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Vibrational modes of sulfur defects in GaP

R. S. Leigh and M. J. L. Sangster*
J. J. Thomson Physical Laboratory, University of Reading, Reading RG6 6AF, United Kingdom

R. C. Newman
Centre for Electronic Materials and Devices, The Blackett Laboratory, Department of Physics, Imperial College, London, SW7 2BW, United Kingdom

J. P. Goss and R. Jones
School of Physics, The University of Exeter, Exeter EX4 4QL, United Kingdom

V. J. B. Torres
Departamento de Fisica, Universidade de Aveiro, 3810 Aveiro, Portugal

S. Öberg
Department of Mathematics, Luleå University of Technology, Luleå S-97187, Sweden

P. R. Briddon
Department of Physics, University of Newcastle upon Tyne, Newcastle upon Tyne, NE1 7RU, United Kingdom

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First principles calculations carried out on GaP containing sulfur donors $^{32}S_P$ (95%) and $^{34}S_P$ (5%) show that both the neutral and ionized donors are located on substitutional sites and have weak S-Ga bonds. For the sulfur impurity in its positive charge state the calculations give gap modes for ^{32}S and ^{34}S at frequencies close to those found experimentally. Modes within the gap are also predicted for neutral sulfur at frequencies within a few cm^{-1} of their charged-state counterparts. However, the S_P^0 donor has a very low apparent charge (i.e. oscillator strength), its calculated integrated absorption cross section being only $\sim 3\%$ of that for the S_P^+ defect. These results support an earlier explanation of the failure to detect gap modes from S_P^0 in infrared measurements. Calculated and observed apparent charges for the S_P^+ donor are compared, and the importance of taking due account of the different geometries that apply to the theoretical calculations and infrared experiments is emphasized.

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It has been shown by electron-nuclear double-resonance (ENDOR) measurements that neutral sulfur donors (S_P^0) in GaP crystals occupy phosphorus lattice sites with tetrahedral T_d symmetry.[1] The presence of these donors is also revealed by infrared (IR) electronic absorption transitions $1s \rightarrow 2p^0$, $2p^{\pm}$, etc., at 10 K when there is carrier freeze-out.[2] The failure[3] to detect an IR-active gap mode from S_P^0, present at concentrations of up to 10^{18} cm^{-3} was initially not surprising. The masses of ^{32}S (95% abundant) and ^{34}S (4.2%) are only slightly greater than that of the replaced ^{31}P (100%), and so it could be argued that the impurity modes are located within the band of optic modes of GaP that extends from 326 to 401 cm^{-1}.[4] However, in partially or completely electrically compensated samples, strong modes from $^{32}S_P^+$ and $^{34}S_P^+$ were detected at 272.5 and 266.2 cm^{-1} in the gap between the acoustic and optic bands (from 255 to 326 cm^{-1}). These modes were simulated[3] by Green's function methods using perfect lattice eigenvectors and frequencies determined by *ab initio* theory and introducing force constant adjustments in the vicinity of the impurity by the Lifshitz procedure.[5] Assuming that S_P^+ also has T_d symmetry, agreement with experiment required that the stretch force constant for bonds between the impurity and its nearest neighbors be reduced to about 50% of that for Ga-P. The reduction in the force constant makes the displacements in the gap mode highly localized: the nearest-neighbor displacements are small and there is a large isotopic shift. These characteristics are more usually found in localized vibrational modes with frequencies above the maximum lattice frequency. Measurements involving two different calibration procedures indicated that an integrated absorption coefficient of 1 cm^{-2} corresponds to a concentration $[S_P^+] = 2.2 \pm 0.3 \times 10^{16}$ cm^{-3}.[3] Since the displacement of the impurity is dominant in the eigenvector of the mode, it is reasonable to approximate the mass associated with the mode as that of the impurity alone. With this assumption, there is no significant distinction between the oscillating charge associated with the mode and the apparent charge for the impurity, as defined in Ref. 6: both will be denoted by η. From the calibrations we deduce that η is about $3.1e$, a value at the high end of the range found for similar centers.[7]

There are clearly outstanding questions to be resolved.

(1) If the mode from S_P^0 is obscured because it lies in the optic band, it is implied that there is a frequency downshift of greater than 50 cm^{-1} when S_P^0 becomes ionized to S_P^+. This would not be expected since the wave function of the bound electron of S_P^0 extends over several nearest-neighbor distances.

