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Theory of the structure and dynamics of the C impurity and C-H complex in GaAs

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Carbon is an important impurity in metalorganic molecular-beam-epitaxy-grown GaAs. C_{As} is a single acceptor that can be passivated by H. We describe local-density-functional cluster calculations on the structure and dynamics of the impurities and passivated complexes. The lowest-energy structure of the passivated acceptor is a H atom located 1.1 Å from C in a bond-centered orientation. The H-Ga distance is 2.1 Å. The other three C-Ga lengths are 2.18 Å. The H stretch frequency is found to be 2605 cm^{-1} and is observed at 2635 cm^{-1}. We have also calculated C-H bend modes that should be visible in Raman but not in infrared experiments. The activation energy for the reorientation of the complex is 0.67 eV. Also described are the local modes of the two substitutional C defects in addition to a C-C pair. Modes of the latter are found around 553 and 425 cm^{-1}, respectively, and have effective charges of about 0.5.

I. INTRODUCTION

Hydrogen can form complexes with intrinsic and extrinsic defects in semiconductors. Some of these defects are then made electrically inactive, and this is of interest from a technological viewpoint. A review of the passivation of impurities with shallow levels in GaAs is found in Ref. 1. Previous theoretical work[2] had shown that H at a *T*-interstitial site has a level below that of bond-centered H. This suggests that H would take up a bond-centered position in the case of shallow acceptor passivation and a *T* site in the case of donor passivation. In fact the situation is somewhat more complex because for the Si donor, Si_{Ga}, the H atom moves away from the *T* site to within 1.6 Å of a displaced Si atom leaving one of the Si—As bonds broken. In the case of a Be acceptor, Be_{Ga}, H moved from the bond-centered site to within 1.54 Å of one of the As neighbors, whereas Be moved in the opposite direction with Be-H becoming 1.77 Å.

Since the complexes are electrically inactive, there are few techniques able to give details of the structure. The changes in bonding described above do, however, imply substantial changes to the local mode frequencies that can be detected by infrared spectroscopy provided the concentrations and effective charges are large enough. The As-H and Si-H stretch frequencies are easily seen, and calculated, but only the Si-H bend frequency lies above the one-phonon peak. However, the back Be—As bonds and Si—As bonds are shortened and lead to *E*-local-mode frequencies higher than those of the substitutional defects.

Clerjaud *et al.*[3] found a C-H stretch frequency at 2635 cm^{-1} in liquid-encapsulated Czochralski (LEC) grown GaAs contaminated by C and H. This was recognized as such by the observation of a shift (≈ 7 cm^{-1}) expected from ^{13}C-H. Further support for this interpretation is given by the isotopic shift in the C-D line at 1969 cm^{-1}.[4] If H lay in a bond-centered orientation, then analogy with the Be $\cdots$ H—As complex suggests low-lying H bend modes and a C local mode *higher* than that due to the substitutional defect should occur. In fact, we find here that the very small C-H length causes the back C—Ga bonds to lengthen and this lowers the C local modes. Moreover, although the C-H bend frequencies are much lower than those of methane, they still lie above the one-phonon peak, but their effective charge is very small and this renders them infrared inactive.

Woodhouse *et al.*[5] found the hole concentration of metalorganic molecular-beam-epitaxy- (MOMBE) grown GaAs containing a high concentration, $\approx 10^{20}$ cm^{-3}, of C as measured by secondary-ion-mass spectroscopy (SIMS), to be only about one-half that of C and this could be further reduced (by a factor up to 5) after a rapid transient anneal in an atmosphere containing AsH_3. Infrared spectroscopy then not only showed lines at 2635 cm^{-1} ascribed to C-H stretch modes and also 582 cm^{-1} due to $^{12}C_{As}$, but also in one sample, two less intense lines at 453 and 563 cm^{-1} called *X* and *Y*, respectively. These lines had relative intensities of almost 1:2, and arose from defects with concentrations about a few percent of C, assuming an effective charge of unity. More recent work[6] shows the relative intensity of these lines is sample dependent indicating that distinct defects are involved. It had previously been shown[7] by an x-ray study that C occupies a substitutional site and the hole activity confirmed its preference for an As one, in contrast to Si. Woodhouse *et al.*[5] suggested that the higher-frequency one is due to C_{Ga}. It is clear that about half of the carbon is present in a form other than C_{As} and possibilities include C_{Ga} and a C-C pair. We find the former would be a donor with modes around 538 cm^{-1}, and the latter has a midgap empty state (possibly leading to a luminescence band) and

TABLE I. Frequencies in cm^{-1} of the vibrational modes of methane.

