The simultaneous recording of current and radiation as a function of electric field strength produces many cases, like that in Fig. 3, which suggest that the instability responsible for the radiation affects the current magnitude.

The dependence of current on electric field during plasma injection (produced by square-wave voltages), Fig. 5, shows that more is to be learned and understood about injection of electron-hole pairs into semiconductors.

ACKNOWLEDGMENTS

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Jahn-Teller Effect for a Single Vacancy in Diamondlike Covalent Solids

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The static Jahn-Teller effect is studied for a monovacancy V^+, V^0, and V^- in diamondlike covalent solids by a new method which applies to the case of linear combinations of atomic orbitals (LCAO) as wave functions. In this "rigid LCAO model" the orbitals are assumed to follow the nuclei rigidly in the deformation. The formal calculation is almost identical to that of the usual treatment of the Jahn-Teller effect by the perturbation method. For the vacancy in diamond we use the electronic structure determined by Coulson and Kearsley in a molecular model. We obtain energy lowerings of the order of 0.1 eV and distortion amplitudes of about 0.05 Å. Finally we compare our results with the experimental data.

INTRODUCTION

It is well known that optical absorption and electron paramagnetic resonance give evidence for the identification of some irradiation defects in diamondlike covalent solids as being vacancies and interstitials. But, in some cases, the question is which defect, either a single vacancy or an interstitial atom, is responsible for a given absorption band or EPR line. Theoretical work then is very useful to guide us in the interpretation of experimental data.

In order to explain the GR 1 absorption band, centered around 2 eV, Coulson and Kearsley[1] have studied theoretically the electronic states associated with a vacancy in a molecularlike model. In a similar way, Yamaguchi[2] has calculated the electronic structure for both vacancies and interstitial atoms. Unfortunately their results do not provide sufficient information to identify the observed centers with certainty.

From electron paramagnetic resonance we can get an idea of the symmetry properties of the defects. Actually there is a lowering of the tetrahedral symmetry due to the distortion of the neighboring atoms. In this work, we shall study that distortion in the case of single vacancies, as arising from static Jahn-Teller effect. Jahn and Teller[3] have shown that if an electronic state of a polyatomic molecule is orbitally degenerate, the nuclear configuration is unstable with respect to small displacements, unless the nuclei lie on a straight line.

It is then necessary to know the electronic structure of the vacancy. We shall first recall the method and results of Coulson and Kearsley, who made use of linear combinations of atomic orbitals (LCAO) for the wave functions. Because the first-order perturbation theory of the Jahn-Teller effect is not very convenient in this case, and it is probably better to assume that the wave functions are rigidly translated according to the atomic displacements, we propose in the second part a new treatment of the Jahn-Teller effect which we shall refer to as the "rigid LCAO model." A great advantage of this model is that the symmetry considerations of the perturbation theory are still valid and the formal results are similar.

In the third section, we shall give our numerical results and conclusions, and then review the experimental data and their interpretation. Finally, the two are compared with one another and with Watkins's

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[1] C. A. Coulson and M. J. Kearsley, Proc. Roy. Soc. (London) **A241**, 433 (1957).

[2] T. Yamaguchi, J. Phys. Soc. Japan **17**, 1359 (1962).

[3] H. A. Jahn and E. Teller, Proc. Roy. Soc., (London) **161**, 220 (1937).

simple models[4] for vacancies in silicon. We hope to give some support to Coulson and Kearsley's conclusion that the GR 1 band arises from V^0 and to Watkins's model for V^+ in silicon.

I. ELECTRONIC STRUCTURE OF THE VACANCY

To determine the new stable configurations of the vacancy, we need the electronic energy levels and the corresponding wave functions. We use Coulson and Kearsley's molecular model in the Hartree-Fock approximation. Having reviewed all of their work, we obtained the same results, except for the ^2E level of V^-, which we think to lie somewhat higher than the ground state, whereas in their work it is in the neighborhood of the fundamental.

Let us now recall the basic assumptions of their model. Each carbon atom in the diamond lattice has four nearest neighbors forming a regular tetrahedron around it. For the perfect lattice we can solve the electronic problem by using sp^3 tetrahedral hybrids pointing from one atom towards its nearest neighbor.

The central atom O (Fig. 1) has four nearest neighbors A, B, C, D. When it is removed to create a vacancy, four bonds are broken. We can assume that the adjacent bonds are not greatly altered and that the deformation of the lattice around the defect is small. Therefore the electrons which are engaged in bonds outside the cube (Fig. 1) are not very much affected by the vacancy.

We may notice here that this localized model neglects the width of the valence band. For instance, the states of high-spin multiplicity must have higher energy values than calculated here. Actually the localization of an electron, added to spin reversal, requires an energy of the order of the valence bandwidth. We can then conclude that the numerical results obtained in the present model may be strongly modified when we make more realistic calculations.