(2) Although there is no evidence that S_P^+ moves off the T_d site, this possibility cannot be ruled out.

(3) It was proposed[3] that [following (1) above] there is only a small difference between the gap mode frequencies for S_P^0 and S_P^+ but the value of η for S_P^0 is no greater than 10% of that for S_P^+. The integrated absorption from S_P^0 would then be only ~1% of that from the same concentration of S_P^+, and it would not be detected. It was argued that, provided certain conditions are satisfied sufficiently well, the dipole moment produced by the displacement of the S_P^+ atom is almost completely canceled by the accompanying displacement of the charge distribution of the added donor electron.

In this Brief Report we investigate these questions by means of *ab initio* density functional calculations for the defect systems. Most of the calculations are for approximately spherical clusters with tetrahedral symmetry consisting of 309 atoms with composition $Ga_{92}P_{93}H_{124}$ but we have also carried out parallel local density functional calculations with supercells of 64 and 216 atoms, in cubic arrangements of $2\times2\times2$ and $3\times3\times3$ conventional unit cells, respectively, or 128 atoms, consisting of $4\times4\times4$ primitive unit cells. The radius of the clusters, ~11 Å, is significantly greater than the radius of the Bohr orbit of the ground-state wave function for S_P^0 (estimated in Ref. 3 to be 5.2 Å) but even our largest supercell is too small for incorporated S_P^0 to be considered as an isolated defect. The computational methods for the cluster calculations and the AIMPRO code for supercell treatments are fully described elsewhere.[8,9] In both cases the atoms are treated using the pseudopotentials of Bachelet *et al.*[10]

For the cluster calculations the wave function basis consisted of 5 and 4 *s*, *p* Gaussian orbitals with different widths sited on S and the inner 16 host atoms, respectively, and a fixed linear combination of these Gaussian orbitals, for the remaining atoms. Two Gaussian orbitals were sited on the terminating H atoms. The charge density was fitted with 8, 3, and 4 Gaussian functions sited respectively at the S, H, and the nuclei of the host atoms. The self-consistent energy was found along with the forces on the atoms. The cluster was relaxed and the second derivatives of the energy with respect to the coordinates of the inner 17 atoms found. These were then used in the construction of the inner parts of the dynamical matrix of the cluster. The remaining entries were described by a Musgrave-Pople potential with parameters deduced by fitting to the second derivatives of a relaxed H-terminated 88-atom cluster containing only Ga and P atoms.

For our supercell calculations the wave function basis consists of sets of five independent s, p_x, p_y, and p_z Gaussian orbitals with different exponents sited at each atom site and an additional set of independent Gaussian orbitals placed at the center of each bond. An MP-2^3 (Ref. 11) set of **k** points was used to sample the band structure for all supercell geometries. The charge density is Fourier transformed using plane waves with a cutoff of 150 Ry. The basis set yields a Ga-P bond length of 2.30 Å, around 2.5% smaller than experiment (2.36 Å). This is within the typical accuracy of the method. As a check, we calculated the energy double derivatives for a bulk cell of 64 atoms and used these values to fit a Musgrove-Pople valence-force potential, as done previously for the cluster. Phonon frequencies at special wave vectors were calculated from the potential model and compared with the accepted values.[4] Apart from neglected LO-TO splitting there is reasonably good agreement and, of particular relevance to our defect calculations, the predicted gap in the phonon density of states lies between around 247 and 324 cm^{-1}, agreeing well with that previously quoted[4] (from 255 to 326 cm^{-1}). The phonon dispersion shows that the 324 cm^{-1} mode lies at the *W* point (1,0.5,0), in agreement with the *ab initio* calculations cited in Ref. 4.

TABLE I. Frequencies of gap modes of S defects in GaP and their downward isotopic shifts when ^{32}S is replaced by ^{34}S (all in cm^{-1}).

	Defect	^{32}S, ^{69}Ga	$^{32}S-{}^{34}S$
Cluster	S_P^+	256.3	4.5
	S_P^0	260.2	5.0
Supercell	S_P^+	275.9	7.0
	S_P^0	271.3	6.5
Experiment [a]	S_P^+	272.5	6.3

[a] Reference 3.