Mode	Theory	Expt. (Ref. 13)
A	2947	2916
F	1180	1306
E	1444	1533
F	3135	3019

vibratory modes close to 563 and 453 cm^{-1}.

To investigate these defects we have carried out *ab initio* local-density-functional cluster calculations of the structure and local modes of vibration of substitutional C in GaAs, three sorts of C-H complexes, and the C-C pair. In addition, the activation energy for the reorientation of H in the bond-centered defect is evaluated as well as the effective charge in a vibrational mode. The method used has been discussed previously.[8–10,2,11] We use clusters ranging in size from 72 atoms to 103. Each cluster is terminated with H to prevent dangling-bond states arising whose occupation would lead to charge transfer from the central impurity atoms to the surface. More details of the method are given in Refs. 8 and 9 and in Sec. II. To illustrate the accuracy involved, we show in Table I the modes for methane. We found the C—H length to be 1.102 Å compared to the observed 1.093 Å. It is seen that the error in the frequencies is worse for the low-frequency F mode but less than about 100 cm^{-1} for the other modes.

II. METHOD

The structures and modes of the isolated substitutional impurities were found with tetrahedral 71-atom clusters. Nontetrahedral clusters can produce an electrical field and stress at the center that may perturb the structure of the isolated impurity. However, such tetrahedral clusters are charged and this requires a modification to the way in which the charge density is expanded. This has been discussed previously.[10] The essential point is to expand the charge density in a basis set of functions of the form

$$(1-\tfrac{2}{3}\alpha_k r^2)\exp(-\alpha_k r^2) \tag{1}$$

together with a term centered on each atom i of the form

$$Q_i(\beta_i/\pi)^{3/2}\exp(-\beta_i r^2)\ . \tag{2}$$

Here, α_k, $k=1,\ldots,$ and β_i are determined by fits to the atomic charge density. Q_i is the national charge on the atom i, which we have taken to be the number of valence electrons except when dealing with charged clusters. The total charge arising from the first set of functions is of course zero and so the total electronic charge in the cluster is just

$$\sum_i Q_i\ . \tag{3}$$

The point of the first set of functions is that they each give rise to a potential of the form

$$\frac{2\pi}{3\alpha_k}\exp(-\alpha_k r^2) \tag{4}$$

and hence matrix elements of this potential with respect to Gaussian orbitals are trivial to compute. The second term gives a long-ranged potential:

$$Q_i \operatorname{erf}(\sqrt{\beta_i}\, r)/r\ . \tag{5}$$

We selected Q_i for H, C, and As to be 1, 4, and 5 and chose it for Ga to be whatever was necessary to account for the cluster charge. Values of α_k and β_i were found from fits to the atomic charge densities. A wave-function basis of four independent s and p Gaussian orbitals was centered on each of the inner atoms (five for the 71-atom clusters and nine in the 87 - and 103-atom clusters) and a fixed linear combination of four s (and likewise p) orbitals was placed on more remote As and Ga atoms. A fixed combination of two s (and p) orbitals was placed on the terminating H atoms, but these were allowed to be a variable combination for the passivating H atom. The charge density was fitted with a basis of five-atom centered Gaussian functions with different α_k on the Ga, As, and C atoms and three Gaussian functions for the H atoms. In addition, orbitals were placed at the center of the innermost bonds. For the 71-atom tetrahedral clusters, five atoms were allowed to move and nine were allowed in the 87-atom cluster. Once the relaxed structures were found, the second derivatives of the energy with respect to the innermost atoms could be evaluated and these were used to construct part of the dynamical matrix for the 71- and 87-atom clusters. The second derivatives between an atom and any more remote atom was taken from the Musgrave-Pople potential:

$$\begin{aligned} V_i = {} & \tfrac{1}{4}\sum_{j} k_r^{(i)}(\Delta r_{ij})^2 + r_0^2/2 \sum_{j>k} k_\theta^{(1)}(\Delta\theta_{jik})^2 \\ & + r_0 \sum_{k>j} k_{r\theta}^{(i)}(\Delta r_{ij}+\Delta r_{ik})\Delta\theta_{jik} \\ & + \sum_{k>j} k_{rr}^{(i)}\Delta r_{ij}\Delta r_{ik} + r_0^2 \sum_{l>k>j} k_{\theta\theta}^{(i)}\Delta\theta_{jik}\Delta\theta_{kil}\ . \end{aligned} \tag{6}$$

