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Calculation of the hyperfine-interaction tensors of the P_{Ga} antisite in GaP

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The tight-binding theory of defects by Hjalmarson *et al.* [Phys. Rev. Lett. **44**, 810 (1980)] is used to calculate the wave function of an electron localized near the P_{Ga} antisite in GaP. The effect of the defect potential is extended to the nearest-neighbor sites, including the effects of lattice relaxation around the antisite phosphorous. From the calculated wave function, the hyperfine interaction of an electron with a P or a Ga nucleus near the defect is obtained and compared with electron-spin-resonance data and optically detected magnetic-resonance data. Good agreement is obtained for antisite phosphorus and nearest-neighbor atoms. The effects of lattice relaxation on the defect energy level, the wave function, and the hyperfine-interaction constants are discussed. The outward relaxation of nearest-neighbor atoms was determined to be 21% of the bond length.

I. INTRODUCTION

An intrinsic defect believed to be important in III-V compound semiconductors is the anion antisite defect, where a group-V atom occupies a group-III atom site, forming a double donor.[1] The first experimental evidence of this defect was for the P_{Ga} antisite defect. In GaP, where via electron-spin resonance[2,3] (ESR) and optically detected magnetic resonance[4,5] (ODMR), the isotropic central-atom phosphorous hyperfine (hf) interaction plus the anisotropic hf interaction of four equivalent phosphorus atoms were resolved and the energy level of the P_{Ga} antisite defect in GaP was obtained through photoresponse ESR.[3] Similar spectra have subsequently been reported for GaAs (Refs. 6–8) and InP.[9–12]

The antisite defects have also been extensively studied theoretically, using, for example, both tight-binding calculations[13–16] and self-consistent pseudopotential Green's-function calculations.[17–19] None of these theories attempted a comparison with the experimental data for the hf-interaction constants as well as with the energy level of the antisite defect. The purpose of this paper will be to provide such a comparison for the P_{Ga} antisite defect in GaP, using the theory of electron-nuclear-double-resonance (ENDOR) and electron-paramagnetic-resonance (EPR) spectra of deep impurity states by Ren *et al.*[20] and the theory of deep energy levels by Hjalmarson *et al.*,[21] extended to allow for the effects of lattice relaxation. A rigorous treatment of lattice relaxation would require a total-energy calculation. However, such a calculation would destroy the simplicity and universality of the theory of Hjalmarson *et al.* Our approach circumvents this problem by treating lattice relaxation phenomenologically. It retains the ability to easily predict chemical trends by treating the diagonal matrix elements of the defect potential using the assumption of Hjalmarson *et al.*: these matrix elements are proportional to atomic-energy differences. The effects of lattice relaxation are included according to Harrison's inverse bond-length-squared scaling law[22] for off-diagonal tight-binding matrix elements. Taking the experimental value of the defect energy level as an input parameter of the approach, the diagonal matrix elements of the defect potential on the nearest-neighbor sites are included, the amount of relaxation of the nearest-neighbor lattice can be determined by comparing calculated results with experimental data. In addition, the energy, wave function, and hf-interaction constant with varying amounts of lattice relaxation are also investigated on the assumption that the diagonal matrix elements on the nearest-neighbor sites is a linear function of lattice relaxation.

The remainder of the paper is organized as follows: Section II describes the method used for the present calculation. Section III gives the formulation of the hf-interaction tensor. The results will be presented in Sec. IV, followed by a discussion of their meaning and comparison to available experiments. A brief summary of our conclusions is contained in Sec. V.

II. WAVE FUNCTION OF THE P_{Ga} ANTISITE DEFECT IN GaP

The ESR and ODMR spectra of the P_{Ga} antisite defect in GaP show that the antisite phosphorus atom is surrounded by a tetrahedron of four equivalent phosphorus atoms and is in an *s*-like state, with the breathing model relaxation. From group theory, the defect state $|\psi\rangle$ is one transforming according to the irreducible representation A_1 of the T_d point group. Hence $|\psi\rangle$ is expanded in a set of bases function $|A_1Rm\rangle$,