In the following we shall use Slater's atomic $2s$ and $2p$ functions, from which we build the hybrid orbitals (we use a zero superscript for quantities involving the coordinates of the nuclei in their perfect-lattice positions)

$$\begin{aligned} a^0&=\tfrac{1}{2}(a_s{}^0-a_x{}^0+a_y{}^0-a_z{}^0)\,,\\ b^0&=\tfrac{1}{2}(b_s{}^0-b_x{}^0-b_y{}^0+b_z{}^0)\,,\\ c^0&=\tfrac{1}{2}(c_s{}^0+c_x{}^0-c_y{}^0-c_z{}^0)\,,\\ d^0&=\tfrac{1}{2}(d_s{}^0+d_x{}^0+d_y{}^0+d_z{}^0)\,. \end{aligned} \tag{1}$$

The Hamiltonian for the n-electron vacancy molecule may be written in atomic units:

$$H^0=\sum_i\,(T_i+V_i{}^0)+\tfrac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}}\,, \tag{2}$$

where $i,\ j=1,\ 2,\cdots,\ n$. T_i is the kinetic energy for electron i. $V_i{}^0$ is the potential energy of interaction between the vacancy electron i, the nuclei, the K-shell electrons of the molecule, and the external electrons surrounding the vacancy atoms A, B, C, D.

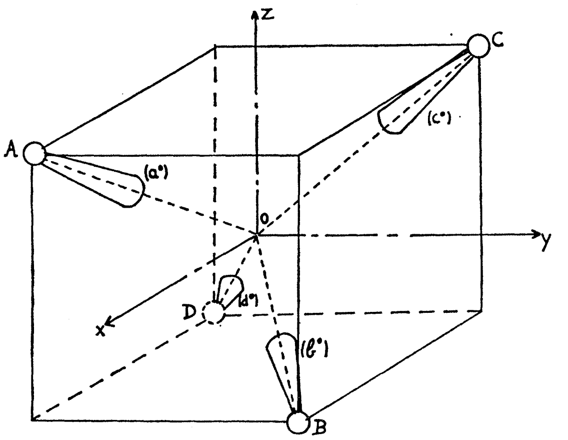

FIG. 1. The vacancy in O is surrounded by four carbon atoms A, B, C, D. The sp^3 hybrid orbitals a°, b°, c°, d° are given, which point from the carbon atoms towards the vacancy.

We may write

$$V_i{}^0=V_{Ai}{}^0+V_{Bi}{}^0+V_{Ci}{}^0+V_{Di}{}^0. \tag{3}$$

Let us now calculate the electronic levels both in the Hartree and Hartree-Fock approximations.

A. Hartree Approximation

Let us form delocalized one electron orbitals:

$$\begin{aligned} v^0&=\tfrac{1}{2}(a^0+b^0+c^0+d^0)\,, && (A_1)\\ t_x{}^0&=\tfrac{1}{2}(a^0+b^0-c^0-d^0)\,, &&\\ t_y{}^0&=\tfrac{1}{2}(-a^0+b^0+c^0-d^0)\,, && (T_2)\\ t_z{}^0&=\tfrac{1}{2}(a^0-b^0+c^0-d^0)\,. && \end{aligned} \tag{4}$$

They transform like basis functions of the irreducible representations A_1 and T_2 of the group T_D; this is a great advantage because it enables us to simplify the energy-level calculation by symmetry considerations.

The energy of the bonding orbital v^0 is about 7 eV lower than for $t_x{}^0$, $t_y{}^0$, $t_z{}^0$. From this, we deduce immediately the electronic energy levels for V^+, V^0, V^- which are, respectively, the vacancies with 3, 4, 5 electrons. In the case of V^+ (Fig. 2), v^0 (A_1) is filled with two electrons (with antiparallel spin) and there

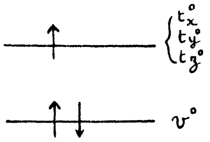

FIG. 2. The electronic srtucture of V^+ in the Hartree case: v^0 is lower in energy than $t_x{}^0$, $t_y{}^0$, $t_z{}^0$. The ground state is given by two electrons in v^0 and an unpaired electron in the threefold degenerate excited state with basis functions $t_x{}^0$, $t_y{}^0$, $t_z{}^0$ (Tz).

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[4] G. D. Watkins, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Academic Press Inc., New York, 1965), Vol. 3, p. 97.

