Identification and Properties of Defects in GaP

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We report an application of self-consistent pseudopotential Green's-function calculations to the problem of identification of defects in GaP. The results are in agreement with and support the EPR-based identification of the P antisite defect, but contradict the assumptions that led to the identification of the Ga vacancy. We reexamine other possibilities using the results of our calculations and find that C at Ga sites is the only center whose properties are consistent with the available data.

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Defects in III-V semiconductors are well known to limit the efficiency of light-emitting diodes and cause the degradation of devices in general. The identification and investigation of the properties of defects in these materials, however, have been hampered by difficulties in using standard experimental techniques such as electron paramagnetic resonance (EPR), luminescence, etc., and by the absence of accurate theoretical calculations.

Recently, Kaufmann, Schneider, and Räuber[1] and Kennedy and Wilsey (KW)[2,3] resolved experimental difficulties and were able to detect EPR signals from defects in GaP. Using standard EPR analysis, Kaufmann, Schneider, and Räuber[1] attributed the observed signals to the P antisite defect (i.e., a P atom occupying a normally Ga site, denoted by P_{Ga}). KW attributed the signals detected in electron-irradiated GaP to the Ga vacancy. More recently, a few more related defects have been identified in III-V semiconductors.[4]

At about the same time, theoretical calculations based on self-consistent Green's-function techniques became possible, giving detailed information about the electronic structure of defects at the same level of accuracy that is possible for perfect crystals.[5,6] In this paper, we report the first application of results of such calculations to the difficult and important problem of defect identification in III-V compounds. We find that the theoretical results are fully consistent with the identification of the P antisite defect,[1] but contradict the assumptions that led to the identification of the Ga vacancy.[2] We then reexamine other possibilities and, using the results of detailed theoretical calculations, conclude that the EPR signals attributed to the Ga vacancy are more likely to originate from carbon impurities occupying Ga sites.

The essential features of the theoretical method used for this work are described in Ref. 5. The method has been reformulated in order to increase its efficiency, flexibility, and accuracy.[7] The ionic pseudopotentials for Ga and P were constructed for the free atoms and then modified slightly so that a self-consistent local-density[8] band-structure calculation yields the measured indirect band gap.[9] For each of the defects studied, the calculation was carried out to self-consistency with no additional approximations.

We begin with the P antisite defect (P_{Ga}). The EPR signal that was attributed to P_{Ga} has been shown[1] to arise from an electron with effective spin $\frac{1}{2}$ coupling to a spin-$\frac{1}{2}$ nucleus at the center and to four spin-$\frac{1}{2}$ nuclei at tetrahedral positions around it (T_d symmetry). The wave function was determined to be s-like at the origin and a mixture of s- and p-like orbitals at the nearest neighbors. The fraction of p-like orbitals was found to be higher than that corresponding to the standard sp^3 hybrid, leading to the suggestion[3] that the nearest neighbors undergo a breathing-mode relaxation away from the central atom.

Our calculations[10] for P_{Ga} show that the neutral center has an A_1 state in the gap at $E_c - 0.45$ eV. This state contains two electrons, and the center is diamagnetic. The positively charged center[11] (P^+) also has an A_1 state in the gap at $E_c - 0.75$ eV, containing one electron, and is paramagnetic. This state is stable with respect to Jahn-Teller distortions. The wave function of the gap state, shown in Fig. 1, clearly has s-like character about the central atom and is a mixture of s-like and p-like orbitals at the nearest neighbors. The fraction of p-like orbital is definitely higher than that corresponding to an sp^3 hybrid, as can be seen by comparing Fig. 1 with the wave function of the gap state of the vacancy in Si, which is almost pure sp^3 (see Refs. 5 and 6). This result shows that it is not necessary to invoke breathing-mode relaxation of the neighbors to explain deviations from sp^3 wave-function character.[12] A small amount of relaxation cannot, of course, be

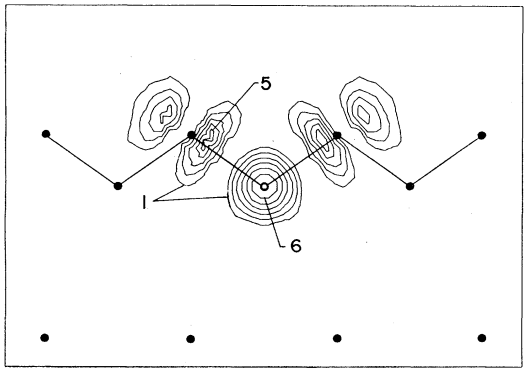

FIG. 1. Contour plot in the (110) plane of the electron density corresponding to the bound-state wave function of GaP:P_{Ga}^{+}. Units are (electrons$\times 10^{-3}$) per unit volume in atomic units.