$$|\psi\rangle=\sum_{Rm}|A_1Rm\rangle\langle A_1Rm|\psi\rangle \ , \tag{1}$$

where $|A_1Rm\rangle$ are orthogonal symmetric combinations of sp^3 hybrid orbitals round the antisite atom. R indexes the Rth shell around the antisite-atom site, e.g., $R=0$ for the antisite atom and $R=1$ for the shell of the nearest neighbors, and m marks the mth basis function of the Rth shell transforming according to the A_1 irreducible representation. For example, the s orbital of the antisite phosphorus atom forms the basis function $|A_1 01\rangle = |S\rangle$. The A_1 combination of four inward-directed hybrids centered at the nearest-neighbor sites constructs $|A_1 11\rangle$, and so on.

The defect electron state $|\psi\rangle$ bound by the short-range potential V satisfies the following equation:

$$|\psi\rangle = G(E)V|\psi\rangle \ , \tag{2}$$

where $G(E)=1/(E-H_0)$ is the Green's function of the host crystal, with matrix elements

$$\langle A_1 Rm|G|A_1 R'm'\rangle = \sum_{n\mathbf{k}} \frac{\langle A_1 Rm|n\mathbf{k}\rangle\langle n\mathbf{k}|A_1 R'm'\rangle}{E-E_{n\mathbf{k}}} \ . \tag{3}$$

Here $E_{n\mathbf{k}}$ and $|n\mathbf{k}\rangle$ are the eigenvalues and the eigenvectors of the host Hamiltonian, which is described by an empirical tight-binding Hamiltonian H_0,[23] and the summation on wave vector $\mathbf{k}$ in the Brillouin zone is performed with use of the special $\mathbf{k}$-point method of Chadi and Cohen.[24]

In the present study, both the diagonal matrix elements of V on the nearest neighbors of the antisite atom and the off-diagonal matrix elements of V, which couple the antisite atom to its nearest neighbors, are included. Thus the potential parameters being introduced are the following: $V_{00}=\langle A_1 01|V|A_1 01\rangle = \langle S|V|S\rangle$, $V_{01}=\langle A_1 01|V|A_1 11\rangle$, $V_{10}=\langle A_1 11|V|A_1 01\rangle$, and $V_{11}=\langle A_1 11|V|A_1 11\rangle$. The solution of Eq. (2) reduces to

$$\begin{aligned}\langle A_1 Rm|\psi\rangle = {} & \langle A_1 Rm|G|A_1 01\rangle V_{00}\langle A_1 01|\psi\rangle \\ & + \langle A_1 Rm|G|A_1 01\rangle V_{01}\langle A_1 11|\psi\rangle \\ & + \langle A_1 Rm|G|A_1 11\rangle V_{10}\langle A_1 01|\psi\rangle \\ & + \langle A_1 Rm|G|A_1 11\rangle V_{11}\langle A_1 11|\psi\rangle \ , \end{aligned} \tag{4}$$

because the defect potential V is only extended up to the atoms of the $R=1$ shell. A set of linear homogeneous equations for $\langle A_1 01|\psi\rangle$ and $\langle A_1 11|\psi\rangle$ may be obtained from Eq. (4),

$$\begin{aligned}\langle A_1 01|\psi\rangle &= (G_{00}V_{00}+G_{01}V_{10})\langle A_1 01|\psi\rangle \\ &\quad + (G_{00}V_{01}+G_{01}V_{11})\langle A_1 11|\psi\rangle \ , \\ \langle A_1 11|\psi\rangle &= (G_{10}V_{00}+G_{11}V_{10})\langle A_1 01|\psi\rangle \\ &\quad + (G_{10}V_{01}+G_{11}V_{11})\langle A_1 11|\psi\rangle \ , \end{aligned} \tag{5}$$

where G_{ij} is the abbreviation of the Green's-function matrix elements, i.e., $G_{00}=\langle A_1 01|G|A_1 01\rangle$, $G_{01}=\langle A_1 01|G|A_1 11\rangle$, $G_{10}=\langle A_1 11|G|A_1 01\rangle$, and $G_{11}=\langle A_1 11|G|A_1 11\rangle$.