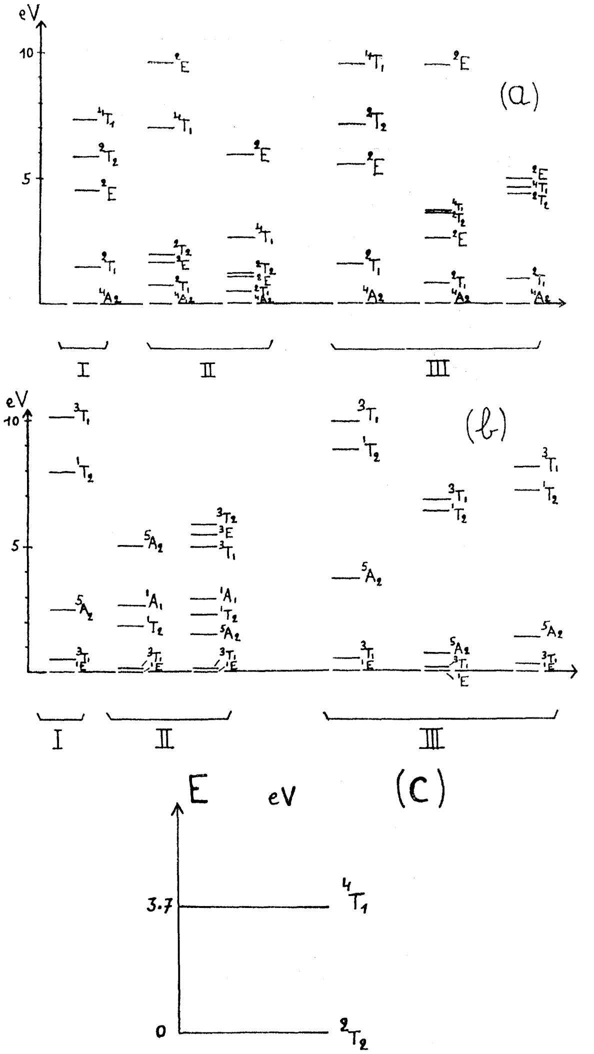

FIG. 3. The electronic structure of V^-, V^0, and V^+ in the molecular model. For V^- [Fig. 3(a)] and V^0 [Fig. 3(b)] the energy levels are given in the following way: (1) in I, Coulson and Kearsley's results with Slater functions; (2) in II, Coulson and Kearsley's results, without or with configuration interaction in their modified semiempirical model [in the V^- case, Fig. 3(a), we give, in I and II, the values which we have recalculated, including the correction of the ^2E level]; (3) in III, Yamaguchi's results. For V^+ [Fig. 3(c)] Slater functions have been used.

is an unpaired electron in the threefold degenerate state (T_2). To obtain V^0 and V^- we add one or two electrons in T_2. Now, we can apply those considerations to the case of the Hartree-Fock approximation.

B. Hartree-Fock Approximation

The many-electron wave functions are Slater determinants built from v^0, t_x^0, t_y^0, t_z^0 in the following way:

$$(v^0\bar{v}^0x^0)=\frac{1}{(3!)^{1/2}}\begin{vmatrix} v^0(1)\alpha(1) & v^0(1)\beta(1) & t_x^0(1)\alpha(1) \\ v^0(2)\alpha(2) & v^0(2)\beta(2) & t_x^0(2)\alpha(2) \\ v^0(3)\alpha(3) & v^0(3)\beta(3) & t_x^0(3)\alpha(3) \end{vmatrix} \tag{5}$$

in the V^+ case. Here v^0 means the orbital with α spin and $\bar{v}^0$ β spin.

Inside a $(v^0)^p(t^0)^{n-p}$ configuration (where $p=0, 1, \cdots, n$) we build linear combinations of Slater determinants transforming like basis functions for irreducible representations of the tetrahedral symmetry group T_D. Then we allow these configurations to interact with each other inside a given irreducible representation with given spin. In this way the maximum matrix to be diagonalized is a 3×3 one.

In a first step Coulson and Kearsley used Slater $2s$ and $2p$ atomic functions, but they obtained no allowed transitions which could account for the GR 1 band of Clark *et al.* (about 1.7 eV). Assuming that the inaccuracy of Slater functions is the chief cause of the discrepancy, they modified in a semiempirical way the values of some integrals according to the experimental data of optical spectra. They found the $V^0\,{}^1E\rightarrow{}^1T_2$ allowed transition to be responsible of the GR 1 band.

Yamaguchi studied a similar model for vacancies and determined his integrals in order to get the minimum value for the binding energy of the whole crystal. He used his integrals as parameters and calculated the level structure in several cases.

In Figs. 3(a), 3(b), and 3(c), we compare Yamaguchi's results to ours using Coulson and Kearsley's model. We note that the two lower levels are always the same in the different models. For V^+ and V^0 the ground state is degenerate, a situation which allows a Jahn-Teller distortion to occur. For V^- we can get distortion only for the excited states. We can notice that Stoneham[5] obtained similar results for V^0 by using the point-ion approximation for the vacancy molecule.

II. RIGID LCAO MODEL

We first detail the basic approximations and then we give the formal results. Finally we develop the cases of the Hartree and Hartree-Fock approximations.

When the nuclei move from their perfect lattice positions their Cartesian coordinates $U_\alpha{}^0$, $V_\alpha{}^0$, $W_\alpha{}^0$ ($\alpha=A, B, C, D$) become U_α, V_α, W_α with

$$\begin{aligned} U_\alpha &= U_\alpha{}^0+X_\alpha\,, \\ V_\alpha &= V_\alpha{}^0+Y_\alpha\,, \\ W_\alpha &= W_\alpha{}^0+Z_\alpha\,, \end{aligned} \tag{6}$$

where X_α, Y_α, Z_α are the Cartesian displacements. The electronic Hamiltonian can still be written

$$H=\sum_i (T_i+V_i)+\tfrac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}}\,, \tag{7}$$

where V_i is identical to the potential $V_i{}^0$, where we replace $U_\alpha{}^0$, $V_\alpha{}^0$, $W_\alpha{}^0$ by U_α, V_α, W_α.

Let us now assume that the sp^3 hybrid orbital named α remains centered on the corresponding nucleus

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[5] A. M. Stoneham, Proc. Phys. Soc. (London), 88, 135 (1966).

when the nucleus is displaced, and that it keeps the same form. That is equivalent to saying that the orbitals follow the atomic displacements rigidly. We then can write that α^0 (centered on the perfect-crystal position) becomes α (identical orbital centered on the displaced position).

Two basis functions $\psi_i{}^0$ and $\psi_j{}^0$ of a degenerate electronic level are combinations of the α^0. We make the assumption that, when the nuclei are displaced, they transform into ψ_i and ψ_j which have the same form but where we replace α^0 by α. The secular problem then is in terms of the matrix elements

$$H_{ij}=\langle\psi_i|H|\psi_j\rangle, \tag{8}$$

which could give the electronic levels as functions of the nuclei positions.