We first investigate the question of possible off-center displacements when a P atom is replaced by S in either of its charge states. In the ionized form, the relaxed S-Ga bond length of the tetrahedral defect from the cluster calculations is 2.48 Å, about 7% greater than that for Ga-P bonds. (The cluster yields 2.32 Å compared to 2.36 Å taken from experiment.) For an S^0 atom at the T_d site the bond length (2.47 Å) is slightly shorter than for S^+ but again significantly larger than the host crystal bond length. The supercell calculations also reveal extended S-Ga bond lengths that are reasonably insensitive to the cell size and charge state, lying between 2.38 and 2.39 Å in all cases, compared to the supercell bulk bond length of 2.30 Å. The lengthening of the bonds to sulfur in either charge state implies some weakening of the bonds, and we need to determine whether the defect moves off the T_d site. Such off-center displacements are known to occur for O^+ in GaAs,[12,13] although, as already mentioned, ENDOR measurements[1] reveal that S^0 in GaP occupies P sites with full T_d symmetry. The impurity was therefore given a trial off-center displacement along a [100] direction, but when the cluster was relaxed, the impurity returned to the T_d site. It is worth noting that in similar calculations with smaller clusters the neutral impurity did not return to the on-center site. It is imperative that in such tests for off-center behavior the cluster is sufficiently large to encompass the extended wave function of an impurity's extra electron. Also, in all our supercell calculations, both the neutral and positive charge states were found to reside on the P site (T_d symmetry) in preference to a trigonal symmetry.

Table I gives the calculated frequencies for the gap modes of the sulfur impurity in both charge states with the observed frequency for $^{32}S^+$ for comparison. The modes quoted for the supercell were obtained from the 128-atom supercell. The modes of the positively charged center obtained from the 64-atom cell were in close agreement with those of Table I, with those of the neutral center being shifted down in frequency by around 10 cm^{-1}. For the neutral charge state, the 216 atom cell yields modes within $\sim 1\ \mathrm{cm}^{-1}$ of those obtained from the 128-atom cell, whereas for the positive charge state the 216 atom cell modes are shifted downwards by around 6 cm^{-1}. For both charge states the isotopic shifts were converged to less than 0.1 cm^{-1}. The small fluctuations in the gap-mode frequencies are not thought to be physically significant.

The $^{32}\mathrm{S}^{+}$-mode frequencies calculated by the two methods correspond well with the detected mode and, of more significance, in both cases there is only a difference of a few cm^{-1} when the extra electron is added to form the neutral defect. Possible reasons for the difference in sign found using the two methods include (a) the cells not being large enough to completely remove the influence of periodicity on the wave function of the extra electron on $\mathrm{S}_{\mathrm{P}}^{0}$ and (b) doubts about the procedure of neutralizing the extra charge of the $\mathrm{S}_{\mathrm{P}}^{+}$ impurity with a uniform background. The assertion in Ref. 3 that very little change in frequency with charge state was to be expected is clearly supported by the calculations. The low frequencies are a consequence of very weak bonding with Ga neighbors. The weak bonding can be inferred from the increase in length of the S-Ga bond over the P-Ga bond and may also be seen more directly by comparing the force constants between the S and its neighbors, as obtained from the second derivatives of the total energy, with those of bulk GaP. It is also reflected in the high degree of localization found for the gap modes: from the cluster-based calculations, the amplitude of the displacements of the Ga nearest neighbors is less than 10% of that for the S impurity and the corresponding ratio from the supercell calculations is less than 2%. The close agreement between experiment and the frequencies of both the gap limits and the gap mode as calculated by the supercell method is encouraging. Although the agreement is less good for the cluster calculation, both methods demonstrate large reductions in the force constant between the impurity and its nearest neighbors.

As shown in Table I, the calculated isotope shifts for the frequency of the S^{+} mode when $^{32}\mathrm{S}$ is replaced by $^{34}\mathrm{S}$ are in fair agreement with the observed shift of 6.3 cm^{-1}. The tabulated frequencies correspond to all four nearest neighbors of the impurity being $^{69}\mathrm{Ga}$ atoms. When one of the neighboring $^{69}\mathrm{Ga}$ atoms is replaced by $^{71}\mathrm{Ga}$ the triplet is split into a doublet and a singlet separated by about 0.1 cm^{-1}. The splitting due to Ga isotopic mixtures has not been observed experimentally because of the large natural width, $\sim 1.5\ \mathrm{cm}^{-1}$, of the absorption band.