The bound-state energies E of the defect satisfy the determinantal equation

$$\begin{vmatrix} G_{00}V_{00}+G_{01}V_{10}-1 & G_{00}V_{01}+G_{01}V_{11} \\ G_{10}V_{00}+G_{11}V_{10} & G_{10}V_{01}+G_{11}V_{11}-1 \end{vmatrix} = 0 \ . \tag{6}$$

Because of the restriction of Eq. (6), only one of the two equations in (5) is independent. The normalization condition $\langle\psi|\psi\rangle=1$ gives another independent equation for $\langle A_1 01|\psi\rangle$ or $\langle A_1 11|\psi\rangle$,

$$\begin{aligned} -(C_1+C_3)^2\frac{dG_{00}}{dE} - (C_2+C_4)^2\frac{dG_{11}}{dE} \\ -2(C_1+C_3)(C_2+C_4)\frac{dG_{01}}{dE} = 1 \ , \end{aligned} \tag{7}$$

where $C_1=V_{00}\langle A_1 01|\psi\rangle$, $C_2=V_{10}\langle A_1 01|\psi\rangle$, $C_3=V_{01}\langle A_1 11|\psi\rangle$, and $C_4=V_{11}\langle A_1 11|\psi\rangle$.

With regard to the matrix elements of V, the diagonal element V_{00} used is the same as given by Hjalmarson *et al.* for the strain-free theory,[21]

$$V_{00}=\beta_S[\omega_S(\mathrm{P})-\omega_S(\mathrm{Ga})] \ , \tag{8}$$

where $\omega_S(\mathrm{P})$ and $\omega_S(\mathrm{Ga})$ are the s-orbital atomic energies for the antisite atom and host atom Ga, respectively. Following Ref. 25, and for the same reason, $\beta_S=1$ is used here.

The off-diagonal matrix elements are written as

$$V_{01}=V_{10}=W[(d_I)^{-2}-(d_H)^{-2}] \ , \tag{9}$$

where d_H and d_I are the bond lengths of the antisite (impurity) containing and the perfect crystal, respectively. W is a proportionality constant, $W=V_{SS\sigma}+V_{SP\sigma}$, which can be obtained from the parameters of Harrison.[22]

The combination of one of the two equations in (5) with Eq. (7) gives the wave functions $\langle A_1 01|\psi\rangle$ and $\langle A_1 11|\psi\rangle$ as a function of the bond length d_I. Then the $\langle A_1 Rm|\psi\rangle$ for each shell can be obtained from Eq. (4).

III. HYPERFINE-INTERACTION TENSOR

In order to use the symmetric wave function $\langle A_1 Rm|\psi\rangle$ to calculate the hf-interaction tensor, we now expand the electronic state $|\psi\rangle$ in terms of the atomic orbitals

$$|\psi\rangle = \sum_j [C_{jS}|jS\rangle + C_{jX}|jX\rangle + C_{jY}|jY\rangle + C_{jZ}|jZ\rangle] \ , \tag{10}$$

where $|jS\rangle$, $|jX\rangle$, $|jY\rangle$, and $|jZ\rangle$ are the nS and nP atomic orbitals of the host or antisite at the jth site, respectively. $C_{jS}=\langle jS|\psi\rangle$, $C_{jX}=\langle jp_X|\psi\rangle$, $C_{jY}=\langle jp_Y|\psi\rangle$, and $C_{jZ}=\langle jp_Z|\psi\rangle$ can be evaluated using the calculated $\langle A_1 Rm|\psi\rangle$.

As usual, the probability of the unpaired electron on the jth atom is represented by

$$\eta_j^2 = C_{jS}^2 + C_{jX}^2 + C_{jY}^2 + C_{jZ}^2 \ , \tag{11}$$

and the percentage s and p character of the wave function by

$$\begin{aligned} \alpha_j^2 &= C_{jS}^2/\eta_j^2 \ , \\ \beta_j^2 &= (C_{jX}^2+C_{jY}^2+C_{jZ}^2)/\eta_j^2 \ , \\ \alpha_j^2+\beta_j^2 &= 1 \ . \end{aligned} \tag{12}$$

