{As}$ pairs. It should be noted that corrections to allow for anharmonicity could not be estimated from isotopic shifts in this simple modeling because of the anticrossing of the E modes.

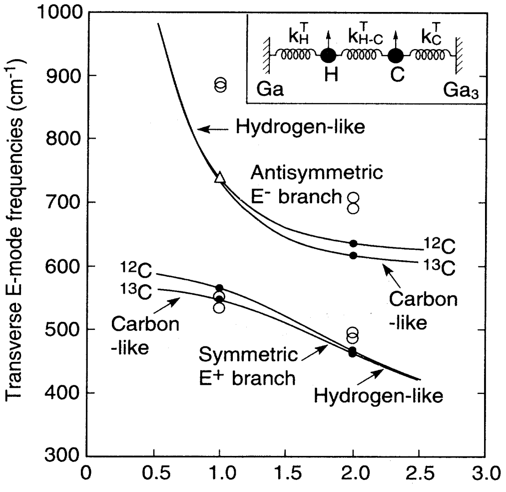

FIG. 10. Vibrational transverse E modes of the coupled masses shown in the inset, used as a simple model to represent the H-C_{As} pair, with force constants of $k_H^T=9.2$ N/m, $k_{H\text{-}C}^T=20.0$ N/m, and $k_C^T=244.6$ N/m. The filled circles are the experimental frequencies as measured by IR spectroscopy; the open triangle is the frequency of the E^- mode of the H-$^{12}C_{As}$ pair (H wag) measured by Raman scattering; the open circles are the results of the updated *ab initio* LDF theory (Refs. 30 and 31). The important feature is the strong anticrossing of the modes which changes their effective identifies as the mass increases.

The coupled oscillator model has also been applied to the modes with A_1 symmetry, for which the force constants refer to displacements of the atoms along the pair axis.[28] The frequencies obtained from this model are reproduced in Table I. It was found that the model overestimated the isotopic shift of the stretch modes for replacement of H with D; however, after correcting the experimentally measured frequencies for anharmonicity, much better agreement was obtained. An anharmonic correction of B/m was added to the measured frequencies, where the anharmonicity factor B was estimated to be 176 amu cm^{-1}, and m was the hydrogen (or deuterium) mass in amu.[28] These frequencies are given in brackets in Table I.

The ratios of the C to H displacement for the various modes obtained by the above modeling are in good agreement with the results of the LDF theory (Table III).[32] The greatest discrepancies are for the E modes of D-C_{As}

TABLE III. Ratio (C/H) of the displacements of C to H for the different local modes of H-C_{As} pairs in GaAs obtained from the normal coordinates of *ab initio* calculations (Refs. 30–32) and the coupled oscillator model.

Mode	*ab initio*	Model
H-$^{12}C_{As}$(A_1^-, stretch)	−0.074	−0.078
H-$^{13}C_{As}$(A_1^-,stretch)	−0.071	−0.072
D-$^{12}C_{As}$(A_1^-,stretch)	−0.16	−0.16
D-$^{13}C_{As}$(A_1^-,stretch)	−0.14	−0.15
H-$^{12}C_{As}$(A_1^+,$^{12}X^H$)	1.11	1.08
H-$^{13}C_{As}$($A_1^+$$^{13}X^H$)	1.11	1.04
D-$^{12}C_{As}$(A_1^+,$^{12}X^D$)	1.06	1.05
D-$^{13}C_{As}$(A_1^+,$^{13}X^D$)	1.05	1.02
H-$^{12}C_{As}$(E^-,$^{12}Y_2^H$)	−0.13	−0.16
H-$^{13}C_{As}$(E^-,$^{13}Y_2^H$)	−0.11	−0.14
D-$^{12}C_{As}$(E^-,$^{12}Y_2^D$)	−0.46	−0.93
D-$^{13}C_{As}$(E^-,$^{13}Y_2^D$)	−0.39	−0.78
H-$^{12}C_{As}$(E^+,$^{12}Y_1^H$)	0.63	0.51
H-$^{13}C_{As}$(E^+,$^{13}Y_1^H$)	0.66	0.38
D-$^{12}C_{As}$(E^+,$^{12}Y_1^D$)	0.35	0.18
D-$^{13}C_{As}$(E^+,$^{13}Y_1^D$)	0.38	0.18

that are the most strongly coupled and show the greatest mixing. It has been demonstrated by theory that these modes also have the largest displacement of the nearest-neighbor Ga atoms of the C_{As} atoms.[32] For the A_1^- mode the average Ga displacement is essentially zero but for the E^- mode it is ~4% of the C displacement while for the symmetric modes this rises to ~8% and there is an even higher value of ~11% for D-E^+ modes. The relatively small displacements of the neighboring Ga atoms in the modes of H-C_{As} pairs, calculated by LDF theory, justifies the use of the coupled oscillator model to give a simple physical interpretation of the various modes, but limitations of the model are also indicated.

V. DISCUSSION AND CONCLUSIONS

The present Raman data give a complete set of LVM frequencies of the H(D)-$^{12/13}C_{As}$ center for all four possible isotopic combinations. This set includes now the hydrogenlike E^- mode for the H-$^{12/13}C_{As}$ isotopic combinations. The assignment of the various LVM Raman lines to specific modes has been confirmed by polarization-dependent Raman measurements which allow the mode symmetries to be determined. Only the low-frequency A_1^+ mode ($X^{H(D)}$ line) of the H-C_{As} center shows a strong resonant enhancement in its scattering strength for incident photon energies of $\simeq 3$ eV.

The coupled oscillator model gives a good physical picture of the character of the modes of H-C_{As} pairs, as shown by the closeness of the predicted frequency of the hydrogen E^- mode to that now measured by Raman spectroscopy, and there is also good agreement of the relative displacements of the C and H atoms with the results of LDF theory.[32] The crossover in the character of the E modes on going from H to D is evident in both the model and the LDF theory (Fig. 10).

A recent plane-wave supercell calculation also led to the result that the H atom should be more stable at the bond-centered site by (0.6 eV) compared with the antibonding site.[44] The plane-wave approach gave H-C_{As} stretch and H-wag (E^-, $^{12}Y_2^H$) frequencies of 2781 and 724 cm^{-1}. These values are close to the frequencies determined experimentally, but are lower than those predicted by the updated LDF theory. Unfortunately, the symmetric mode frequencies were not given in Ref. 44, and so a more complete comparison of the plane-wave supercell calculation with experimental results is not possible. No account of the effects of anharmonicity was taken in this theoretical work.

The combination of specially grown samples suitable for IR and Raman measurements has resulted in a significant advance in the characterization of H-C_{As} pairs in GaAs, and demonstrates the value of applying more than one technique to the study of a particular system.

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