A. Method of Calculation

Let us first define normal displacements Q_s (Fig. 4) which are basis functions for irreducible representations of T_D. They are linear combinations of the Cartesian displacements X_α, Y_α, Z_α and their symmetry properties will allow us to simplify the calculations. The matrix elements H_{ij} [Eq. (8)] are functions of the new nuclear coordinates, i.e., of the Q_s. If we assume the atomic displacements to be small, then in order to simplify the secular problem, we can use the expansions to first order:

$$\begin{aligned}\alpha&=\alpha^0+\sum_s\left(\frac{\partial\alpha}{\partial Q_s}\right)_0 Q_s,\\ H&=H^0+\sum_s\left(\frac{\partial H}{\partial Q_s}\right)_0 Q_s.\end{aligned} \tag{9}$$

In the matrix element H_{ij}, we replace α and H by their approximated forms (9). In this way we obtain for H_{ij} an explicit function of the Q_s in which we only keep the terms up to first order in the Q_s. In both the Hartree and the Hartree-Fock approximations, it is equivalent to write

$$H_{ij}=\langle\psi_i{}^0|H^0|\psi_j{}^0\rangle+\sum_s Q_s\left(\frac{\partial}{\partial Q_s}\langle\psi_i|H|\psi_j\rangle\right)_0. \tag{10}$$

The first term is a diagonal one and gives the energy E^0 before distortion. To know the new electronic energy values we merely have to diagonalize the matrix whose general term is

$$\sum_s Q_s\left(\frac{\partial}{\partial Q_s}\langle\psi_i|H|\psi_j\rangle\right)_0. \tag{11}$$

If we denote by $\epsilon_n(Q_s)$ the eigenvalues of this matrix, the new electronic energy values after deformation become

$$E_n(Q_s)=E_n{}^0+\epsilon_n(Q_s). \tag{12}$$

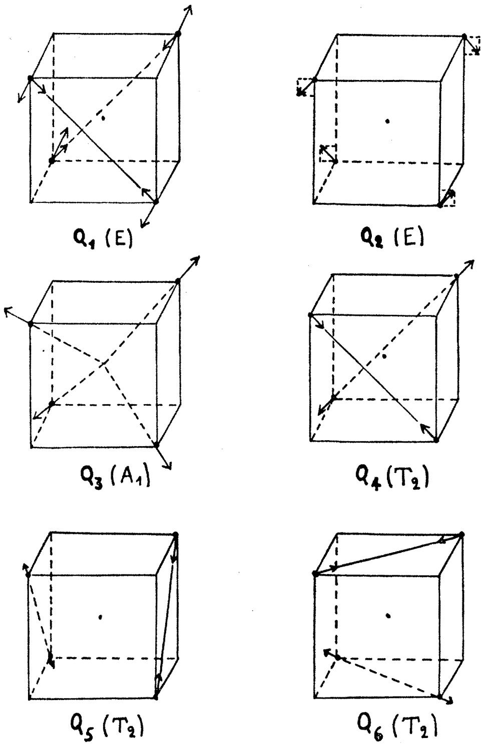

FIG. 4. Geometrical representation of the normal displacements: Q_1 and Q_2 transform like $2x^2-y^2-z^2$ and $\sqrt{3}(y^2-z^2)$ (E), Q_3 like $x^2+y^2+z^2(A_1)$; Q_4, Q_5, and Q_6 like x, y, and z ($T2$).

The potential energy for the motion of the nuclei is obtained in the simple form

$$W_n(Q_s)=E_n(Q_s)+\tfrac{1}{2}M\sum_s\omega_s{}^2Q_s{}^2, \tag{13}$$

where the second term gives, in the harmonic approximation, the interaction between A, B, C, D and the remaining part of the lattice. The frequencies ω_s have to be determined from the force constants of the perfect crystal. In practice we shall be concerned only with ω_A (symmetrical mode), ω_E (twofold degenerate mode), and ω_T (threefold degenerate mode of symmetry T_2).

The equilibrium configurations then will be obtained by resolving the set of simultaneous equations

$$\partial W_n/\partial Q_s=\partial E_n/\partial Q_s+M\omega_s{}^2Q_s=0, \tag{14}$$

which are valid only within the Born-Oppenheimer approximation.

From (14) we first calculate all the Q_s and then the splitting in energy due to the distortion. It is thus possible to determine the symmetries of the new stable configurations of the defect. We now consider the cases of twofold and threefold degenerate electronic levels.

B. Symmetry Considerations

Each energy level belongs to a given irreducible representation which is at most threefold degenerate.

TABLE I. Solutions for the threefold degenerate state. We have simplified our notations by putting $e_1=(I_2)^2/2M(\omega_{\mathrm{E}})^2$, $e_3=(I_3)^2/2M(\omega_T)^2$, $q_1=I_2/M(\omega_{\mathrm{E}})^2$, $q_3=I_3/M(\omega_T)^2$.