The hf-interaction tensor can be represented in the following form:

$$A=\begin{vmatrix} A_{XX}\,A_{XY}\,A_{XZ} \\ A_{YX}\,A_{YY}\,A_{YZ} \\ A_{ZX}\,A_{ZY}\,A_{ZZ} \end{vmatrix} . \tag{13}$$

As is commonly adopted, only the atomic orbitals centered on the jth atom contribute to A_j and the contributions from the other atomic orbitals are neglected. Under this assumption, the hf-interaction tensor arising from the wave function of the gap state alone is an asymmetric tensor. Then we can obtain the following relationships among all components of A_j and the coefficients C_{jS}, C_{jX}, C_{jY}, and C_{jZ}:

$$\begin{aligned} A_{XX}&=C_S^2A_f+(2C_X^2-C_Y^2-C_Z^2)B_f\ , \\ A_{XY}&=A_{YX}=3C_XC_YB_f\ , \\ A_{YY}&=C_S^2A_f+(2C_Y^2-C_Z^2-C_X^2)B_f\ , \\ A_{YZ}&=A_{ZY}=3C_YC_ZB_f\ , \\ A_{ZZ}&=C_S^2A_f+(2C_Z^2-C_X^2-C_Y^2)B_f\ , \\ A_{ZX}&=A_{XZ}=3C_ZC_XB_f\ , \end{aligned} \tag{14}$$

with

$$\begin{aligned} A_{jf}&=(16\pi/3)(\mu_j/I_j)\mu_B|\psi_{nS}(0)|_j^2\ , \\ B_{jf}&=4/5(\mu_j/I_j)\mu_B\langle r_{nP}^{-3}\rangle_j\ . \end{aligned} \tag{15}$$

All subscripts j are dropped in Eqs. (13) and (14). In Eq. (15), μ_B is the Bohr magneton and μ_j and I_j are the nuclear magneton and nuclear spin of the jth atom, respectively. $|\psi_{nS}(0)|_j^2$ and $\langle r_{nP}^{-3}\rangle_j$ are the probability density of the nS orbital of the jth atom at its nucleus site and the expectation value of r^{-3} weighted over the nP orbital of the jth atom, respectively. For ^{31}P, its natural abundance is 100%, $I=\frac{1}{2}$, $\mu=1.1316$ nm, $|\psi_{3S}(0)|^2=41.6\times10^{24}$ cm^{-3}, $\langle r_{3P}^{-3}\rangle=24.2\times10^{24}$ cm^{-3} (these values are taken from Ref. 26). The free-ion values for ^{69}Ga were taken as $A_f=2477\times10^{-4}$ cm^{-1}, $B_f=49\times10^{-4}$ cm^{-1}.[27]

In ESR, ODMR, and ENDOR experiments, each hf-interaction tensor is usually reduced to diagonal form by a coordinate transformation to its principal axes. The largest principal value is taken as A_1, the second largest and the smallest are taken as A_2 and A_3, respectively. Thus (13) becomes a diagonal matrix and new parameters a, b, and c are determined by

$$A=\begin{vmatrix} A_1 & & \\ & A_2 & \\ & & A_3 \end{vmatrix}=\begin{vmatrix} a+2b & & \\ & a-b+c & \\ & & a-b-c \end{vmatrix} . \tag{16}$$

Here $a=1/3\,\mathrm{Tr}\,A$ represents the isotropic part of the hf interaction, b gives the purely axially symmetric part of the hf-interaction tensor, and c takes account of the deviation from axially symmetry. Generally, the hf tensor is a nearly axially symmetric tensor, i.e., $c \ll b$.

It has been found in ESR experiments that the hf-interaction tensor of the $\mathrm{P_{Ga}}$ antisite defect in GaP is an axially symmetric one along the p-orbital axis, $c=0$ and the principal values can then be parametrized as

$$(A_{\parallel})_j=a_j+2b_j\ ,\quad (A_{\perp})_j=a_j-b_j\ , \tag{17}$$

where the hf-interaction parameters a_j and b_j are given by

$$a_j=\alpha_j^2\eta_j^2A_{jf}\ ,\quad b_j=\beta_j^2\eta_j^2B_{jf}\ . \tag{18}$$

The hf-interaction tensor is purely axially symmetric and the axial direction is determined by the direction cosines. The direction cosines of the first-principal axis of the hf-interaction tensor, on which the hf-interaction tensor has the largest principal values, are

$$\begin{aligned} l&=C_{jX}/(C_{jX}^2+C_{jY}^2+C_{jZ}^2)^{1/2}\ , \\ m&=C_{jY}/(C_{jX}^2+C_{jY}^2+C_{jZ}^2)^{1/2}\ , \\ n&=C_{jZ}/(C_{jX}^2+C_{jY}^2+C_{jZ}^2)^{1/2}\ . \end{aligned} \tag{19}$$