It was previously argued[3] that the absence of detectable IR absorption arising from the neutral center was due to its very low oscillator strength or, in other words, we expected the effective charge associated with the gap mode for neutral S to be significantly smaller than that for S^{+}. We now consider supporting evidence provided by our calculations.

We may define an effective charge associated with a highly localized mode as the dipole moment corresponding to unit displacement of the normal coordinate of the mode. We have calculated the induced dipole moment when the atoms in the cluster are displaced according to the normal coordinate of the (T_2 symmetry) gap mode. If the magnitude of this displacement is u, the total dipole moment for the complete spherical cluster may be written as $\mu_s = \eta_s u$. The charge η_s is found to be $0.57e$ for the ionized ($^{32}\mathrm{S}$) defect but for the neutral defect it is only $0.1e$. Consequently the strength of the absorption from the mode for the neutral defect is predicted to be $\sim 3\%$ of that for the ionized defect according to the model. The reduced value of the dipole therefore supports the proposal[3] that the induced dipole moment is largely canceled by the addition of the donor electron.

The value of η_s for the ionized defect, $0.57e$, is much smaller than the large value for η, $3.1e$, deduced from infrared absorption measurements. This is to be expected since the coupling of an external field to a redistribution of charge in a sample, as measured by infrared absorption, depends on the shape of the sample. In standard experimental measurements, the light enters (at normal incidence) a slab with parallel faces of extent large compared with the thickness. Under these boundary conditions the external field E_{ext} is equal to E_{mac}, the macroscopically averaged electric field inside the sample. We may therefore achieve a definition of η, the effective (or "apparent") charge, which is both independent of shape and consistent with measurement, if we define the coupling of the gap mode to E_{mac} by $-\eta u E_{\mathrm{mac}}$.

The connection between the effective charge η_s calculated from our spherical cluster and the measured apparent charge η may be established in several ways. In all arguments, it is essential to mirror the experimental determination of η by considering the coupling to electric fields. Probably the simplest way of deducing the correction factor is to note that for a sphere of dielectric constant ε in a uniform external field E_{ext}, the (uniform) field inside is $E_{\mathrm{mac}} = [3/(\varepsilon + 2)]E_{\mathrm{ext}}$: see, for example, Ref. 14. The coupling of our calculated dipole moment, $\mu_s = \eta_s u$, to E_{ext} is $-\eta_s u E_{\mathrm{ext}}$ which can be reexpressed as $-[(\varepsilon+2)/3]\eta_s u E_{\mathrm{mac}}$. Comparison with the definition above immediately gives

$$\eta = \eta_s \frac{\varepsilon + 2}{3}.$$

Another version of the argument, in which electric fields are introduced at a later stage, involves relating μ_s to the actual dipole moment when the cluster is embedded in a medium of dielectric constant ε. The latter dipole corresponds to the "internal moment" μ_i in Appendix A 2 of Fröhlich[15] and the relation is given [Fröhlich's equation (A2.32)] as $\mu_s = [3/(\varepsilon+2)]\mu_i$. The coupling to E_{mac}, the macroscopically averaged electric field inside the medium, is $-\mu_i E_{\mathrm{mac}}$, from which the above connection between η and η_s follows immediately.

The use of this correction factor assumes that the calculated dipole moment has converged with increasing cluster size and that a macroscopic dielectric treatment is appropriate.

The constant required for the correction factor is the purely electronic dielectric constant, since the nuclear positions are independent variables in the expression for the coupling energy. With $\varepsilon=8.85$ (a value deduced from the low temperature data and interpolation scheme given in Ref. 16) and $\eta_s=0.57e$ we obtain $\eta=2.06e$, in better agreement with the value of $3.1e$ deduced from the infrared absorption measurements.

In summary, the calculations show (a) that the ionized and neutral S donors in GaP are both on-site defects and (b) that there are gap modes associated with each charge state arising as a consequence of very weak bonding with Ga neighbors. The frequencies of the gap modes are essentially independent of the charge state but the effective charges of the defect in the two charge states are very different with that for the neutral defect η_s being greatly reduced. This demonstrates that the conditions for the argument of Ref. 3 to hold are sufficiently well satisfied. Finally, when a shape-dependent correction factor is included, the agreement between the calculated effective charge for the S_P^+ gap mode and the value deduced from absorption measurements is greatly improved.

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*Electronic address: m.j.l.sangster@reading.ac.uk

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