Here, Δr_{ij} and $\Delta\theta_{ijk}$ are the changes in the length of the i—j bond and the angle between the i—j and i—k bonds, respectively. The sum is over the nearest-neighbor atoms only. Table II gives the coefficients $k_r^{(i)}$, $k_\theta^{(i)}$, $k_{r\theta}^{(i)}$, $k_{rr}^{(i)}$, and $k_{\theta\theta}^{(i)}$ derived earlier.[11] This potential results in the highest optic mode at 293 cm^{-1}, in agreement with observation. The atomic masses of Ga and As were taken as 70 and 75, respectively. The surface H atoms were given a very large mass and previous applications[2] have shown that these clusters are sufficiently large for the effects of the vibrations of the surface H to be negligible for localized modes.

We have previously shown that the method can evaluate accurately the dipole moments[8] for molecules like water. Thus, in principle, we can evaluate the effective

TABLE II. Parameters for the Musgrave-Pople potential for GaAs in eV/Å^2, $r_0=2.37$ Å.

	k_r	k_θ	$k_{r\theta}$	k_{rr}	$k_{\theta\theta}$
Ga	8.07	0.974	0.153	0.373	0.491
As	8.07	−0.111	0.219	0.373	−0.250

charge η, which governs the intensity of infrared absorption.[12] η is found by computing the change in the adiabatic dipole moment of the cluster when the ions are displaced by $\pm u_{l,i}/\sqrt{M_i}$. Here, $u_{l,i}$ is the normal mode coordinate of atom i, with mass M_i, along the direction l. In addition, the polarizability, which is just the derivative of η with respect to the displacement, can also be found and relates to the intensity of the Raman line.

III. THE SUBSTITUTIONAL DEFECTS: C_{As} AND C_{Ga}

We used the tetrahedral 71-atom cluster $C^-Ga_{16}As_{18}H_{36}$ where C replaces the central As atom. This cluster has the central C atom surrounded by four Ga atoms, which are themselves surrounded by twelve As atoms. These are in turn joined to twelve more distant Ga and H atoms. These Ga atoms were joined to six As atoms and a further 24 H atoms saturated the surface bonds. Each of C, As, and Ga has four occupied covalent bonds and H has one, thus the cluster contains 176 electrons. Hence there is a net charge of two protons as there are 178 of the latter. The forces on the innermost five atoms were found and the structure relaxed. We found the C atom remained on site, the four C—Ga bonds being 2.03 Å. The gap was clear of levels, showing that the acceptor level of the C impurity is very low indeed. The triplet vibratory modes for ^{12}C were found at 556, 543, and 533 cm^{-1}. Their splitting indicated the numerical errors in locating the T_d relaxed structure and in evaluating the second derivatives numerically. The average mode is then at 544 cm^{-1} and is to be compared with the observed one at 582 cm^{-1}.

For the unreported donor, C_{Ga}, we used the cluster $C^+As_{16}Ga_{18}H_{36}$, which is now charged with two electrons. The relaxed structure again has a clear gap showing that the neutral C atom would be a shallow donor. The C—As bond is 2.08 Å and the three local modes for ^{12}C are 533, 540, and 542 cm^{-1}. Thus the mean is 538 cm^{-1}, slightly lower than that of the acceptor. These results are similar to the case of Si (Ref. 12), where the frequency of Si_{Ga} at 384 cm^{-1} is just below that of Si_{As} at 399 cm^{-1}.

IV. THE C_{As}-H COMPLEX

A stoichiometric 87-atom cluster centered on a bond center, with C placed at a central As site and H placed in the bond-centered position, was relaxed and led to a stable configuration with C—H, H—Ga, and the three C—Ga bonds equal to 1.12, 2.05, and 2.18 Å, respectively. The Ga-C-H and H-Ga-As angles are close to 99°. Thus H has been considerably displaced from the bond center and the C-Ga lengths are longer than in the substitutional centers, suggesting lower C vibrational modes. The gap was cleared of levels thus showing very effective passivation. The effect of cluster size was investigated using a larger 103-atom cluster, where we found these lengths to be 1.13, 2.20, and 2.17 Å, respectively. The greatest difference involves the weak H-Ga distance. The second derivatives of the energy were evaluated between the inner six atoms, i.e., H, C, and their neighbors. The resulting local modes are given in Table III.