If a point defect in diamond or zinc-blende structure semiconductors has a mirror plane, two of the quantities $|C_{jX}|$, $|C_{jY}|$, and $|C_{jZ}|$, when the coordinate directions are along the cubic axes, should be equal to each other for an atom located in the mirror plane. In the case of the $\mathrm{P_{Ga}}$ antisite defect in GaP, the wave function belongs to the A_1 representation of T_d point group, so the nearest-neighbor P atom and the next-nearest-neighbor Ga atoms are all in a mirror plane. Thus, the direction of the first principal axis of the hf-interaction tensor is in the mirror plane, and it can be represented by an angle θ between it and the [011] direction. Assuming $|C_{jX}|\neq|C_{jY}|=|C_{jZ}|$, θ can be given by

$$\theta=\tan^{-1}\frac{|C_{jX}|}{|\sqrt{2}C_{jY}|}\ . \tag{20}$$

The relationship of the hf constant A to the direction of the externally applied magnetic field is given by

$$A=(A_1^2n_1^2+A_2^2n_2^2+A_3^2n_3^2)^{1/2}\ , \tag{21}$$

where A_1, A_2, A_3 are the principal values of the hf tensor A and n_1,n_2,n_3 are the direction cosines of the magnetic-field direction with respect to the 1,2,3 principal axes of the A tensor.

IV. RESULTS AND DISCUSSION

To make an improvement for calculating the defect wave function, the formulations described in Secs. II and III include two parameters to be determined after the V_{00} is specified; one is V_{11}, the diagonal matrix elements of the defect potential at the nearest-neighbor sites, and another is d_I/d_H, the ratio of the nearest-neighbor distances in the impurity and host clusters. How do we determine the proper values of the two parameters and further calculate the wave function?

First of all, it should be noted that Eq. (6) may be regarded as an implicit function of the arguments E, V_{11},

TABLE I. The probabilities η^2 of the unpaired electron, the s-character percentage α^2 and p-character percentage β^2 of the wave functions on antisite phosphorus, the nearest-neighbor and the next-nearest-neighbor atoms in GaP, and the hf interactions $A_{\parallel}$, $A_{\perp}$, a, and b (in 10^{-4} cm^{-1}), the direction angle θ (in degrees) of the first principal axis of the hf tensor in the mirror plane from the [011] direction. The corresponding experimental results are taken from Refs. 2–5. The deep energy level is at $E_v + 1.25$ eV[3], where E_v denotes the top of the valence band. The outward relaxation of the nearest neighbor is at 21% of the bond length.

Atom	$A_{\parallel}$	$A_{\perp}$	a	b	α^2 (%)	β^2 (%)	η^2 (%)	θ	Ref.
P_{Ga}	966±13			0	100	0			2
	996±3			0	100	0			4
	988±15			0	100	0	26		5
	982.8			0	100	0	26.4		this work
P_4	105	60	75	15	11.8	88.2	15.7		3
	105	62	76	14	13.0	87.0	15.8	35.3	this work
Ga_{12}	0.7	0.3	0.4	0.15	5.4	94.6	0.3		this work