	Tetragonal case			Intermediate case						Trigonal case			
Q_1	$\frac{q_1}{6}$	$\frac{q_1}{6}$	$-\frac{q_1}{3}$	$-\frac{q_1}{12}$	$-\frac{q_1}{12}$	$-\frac{q_1}{12}$	$-\frac{q_1}{12}$	$\frac{q_1}{6}$	$\frac{q_1}{6}$	0	0	0	0
Q_2	$\frac{q_1}{2\sqrt{3}}$	$-\frac{q_1}{2\sqrt{3}}$	0	$-\frac{q_1}{4\sqrt{3}}$	$-\frac{q_1}{4\sqrt{3}}$	$\frac{q_1}{4\sqrt{3}}$	$\frac{q_1}{4\sqrt{3}}$	0	0	0	0	0	0
Q_4	0	0	0	0	0	0	0	$-q_3$	q_3	$-\frac{2}{3}q_3$	$\frac{2}{3}q_3$	$\frac{2}{3}q_3$	$-\frac{2}{3}q_3$
Q_5	0	0	0	0	0	$-q_3$	q_3	0	0	$-\frac{2}{3}q_3$	$\frac{2}{3}q_3$	$-\frac{2}{3}q_3$	$\frac{2}{3}q_3$
Q_6	0	0	0	$-q_3$	q_3	0	0	0	0	$-\frac{2}{3}q_3$	$-\frac{2}{3}q_3$	$\frac{2}{3}q_3$	$\frac{2}{3}q_3$
Energy lowering		$-\frac{e_1}{9}$				$-\frac{e_1}{36}-e_3$					$-\frac{4}{3}e_3$		

We will consider only E and T levels because nondegenerate levels like A_1 and A_2 cannot give rise to distortions. The only term which does not vanish in this case is the totally symmetrical displacement. This displacement Q_3 also arises in the case of degenerate levels, but as the term $E_n(Q_s)$ in Eq. (13) is linear in the Q_s in the first order approximation, the problem can be separated and the value of the other Q_s does not depend on Q_3. We will then restrict ourselves to the case where Q_3 vanishes in order to simplify the calculations. We will further give the value of the additional term due to Q_3 in a particular case (ground state of V^0).

We notice that the quantities

$$\left(\frac{\partial}{\partial Q_s}\langle\psi_i|H|\psi_j\rangle\right)_0 \tag{15}$$

have the same symmetry properties as the terms

$$\langle\psi_i{}^0|\left(\frac{\partial H}{\partial Q_s}\right)_0|\psi_j{}^0\rangle, \tag{16}$$

which we should find in the usual perturbation treatment of the Jahn-Teller effect. We then find similar results (see Appendix B).

1. E Level

For this twofold degenerate energy level, the basis functions $\psi_1{}^0$ and $\psi_2{}^0$ transform like $(2x^2-y^2-z^2)$ and $\sqrt{3}(y^2-z^2)$. By putting

$$I_1=\left(\frac{\partial}{\partial Q_2}\langle\psi_1|H|\psi_2\rangle\right)_0, \tag{17}$$

we obtain[6] for the matrix (11)

$$\begin{pmatrix} -I_1Q_1 & I_1Q_2 \\ I_1Q_2 & I_1Q_1 \end{pmatrix}. \tag{18}$$

If we introduce ρ and θ given by

$$Q_1=\rho\cos\theta\,,\quad Q_2=\rho\sin\theta\,, \tag{19}$$

we find by using (14), (18), and (19) that the equilibrium configurations correspond to

$$\rho=|I_1|/M\omega_E{}^2\,,\quad W_n=E^0\pm I_1{}^2/2M\omega_E{}^2\,. \tag{20}$$

From these equations we cannot get the values of Q_1 and Q_2 explicitly. To determine θ it is necessary to make a formal calculation up to second order. As a standard result we find

$$\theta=j\pi/3\,, \tag{21}$$

where j is an integer. We then obtain three equivalent tetragonal configurations which have ⟨100⟩, ⟨010⟩, and ⟨001⟩ symmetry axes.

2. T level

We treat both T_1 and T_2 levels which lead to the same results. The three basis functions $\psi_1{}^0$, $\psi_2{}^0$, and $\psi_3{}^0$ transform like x, y, z (T_2) or yz, zx, sy (T_1). If we define

$$I_2=\sqrt{3}\left[\frac{\partial}{\partial Q_2}(\langle\psi_2|H|\psi_2\rangle-\langle\psi_3|H|\psi_3\rangle)\right]_0,$$
$$I_3=\left(\frac{\partial}{\partial Q_4}\langle\psi_2|H|\psi_3\rangle\right)_0, \tag{22}$$

we are concerned with the more complicated matrix

$$\begin{bmatrix} (I_2/3)Q_1 & I_3Q_6 & I_3Q_5 \\ I_3Q_6 & -(I_2/6)Q_1+(I_2/2\sqrt{3})Q_2 & I_3Q_4 \\ I_3Q_5 & I_3Q_4 & -(I_2/6)Q_1-(I_2/2\sqrt{3})Q_2 \end{bmatrix}. \tag{23}$$

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[6] U. Opik and M. H. L. Pryce, Proc. Roy. Soc. (London) **A238**, 425 (1957).

To solve the set of Eqs. (14), we use the method of Opik and Pryce.[6] We obtain similar results (Table I). There are three possible solutions for the lowering in energy, i.e., a tetragonal, a trigonal, and an intermediate case. The last one gives a lowering in energy midway between the other two and has no practical interest. The choice between tetragonal and trigonal distortions only depends on the numerical values of I_2 and I_3. As for the E level, there are three equivalent tetragonal configurations with symmetry axes ⟨100⟩, ⟨010⟩, and ⟨001⟩. On the other hand, there are four equivalent trigonal configurations with symmetry axes in the four equivalent ⟨111⟩ directions.