The resulting C-H stretch modes agree well with the observed ones. The slightly larger C-H length accounts for the drop in the stretch frequency from that of methane. The angle force constant drops by a factor of almost 4 leading to H bend modes around 720 cm^{-1}. However, there are no reports of these modes or of combination bands at 3300 cm^{-1}.

If the C-H distance was infinitesimal, then the complex is isoelectronic with As. This would result in equal C—Ga bond lengths. The complex appears to possess a large radius as these lengths are longer than 2.03 Å, and hence the triplet mode is lower than the 582 cm^{-1} attributed to C_{As}. This can explain why no C local modes would arise beyond this frequency, in contrast to the passivated Be_{Ga} complex.[2] We find the three modes lower than 582 cm^{-1} and rather close together. These low-frequency modes might be difficult to detect because of the interference from lattice absorption. The carbon *A* mode involves a displacement of C in phase with H but out of phase with the three Ga neighbors. Surprisingly, it is at a higher frequency than the *E* mode.

The activation energy for H reorientation among the four bond centers was then calculated in the following way: we moved H to the *C* site, i.e., a site equidistant with two Ga neighbors of the C atom. The inner 12 atoms were then relaxed with constraints that required both H and C to remain equidistant from these neighbors. This procedure was followed previously in the case of O diffusion in Si (Ref. 14), where it was shown that the resulting structure was indeed a saddle-point one. The energy difference with the starting configuration is 0.67 eV. This is close to the observed energy[15] of 0.5 eV.

The agreement with experiment here suggests that high frequency of the H bend modes is correct and their invisibility stems from a small effective charge. We calculated this quantity for the H modes as described above. For the stretch mode we found η to be 0.96, whereas for the bend modes η is 0.036. Thus the ir intensity of the bend modes would be only about 0.3% that of the stretch mode. This explains why they have not been observed. On the other hand, the polarizabilities of the modes are much closer together so they should be observable by Raman spectroscopy. It is likely that the small value of η arises from an occupied carbon *p* orbital pointing towards H, which easily follows the H motion. This would explain why the dipole moment is largely unaltered when H

TABLE III. Frequencies in cm^{-1} of the local modes of the bond-centered C-H-Ga complex.

Mode	^{12}C-^1H	^{13}C-^1H	^{12}C-^2H
H, stretch	2605	2598	1905
H, bend	730	729	540
	707	704	528
C, *A*	413	399	402
C, *E*	392	379	376
	367	355	355
Observed (Refs. 3 and 4)			
H, stretch	2635	2628	1969

TABLE IV. Frequencies in cm^{-1} of the local modes of the antibonding H-C-Ga complex.

Mode	^{12}C-^{1}H	^{13}C-^{1}H	^{12}C-^{2}H
H, stretch	3261	3252	2384
H, bend	728	728	520
	685	685	493
C,*E*	333	323	332
	304	299	303
C,*A*	296	293	293

moves in a direction perpendicular to the C—H bond, as well as the low bending force constant compared to methane.

H was then placed at an antibonding site of the 87-atom cluster, which when relaxed, yielded an energy 0.5 eV greater than the bond-centered defect above. However, the gap was also cleared of energy levels showing that this metastable complex would also be electrically inactive. Its structure consists of the C atom being displaced towards the H site with the H—C, C—Ga(1), and C—Ga(3) bond lengths being 1.08, 2.82, and 2.24 Å, respectively. The local modes are given in Table IV.

It is clear that they are further from the observed ones and this confirms the assignment[3] of the 2635-cm^{-1} mode to a bond-centered C-H-Ga complex.

V. THE PASSIVATED C_{Ga} COMPLEX

There are no reports of the C_{Ga} donor or its complex with H but we have calculated their properties. In analogy with previous work on the Si donor,[2,11] H is expected to lie at an antibonding site with a lengthening of one of the C—As bonds. Calculations carried out on the 87-atom cluster showed this had a length of 3.16 Å and is clearly broken. The H-C and other C-As lengths were 1.08 and 2.12 Å. The local modes are given in Table V. It is again unlikely that the *E* and *A* local modes account for the *X* and *Y* lines as the high-frequency C-H stretch mode is not observed.

VI. THE C-C PAIR DEFECT

A pair of C atoms placed next to one another in an 86-atom cluster and relaxed together with their six neighbors gave C-Ga, C-As, and C-C lengths of 2.12, 2.27, and 1.83 Å, respectively. The former are greater than those of the isolated defects and the C—C bond is longer than in diamond (1.54 Å). The longer C-Ga and C-As lengths suggest lower frequencies than the isolated substitutional defects. There is in fact a metastable defect with short C—As and C—Ga bonds and a much longer C—C bond having energy 0.5 eV greater.