and d_I/d_H ($d_H = 2.36$ Å), which is a surface in the geometric interpretation. Assuming that the E that appears in Eq. (6) is equal to the experimental defect energy level, thus it follows from $F(E, V_{11}, d_I/d_H) = 0$ and $E = 1.25$ eV[3] that the cut line describes the functional relation between V_{11} and d_I/d_H. That is to say, under the condition of fixed E, Eq. (6) gives an infinite set of pairs $(V_{11}, d_I/d_H)$. Thus, for each given d_I/d_H, the V_{01} (V_{10}) can be evaluated from Eq. (9), the V_{11} can be obtained by virtue of Eq. (6); and then we obtain, on substitution into one of Eqs. (5) and (9), the wave function and theoretical values of the η^2, α^2, and A, $A_{\parallel}$, and $A_{\perp}$ for P_{Ga} and P_4 can be calculated from Eqs. (11), (12), and (18) in an orderly way. Compared with their experimental values, the optimum theoretical results are obtained when d_I/d_H is about 1.21. By this time $V_{11} = -2.82$ eV.

The calculations show that $\langle A_1 01 | \psi \rangle$ and $\langle A_1 11 | \psi \rangle$ are of opposite sign, e.g., when $d_I/d_H = 1.21$. They are equal to -0.514 and $+0.786$, which just highlights the antibonding character of the P_{Ga} defect electron wave function. The corresponding other physical quantities are listed in Table I. The experimental values from Refs. 2–5 are also summarized in the table for comparison. These values show that both the theory and experiment agree very well. The direction angle θ for each of the four phosphorus atoms in the mirror plane from the [011] direction is calculated to be 35.26°. This shows that the first-principal axis remains in [111] direction.

The calculated results of the hf-interaction tensor are listed in Table II. As seen from this table, the hf-interaction tensor of P_{Ga} is isotropic; those of the four nearest-neighbors P_4 are symmetric, and their first principal-axis direction is in a different [111] direction. The angular dependence of the P_4 lines has been obtained from Eq. (21), and is shown in Fig. 1. It reveals the characteristic four-line (two of them are coincident) spectrum of the four P_4, each with a different [111] axis of symmetry.

It is worth noticing that the $d_I/d_H = 1.21$ means that the relaxation direction of P_4 is outward and the amount is about 21% of the host bond length. This result shows that the defect GaP:P_{Ga} may be another example of outward relaxation caused by substituting a smaller atom for a larger one. Li and Myles[28] and Morgan[29] have predicted a similar trend for O in GaP:O_P, in which the nearest-neighbor Ga atoms move away from the O impurity by

TABLE II. Parameters (in 10^{-4} cm^{-1}) and orientations of hf tensors of ^{31}P atoms of P_{Ga} in GaP.

Atom	A			i	A_i	(l,m,n)
P_{Ga}	983	0	0	1	983	(1.000,0.000,0.000)
(000)	0	983	0	2	983	(0.000,1.000,0.000)
	0	0	983	3	983	(0.000,0.000,1.000)
P(1)	77	14	14	1	105	(−0.577,−0.577,−0.577)
$(\bar{1}\bar{1}\bar{1})$	14	77	14	2	62	(0.071,−0.740,0.669)
	14	14	77	3	62	(−0.813,0.346,0.468)
P(2)	77	14	−14	1	105	(0.577,0.577,−0.577)
$(11\bar{1})$	14	77	−14	2	62	(−0.071,0.740,0.669)
	−14	−14	77	3	62	(−0.813,0.346,−0.468)
P(3)	77	−14	14	1	105	(0.577,−0.577,0.577)
$(1\bar{1}1)$	−14	77	−14	2	62	(0.071,0.740,0.669)
	14	−14	77	3	62	(−0.813,−0.346,0.468)
P(4)	77	−14	−14	1	105	(−0.577,0.577,0.577)
$(\bar{1}11)$	−14	77	14	2	62	(−0.071,−0.740,0.669)
	−14	14	77	3	62	(−0.813,−0.346,−0.468)

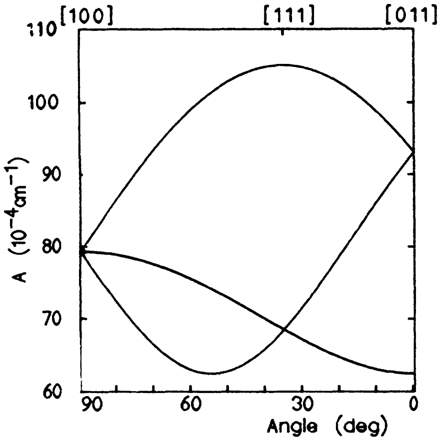

FIG. 1. The angular dependence lines [**B** in $(0\bar{1}1)$ plane].