C. Application of the Method

We detail here the application to the Hartree and the Hartree-Fock approximations.

Hartree Approximation

Let us consider the case of V^+ in the Hartree approximation. We choose this case only because it is the simplest one and because it is the most important one in Watkin's[4] EPR study on silicon. This center has one unpaired electron in a threefold degenerate state with basis functions t_x^0, t_y^0, and t_z^0. From the above considerations the problem is reduced to the determination of the following integrals (H_1 is the part of the total Hamiltonian involving the coordinates of electron 1):

$$I_2=\sqrt{3}\left[\frac{\partial}{\partial Q_2}(\langle t_y|H_1|t_y\rangle-\langle t_z|H_1|t_z\rangle)\right]_0,$$
$$I_3=\left(\frac{\partial}{\partial Q_4}\langle t_y|H_1|t_z\rangle\right)_0. \tag{24}$$

As t_x, t_y, t_z are linear combinations (4) of α, the two integrals (29) break down into a series of

$$\left(\frac{\partial}{\partial Q_s}\langle\alpha|H_1|\alpha\rangle\right)_0 \tag{25}$$

and

$$\left(\frac{\partial}{\partial Q_s}\langle\alpha|H_1|\beta\rangle\right)_0, \tag{26}$$

β being an sp^3 tetrahedral hybrid different from α. The term (26) involves only two- and three-center integrals while the first one [Eq. (29)] can be broken down in the following way into

$$\left(\frac{\partial}{\partial Q_s}\langle\alpha|-\frac{\Delta}{2}+V_{\alpha 1}|\alpha\rangle\right)_0+\sum_{\beta\neq\alpha}\left(\frac{\partial}{\partial Q_s}\langle\alpha|V_{\beta 1}|\alpha\rangle\right)_0. \tag{27}$$

The first part of (27) is a one-center integral which does not depend on the nuclear position, so that

$$\left(\frac{\partial}{\partial Q_s}\langle\alpha|-\frac{\Delta}{2}+V_{\alpha 1}|\alpha\rangle\right)_0=0. \tag{28}$$

The second term in (27) is a sum of two-center integrals. We then have shown that there is no contribution of the one-center integrals in the "rigid LCAO model," while in the perturbation treatment (Appendix B) we can see that those integrals lead to very large values of the energy lowering in trigonal distortions.

Hartree-Fock Approximation

Let us now discuss the application of the model to the Hartree-Fock approximation for the general case. In the matrix element (15), the wave functions ψ_i and ψ_j are now linear combinations of Slater determinants and the Hamiltonian is built with one- and two-electron operators. The one-electron operators have matrix elements similar to those obtained in the Hartree problem. We still have to investigate the matrix elements of $1/r_{ij}$,

$$\left(\frac{\partial}{\partial Q_s}\langle\psi_k|\tfrac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}}|\psi_l\rangle\right)_0, \tag{29}$$

which break down into integrals of the type

$$\left(\frac{\partial}{\partial Q_s}\int\alpha(1)\beta(2)\frac{1}{r_{12}}\gamma(1)\delta(2)d\tau_1 d\tau_2\right)_0, \tag{30}$$

with α, β, γ, $\delta=a$, b, c, or d. The one-center integrals vanish as in (28).

In the Hartree-Fock case we see another fundamental difference between the present model and the perturbation treatment. In the latter case, the electron interaction gives no contribution to the Jahn-Teller effect because $1/r_{ij}$ does not depend on the nuclear coordinates, while we now have some matrix elements (30) which can play an important role. More details on the calculations are given in the Appendix A.

III. NUMERICAL RESULTS AND DISCUSSION

We first give the numerical results for diamond in the "rigid LCAO model" with Slater atomic wave functions. We then review the main experimental results and discuss in some detail the identification of the defects.

A. Numerical Results in the LCAO Model

It is first necessary to find the order of magnitude of the frequencies ω_E and ω_T.

We can assume that both frequencies are of the order of the maximum optical value of the phonon spectrum,

$$2.5\times 10^{14}\ \text{rad/sec}. \tag{31}$$

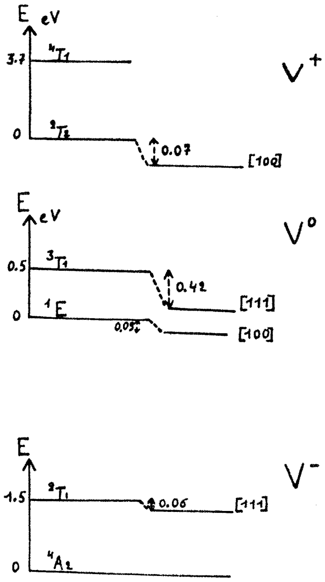

FIG. 5. The first energy levels of V^+, V^0, and V^- before and after distortion.

However, as Lidiard and Stoneham[7] have pointed out, in a simple model where we keep all the atoms fixed except A, B, C, D, we can show that

$$\omega_E=\sqrt{2}\omega_T. \tag{32}$$

However, for ω_E we will keep the value (31) which is not very different from

$$\omega_E=2.24\times10^{14}\ \text{rad/sec}$$

deduced by Lidiard and Stoneham[7] by using the force constants of Swalin. The numerical values of I_1, I_2, I_3 were computed from the tables of Kotani, Amemiya, and Simose[8] and of Von Hermann and Kopineck.[9] Some details are reported in Appendix A.