TABLE V. Frequencies in cm^{-1} of the local modes of the antibonding H-C-As complex.

Mode	^{12}C-^{1}H	^{13}C-^{1}H	^{12}C-^{2}H
87-atom cluster			
H, stretch	3246	3236	2380
H, bend	1115	1115	795
	1105	1105	787
C,*E*	516	497	514
	477	459	476
C,*A*	414	401	401

TABLE VI. Frequencies in cm^{-1} of the local modes of the C-C pair defect.

Mode	^{12}C	^{13}C
E	556	534
	551	530
A	425	410
E	383	370
	381	367

The gap contained a filled level very close to the top of the valence band but there is an empty level around midgap whose wave function is an antibonding combination of sp^3 orbitals on the C atoms. This reflects the weakness of the C—C bond. The local mode frequencies are given in Table VI. There are six frequencies due to these two atoms and five could be clearly seen above the one-phonon peak. Because of the C_{3v} symmetry, the six modes are composed of two *E* and two *A* modes. The highest is the *E* mode with displacements of the C atoms, out of phase with each other, in transverse directions. The only *A* mode above the one-phonon peak is one in which the two C atoms move in phase. The other mode for which the C-C distance increases is presumably a soft mode due to the existence of the metastable state above. The second *E* mode, consisting of transverse motion of the two C atoms in phase with one another, occurs at a lower frequency. The higher modes are close to *Y* and *X* observed at 563 and 453 cm^{-1}, respectively. The effective charges of the modes are 0.48 and 0.55, respectively. Thus concentration of the pairs would be seriously underestimated by assuming a charge of unity. They should give lines with a relative intensity of 2:1.

VII. DISCUSSION

From the computed bond lengths of the substitutional defects, we infer that the elastic strain energy of C_{Ga} should be less than that of C_{As}. The formation energy of the former defect is presumably larger than the latter because of the energies necessary to move the host atoms to the surface. However, this is contradicted by the behavior of Si, which, at low concentrations, prefers to substitute for Ga and is likely to have a lower strain energy. We are then puzzled why C prefers to occupy an As site.

We find the donor species has a vibratory mode just below that of the acceptor (582 cm^{-1}) and is not inconsistent with the suggestion that the *Y* mode[5] at 563 cm^{-1} is due to this defect.

If the donor species is formed, then one expects a pairing to eventually occur. The structure of the C-C pair is unexpected since the C-C length is rather long: 1.83 Å compared to 1.54 Å in diamond. It suggests that the bonding is weak as in graphite. The weak C—C resulted in a midgap state whose wave function is made up of antibonding combinations of C sp^3 orbitals. This defect then should lead to subgap absorption. It would be interesting for luminescence and deep-level transient spectroscopy (DLTS) studies to be carried out.

The pair gives transverse and longitudinal modes at 553 and 425 cm^{-1} that are close to the Y and X lines at 563 and 453 cm^{-1}. However, they should always be observed with an intensity ratio 2:1, which is not apparently the case. To be observed by ir spectroscopy, pairs need to be present in high concentrations because their effective charges are rather low, around 0.5. Another mode at 382 cm^{-1} is due to the transverse vibrations of the C atoms out of phase with each other. The existence of C-C pairs[16] in C-rich GaAs may explain why the hole concentration should be only a fraction of that of the total C.

For the passivated C_{As} defect we find the following.

(1) H prefers to lie in the bond-centered position with a slightly lengthened, 1.14 Å C—H bond, and a long H—Ga (2.05 Å) bond. The shortness of this bond accounts for carbon local modes falling below those of the substitutional defect.

(2) C-H bend modes occur at 718 cm^{-1}. They represent a reduction in the bending force constant of methane by a factor of almost 4. The effective charge of these modes is very small, explaining why they have not been observed by infrared spectroscopy. However, we find that they should be Raman active.

In the bond-centered complex, Be_{Ga}-H-As, where H is much more strongly bonded to As than Be, the bend mode lies below the one-phonon peak, but there the As-H length is 1.54 Å.

(3) The reorientation energy of the defect is 0.67 eV, rather close to that observed at 0.5 eV. The size of this energy suggests the bond-centered defect is exceptionally stable. H passivates the donor in the antibonding position. The C-H modes are much higher and closer to those of methane.

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