0.42 Å, or about 18% of the GaP bond length.[28,29] Following Li and Myles, the simple interpretation is that, partially due to the fact that ${P_{Ga}}^{4+}$ is much more electronegative than the P and Ga atoms, and partially due to the smaller radii of the ${P_{Ga}}^{4+}$ orbitals in comparison with those for Ga, which causes a smaller overlap between the antisite ${P_{Ga}}^{4+}$ and P orbitals, the ${P_{Ga}}^{4+}$-P bond is much weaker than the Ga-P bond, so that the nearest-neighbor P atoms relax away from the antisite ${P_{Ga}}^{4+}$.

Now we investigate the effect of lattice relaxation on defect energy level, wave function, and hf interactions. For this end, we need to know the function V_{11} as the argument d_I/d_H. This problem is so difficult that no one can give the expression as yet. As a rough approximation, we assume that V_{11} is independent of E and depends only on d_I/d_H linearly. Thus, this may be done by requiring that $V_{11}=0$, when $d_I/d_H=1$ (the nearest-neighbor atom has no relaxation), and $V_{11}=-2.82$ eV, when $d_I/d_H=1.21$ (as has been determined above). Then the equation of a straight line passing through two points (1,0) and (1.21, −2.82) in the $V_{11}\sim d_I/d_H$ plane has the form

$$V_{11}=k(d_I/d_H-1)\ , \tag{22}$$

where $k\approx-13.4$, is the slope of the straight line. The validity of Eq. (22) will be illustrated by the following theoretical results and discussions.

The effect of lattice relaxation on the A_1 level of the GaP:P_{Ga}, obtained from Eq. (6), is shown in Fig. 2. This curve indicates that the energy level moves closer to the conduction-band edge for inward relaxation, while it moves deeper into the band gap for outward relaxation. We note that a similar trend has been predicted for various Ga- and P-site impurities in GaP and S, Se, and Te in Si by Li and Myles,[30] for N in GaP by Shen, Ren, and Dow,[25] and for P_{Ga}, As_{Ga}, and Sb_{Ga} in GaAs by Caldas *et al.*[31]

We have also calculated the trends of the $\langle A_1Rm|\psi\rangle$ with relative lattice relaxation d_I/d_H. Shown in Figs. 3(a) and 3(b) are the curves for η^2 and α_j^2 vs d_I/d_H for the P_{Ga}, P_4, and Ga_{12}. From the curves for η_j^2, it can be seen that the η^2 of P_{Ga} increases almost linearly for outward relaxation and decreases for inward relaxation. But the η^2 of P_4 (each of four P atoms on the $R=1$ shell) is opposite to the η^2 of the P_{Ga}. This then led to a conclusion that because of the antibonding character of the A_1 state of GaP:P_{Ga} an increase in the bond length causes an increase in localization of its wave function, which is identical to the result of density-functional-theory calculations for P, As, and Sb in GaAs and InP, by Caldas *et al.*[31]

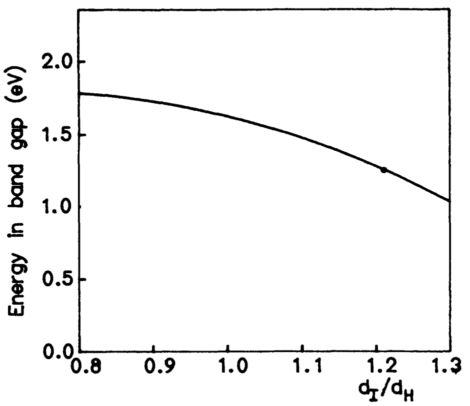

FIG. 2. Energy level of A_1 symmetry produced by P_{Ga} in GaP. The abscissa is the ratio of d_I/d_H between the antisite impurity and the host bond length. The ordinate is the band-gap energy with the zero of energy equal to the top of the valence band. Since d_I/d_H is a measure of the nearest-neighbor lattice relaxation around the antisite, this figure gives the dependence of the deep levels of the antisite on this relaxation. The dot corresponds to $E=E_v+1.25$ eV and $d_I/d_H=1.21$.