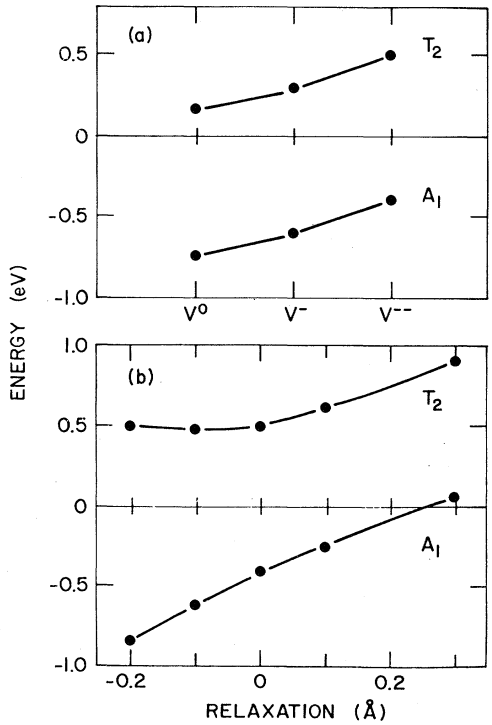

FIG. 2. (a) The variation of the T_2 and A_1 levels of the unrelaxed Ga vacancy in GaP (V_{Ga}) for three different charged states. The calculated points are connected for visual clarity. (b) The variation of the T_2 and A_1 levels of V_{Ga}^{--} as a function of inward and outward relaxation of the nearest neighbors. The zero of energy is the top of the valence bands.

ruled out.

Very recently, Kaufmann *et al.*[13] determined the first and second ionization energies of P_{Ga} to be <0.8 and 1.1 ± 0.1 eV, respectively. The corresponding theoretical numbers, based on transition-state calculations,[11] are 0.6 and 1.1 eV. Thus, the results of our calculations are in full agreement with the evidence that has been associated with P_{Ga}, and hence further support its identification.

We turn now to the Ga vacancy (V_{Ga}). The EPR signal that has been attributed[2,3] to V_{Ga} has been shown to arise from an electron with effective spin $\frac{1}{2}$ at a center with T_d symmetry, no nuclear spin at the origin, and four spin-$\frac{1}{2}$ nuclei at the nearest-neighbor sites. The character of the wave function at the nearest-neighbor sites was determined to be predominantly p-like, with a very small s admixture. KW's identification of this center as the V_{Ga} was based on several assumptions, one of which concerned the energy ordering of the vacancy A_1 and T_2 dangling-bond states. KW proposed that, in partially ionic semiconductors, it is possible to have the A_1 level above the T_2 level, i.e., in reverse order of what is known to occur in Si. With such an assumption, the doubly negatively charged state of V_{Ga} would be in agreement with the EPR data.

We have carried out calculations for the neutral Ga vacancy and found a T_2 level in the gap at $E_v + 0.15$ eV and an A_1 resonance at $E_v - 0.75$ eV, i.e., the same ordering as in the case of the Si vacancy. We repeated the calculation for V_{Ga}^{-} and V_{Ga}^{--} and found that both the T_2 and A_1 levels move up, maintaining a virtually identical splitting of 0.9 eV [Fig. 2(a)] which is far larger than the accuracy of the calculation or possible spin-orbit splittings. As a further check, we repeated the calculation for V_{Ga}^{--}, allowing the nearest neighbors to relax either toward or away from the vacancy. The ordering of the levels did not change, with the A_1-T_2 splitting remaining at about 0.9 eV or getting even larger [Fig. 2(b)]. These results strongly suggest that the assumption of reverse A_1-T_2 ordering is incorrect. The partial occupation of the T_2 level would in turn trigger a Jahn-Teller distortion and hence an anisotropic EPR signal, contrary to what is observed.[2,3]

KW also considered the possibility that the EPR spectrum appears to arise from a center with T_d symmetry by being a motional average of a set of anisotropic spectra corresponding to different modes of distortion (see also Ref. 4). Such a model would require small barriers for reorientation. By going to a low enough temperature, it should be possible to freeze the vacancy in one of the possible distorted configurations. Experi-

ments at 4.2 K (Ref. 2) and, more recently, at 1.4 K (Ref. 3), however, failed to produce support for the idea.

The above results suggest strongly that the EPR spectrum arises from a center other than the Ga vacancy. Indeed, KW recognized that the EPR data cannot differentiate between a vacant Ga site and a substitutional impurity with zero nuclear spin. They identified all impurities that are present in adequate concentrations, but ruled them all out for reasons that we consider valid, with one exception: Carbon was ruled out[2,3] on the grounds that C_{Ga}, like Si_{Ga}, is a shallow donor and thus would give a totally different and well-known spectrum. In Ref. 3, an additional reason was given, namely that C is not known to occupy Ga sites in GaP and, according to infrared-absorption data by Thompson, Morrison, and Newman,[14] upon irradiation, C_P changes to a trigonal center.