The numerical results and the corresponding distortion are given in Table II and Figs. 5 and 6 for the low-lying states of V^+, V^0, and V^- in the Hartree-Fock approximation and for V^+ in the Hartree one. Let us summarize these fesults in the following way:

(a) Energy lowering: In Fig. 5 we give the considered levels before and after distortion and in Table II we give the numerical results for the energy lowering in each case.

For V^+ in the Hartree-Fock approximation the ground state $^2T_2$ is 4 eV deeper than the first excited state $^4T_1$. So we have studied only the former which gives rise to tetragonal configurations. In the Hartree treatment of V^+ we obtain similar results.

For V^0 the ground state ^1E is 0.5 eV lower than the first excited state $^3T_1$. We have determined the energy lowering for both levels. The numerical values are about 0.1 eV for ^1E in a tetragonal configuration and 0.4 eV for $^3T_1$ in a trigonal one. We then see (Fig. 5) that both levels give almost the same energy, $^3T_1$ being about 0.17 eV above ^1E.

The $^4A_2$ ground state of V^- is not degenerate and so gives no distortion terms. The first excited state $^2T_1$ favors a trigonal distortion.

(b) Distortion amplitude: In Table II, we indicate the distortion amplitudes for the equilibrium configurations in each case.

For a tetragonal distortion we have three equivalent configurations with symmetry axes along the $\langle100\rangle$, $\langle010\rangle$, and $\langle001\rangle$ directions, from which we choose the first. In this case, $Q_2=0$, and only Q_1 does not vanish. We see [Fig. 6(a)] that the increases of the interatomic distances ΔR_{AB} and ΔR_{AD} are sufficient to determine the configuration. Their numerical values are given in Table II, except for an E level where we give only their absolute value because we cannot determine the sign of Q_1 to first order (20).

In the trigonal case we have four equivalent configurations (Table I): We choose the one which corresponds to $Q_4=Q_5=Q_6$. Then the three atoms A, B, C form an equilateral triangle [Fig. 6(b)] and D is on its symmetry axis. Once more we determine the new configuration by the numerical value of ΔR_{AB} and ΔR_{AD}.

(c) The symmetrical term Q_3: Up to now we have not considered this term in detail though it exists for each electronic level. From symmetry considerations the linear term in Q_3 can be written

$$\left(\frac{\partial}{\partial Q_3}\langle\psi_i|H|\psi_j\rangle\right)_0=I\delta_{ij} \tag{33}$$

both for E and T levels, and from Eq. (14) we obtain

$$\frac{\partial}{\partial Q_3}(\tfrac{1}{2}M\omega_A{}^2Q_3{}^2+IQ_3)=0, \tag{34}$$

where ω_A is the frequency of this symmetrical mode.

TABLE II. Numerical results in the "rigid LCAO model." For a T level we give ΔR_{AB} and ΔR_{AD} only for the most stable configuration.

Approximation	Center	Electronic level	ΔE tetragonal (eV)	ΔE trigonal (eV)	ΔR, Å
Hartree	V^+	T_2	0.33	0.18	$\Delta R_{AB}=-0.05$ $\Delta R_{AD}=0.025$
Hartree-Fock	V^+	$^2T_2$	0.09	0.05	$\Delta R_{AB}=-0.028$ $\Delta R_{AD}=0.014$
			0.09		$\Delta R_{AB}=0.028$ $\Delta R_{AD}=0.014$
	V^0	$^3T_1$	0.005	0.42	$\Delta R_{AB}=0.084$ $R_{AD}=-0.084$
	V^-	$^2T_1$	0.014	0.06	$\Delta R_{AB}=-0.033$ $\Delta R_{AD}=0.033$

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[7] A. B. Lidiard and A. M. Stoneham, in International Industrial Diamond Conference, Oxford, 1966 (unpublished).

[8] Kotani, Amemiya, and Simose, Proc. Phys. Math. Soc. Japan **20**, Extra 1 (1938).

[9] Von Hermann and Josef Kopineck, Z. Naturforsch **5a**, 420 (1950).

From (34) it follows that

$$Q_3 = -I/M\omega_A^2, \tag{35}$$

and the lowering in energy is given by

$$I^2/2M\omega_A^2. \tag{36}$$

The whole problem lies in the determination of I and ω_A. We have attempted to calculate this term only in the case of the ${}^1E$ ground state of V^0. The integral I can be put in the form

$$I = \left(\frac{\partial}{\partial Q_3}\langle\psi_i|H|\psi_i\rangle\right)_0 + \left[\frac{\partial}{\partial Q_3}\left(\sum_{\alpha\neq\beta} F_{\alpha\beta}\right)\right]_0, \tag{37}$$

where $F_{\alpha\beta}$ represents the repulsion between nuclei α and β. We give some details of the calculation in Appendix A. We notice that such a term does not appear in the calculation of I_1, I_2, I_3 because it vanishes by symmetry. For ω_A we have taken the value

$$\omega_A = 2.5\times10^{14}\ \text{rad/sec}. \tag{38}$$

For the ${}^1E$ level of V^0 we obtain a lowering in energy of about 1.2 eV and a symmetrical contraction of the vacancy molecule with amplitude 0.2 Å. From this estimate we can conclude that we obtain the right sign (contraction) and a reasonable order of magnitude despite the crudeness of the model (which is probably better for distortion terms than for Q_3).