From Fig. 3(b), it is clear that the α^2 of P_4 decreases rapidly with an increase in d_I/d_H. Such a trend is similar to the argument proposed by Watkins and Corbett.[26] For P_{Ga}, its α^2 remains unaltered and equal to 100%. This means that in the process of the breathing model relaxation, the P_{Ga} will not be polarized and the P_4 will be polarized highly, so that a portion of the *s* character of the wave function on P_4 is transformed to the *p* character.

The changes of the hf-interaction constant vs d_I/d_H are shown in Fig. 3(c). The A of P_{Ga} is monotonically increasing, while the $A_\parallel$ and $A_\perp$ of P_4 are monotonically decreasing. In addition, the calculated results for Ga atoms on the $R=2$ shell are also shown in Fig. 3. From the curves of Ga_{12}, its η^2 and α^2 are smaller than those of P_{Ga} or P_4. Especially, its a and b are several orders of magnitude smaller than the A of P_{Ga}, which has not been measured by experiment. Because of this, a simple molecular model[32] can be used to estimate A.

V. CONCLUSIONS

The theory of the ENDOR and EPR spectra of deep impurity states has been extended to include the effects of lattice relaxation and applied to investigate the electronic

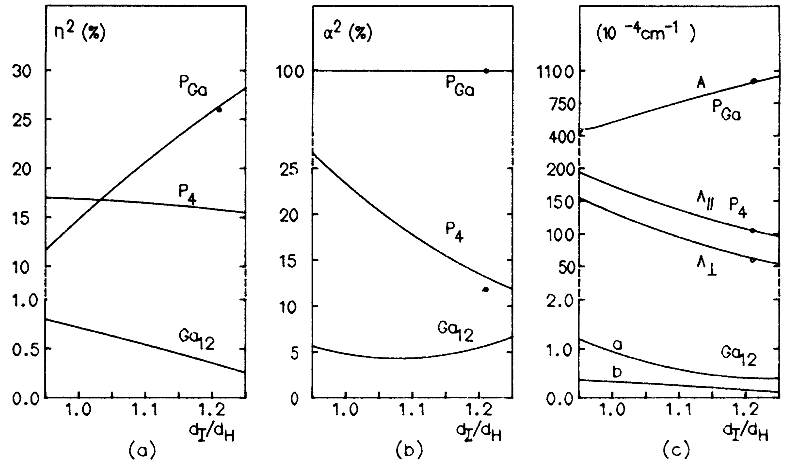

FIG. 3. Wave functions and hf interactions of A_1 symmetry produced by P_{Ga} in GaP. The abscissa is the ratio of d_I/d_H between the antisite and the host bond lengths. The ordinates are (a) the probabilities (η^2) of the unpaired electron and (b) s-character percentage (α^2) of the wave functions on antisite phosphorus (P_{Ga}), nearest-neighbor phosphorus (P_4), and next-nearest-neighbor Ga (Ga_{12}) atoms, and (c) the hf interactions A of antisite phosphorus, $A_{\parallel}$ and $A_{\perp}$ for each of four equivalent phosphorus atoms, a and b for each of the 12 atoms in the nearest Ga shell surround the substitutional P_{Ga} antisite. Since d_I/d_H is a measure of the nearest-neighbor lattice relaxation around the antisite, this figure gives the dependence of the wave functions and the hf interactions of the antisite on this relaxation. The dots are the experimental data taken from Refs. 3 and 5, and the lines are theoretical curves.

structure of the antisite defect GaP:P_{Ga}. By comparison of the theoretical results with experiments, satisfactory results are obtained, when the amount of the relaxation is determined to be about 21% of the host bond length. We have reproduced the angular dependence of the P_4 lines. The trend of the defect energy level E with the lattice relaxation has been discussed. The trends of the wave function and the hf interaction with varying amounts of lattice relaxation also have been systematically explored. So our calculation is successful. We also have applied this approach to the antisite defect GaAs:As_{Ga}. The theoretical results, which are in good agreement with EPR and ENDOR experiments, will be published elsewhere.

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