Concerning the question of the C_{Ga} energy level, we note that there exists no evidence that it is shallow. The center has not been detected experimentally and Dean, Frosch, and Henry[15] have suggested that it is likely to be deep, because of the large electronegativity difference between C and Ga. The argument is supported by the fact that Si:N and GaP:O_P are deep, whereas all the other corresponding single donors are shallow. In order to settle this question, we carried out self-consistent calculations[16] for C_{Ga}. The result was a deep A_1 state in the gap at $E_c - 1.3$ eV containing one electron and thus being paramagnetic. The center is stable against Jahn-Teller distortions. The wave function of the gap state is shown in Fig. 3. It is clearly very similar to that of P_{Ga}. This similarity, together with the fact that C is deeper, allow us to conclude[17] that the g shift of C should be larger than that of P, as is indeed the case for the center observed by KW. We conclude, therefore, that C_{Ga} is the only center with T_d symmetry whose electronic properties are in full accord with KW's data.

Concerning the data of Ref. 14, we note that they were taken at fluences considerably higher than those used by KW. These data[14] show that, at very high fluences, a fraction of C_P's convert to a center which is not the one detected by KW. They do not, however, yield information about the relative concentrations of different carbon centers (e.g., C_P, C_{Ga}, $C_{interstitial}$, etc.) at the experimental conditions of KW, and thus do not rule out the possibility that the EPR-active center is C_{Ga}.

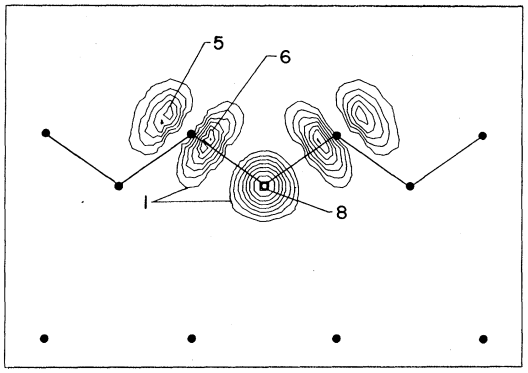

FIG. 3. Contour plot in the (110) plane of the electron density corresponding to the bound-state wave function of GaP:PC_{Ga}. Units as in Fig. 1.

Finally, we address the question of how C_{Ga} centers are formed. A small concentration of such centers may already exist at concentrations which are too small to be detected. During irradiation, a fraction of C atoms are likely to be dislodged from the normal P sites by a combination of direct and indirect processes and be captured by Ga vacancies. Finally, a fraction of C atoms initially occupy interstitial positions and are then captured by Ga vacancies created by irradiation. Detailed discussion of these issues is given elsewhere,[18] where a specific model of the dynamics of carbon atoms in irradiated GaP is constructed which is fully consistent with all of KW's observations regarding the temperature, illumination, and annealing-stage dependences of the EPR signals.

In summary, we have shown that the electronic structure of the Ga vacancy implies a Jahn-Teller distortion which is not consistent with the observed isotropic EPR signal. On the other hand, we have shown that, from among the alternative possibilities, C_{Ga} is the only center which is fully consistent with the available data. Additional experiments would be desirable to test further the present identification. In particular, it would be desirable to determine the relative concentrations of the different carbon centers before and after irradiation by combining mass spectroscopy, infrared absorption, and pair luminescence,[15] and compare with the concentration of the EPR-active center. It would also be desirable to repeat the EPR measurements with different C concentrations using crystal-growing techniques described in Ref. 15, and using samples enriched with ^{13}C, which has nuclear spin $\frac{1}{2}$. Finally, uniaxial-stress

experiments may help test further the motional-average model of V_{Ga} by increasing the likelihood of freezing in one of the presumed modes of distortions.

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[7]The band-structure calculation is carried out using a plane-wave basis which allows systematic convergence tests. Gaussian-type basis functions are used to represent all operators needed for the defect calculation. An arbitrary number of such orbitals can be used at arbitrary positions in the vicinity of the defect. Details of the calculations and of the electronic structure of several defects will be given elsewhere.

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[9]Most ionic pseudopotentials yield band gaps that are too small, which is a fault of the local-density approximation for the effective single-particle potential [see, e.g., D. R. Hamann, Phys. Rev. Lett. 42, 662 (1979)]. For point-defect calculations, it is important to have the correct band gap. Modifying the ionic pseudopotentials is a convenient way to incorporate the necessary correction. An alternative way (rigid shift of bands) has been tested and found to give essentially identical results.

[10]A non–self-consistent calculation for P_{Ga} was previously reported by M. Jaros, J. Phys. C 11, L216 (1978). An A_1 level at $E_c - 0.2$ eV was found.

[11]The Coulombic tail that is present in the potentials of charged states was included by perturbation theory.

[12]Our calculations on vacancies, antisites, and impurities show that deviations from sp^3 character are possible, in fact common, without relaxation of the nearest neighbors. In the past, such deviations were viewed as evidence for relaxation.

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