From Table II and the values of this symmetrical contraction we conclude that we have obtained a reasonable set of results, while in the perturbation theory, the energy lowering in the case of trigonal distortions is about 5 to 10 eV (Appendix B). Finally, we notice that all this study concerns the static Jahn-Teller effect. A complete discussion of the static and dynamic cases would require the calculation of second order terms which can possibly alter some of the above theoretical conclusions.

B. Review of Experimental Results

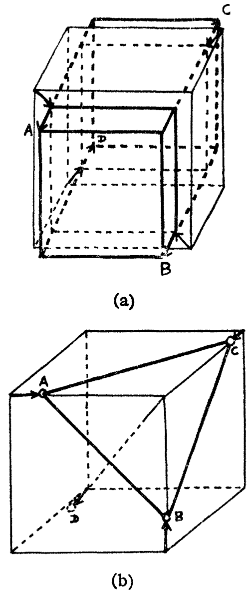

FIG. 6. Stable configurations of the vacancy: (a) tetragonal case; (b) trigonal case.

In 1957, Mitchell[10] suggested that the GR 1 absorption band of Clark *et al.*[11] centered about 2 eV could be due to electronic transitions in single vacancies. We have seen that Coulson and Kearsley found this value for the allowed transition ${}^1E\rightarrow{}^1T_2$ of V^0. But V^0 has also been proposed for other centers. We first examine the important B spectrum (or "c" system) observed in EPR (Harris, Owen, and Windsor[12]). The corresponding center has spin $S=1$ and a ⟨100⟩ symmetry axis. The study of its intensity[13] versus temperature leads to the conclusion that it corresponds to an excited state about 300 cm^{-1} higher than the ground state which is not seen by resonance. The last point is consistent with the electronic structure determined theoretically for V^0 and C^0,[1,2] but room for doubt remains. More recently, by studying the correlation between the GR 1 band and the "c" system, Clark *et al.*[14] strengthened the idea that the former was produced by V^0. They attributed this correlation to the formation of interstitial-vacancy pairs by irradiation. The vacancies would be responsible for the GR 1 band and the interstitial for the "c" system. However, we notice that Owen does not rule out the hypothesis of V^0 for the latter. The C spectrum ("b" system) with spin $S=1$ observed by Faulkner and Lomer[15] could also be attributed to V^0. As to the A spectrum ("d" system) whose spin is $S=\frac{1}{2}$, Yamaguchi[2] suggested that V^- is responsible for most of it. The centers associated with C and A spectra have a symmetry axis close to the ⟨322⟩ and ⟨311⟩ directions. Another A spectrum has been observed by Baldwin[13] who has interpreted it in terms of V^+ in a tetragonal configuration, but those results have not yet been confirmed.

Let us now summarize Watkin's EPR study[4] in silicon. He was able to identify a great number of EPR spectra in irradiated silicon. In particular, he attributed the spectra G_1 and G_2, respectively, to V^+ and V^-. The case of G_1 seems to be the most important one in this study. The corresponding defect has tetragonal symmetry and Watkins[4] has interpreted the whole G_1 spectrum by a simple Hartree model for V^+ (Fig. 2). He estimated the potential barrier between two tetragonal configurations to be of the order of 0.02 eV. It is possible that this value corresponds to the difference in energy between tetragonal and trigonal distortions.

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[10] E. W. J. Mitchell, Brit. J. Appl. Phys. **8**, 179 (1957).

[11] C. D. Clark, R. W. Ditchburn, and H. E. Dyer, Proc. Roy. Soc. (London) **A234**, 363 (1956); **A237**, 75 (1956).

[12] E. A. Harris, J. Owen, and C. Windsor, Bull. Am. Phys. Soc. **8**, 252 (1963).

[13] J. Owen, in *Physical Properties of Diamond*, edited by R. Berman (Oxford University Press, London, 1965), p. 274.

[14] C. D. Clark, I. Duncan, J. N. Lomer, and P. W. Whippey, Proc. Brit. Ceram. Soc. **1**, 85 (1964).

[15] E. A. Faulkner and J. N. Lomer, Phil. Mag. **7**, 1995 (1962).

C. Discussion of the Results

We first consider the case of V^0 which has a ${}^1E$ ground state and a ${}^3T_1$ level about 0.3 eV above it. V^0 can be responsible for the "c" system if the ${}^3T_1$ level favors a tetragonal stable distortion. Actually, we find that the new stable configurations are trigonal and since experimental results give no evidence of such distortions it is possible that the dynamic effect is important enough to prevent the static one. Nevertheless, the logical interpretation is that the neutral interstitial can account for the "c" system and V^0 for the GR 1 band of Clark *et al.*[11] This conclusion could then give some support to Coulson and Kearsley's calculation for the ${}^1E \rightarrow {}^1T_2$ transition in V^0 which appears to be of the same order of magnitude as the GR 1 band (2 eV). However, a more confident conclusion would require some knowledge about the Jahn-Teller effect on the first excited state ${}^3T_1$ of C^0 (predicted by Yamaguchi).[16]

We now can give some interesting conclusions for V^+. In this case the predicted configurations have tetragonal symmetry. Unfortunately, the theoretical studies of the electronic structure lead to the conclusion that, in irradiated diamonds, V^+ is much less stable than V^0 and V^-. However, as the ${}^2T_2$ ground state is very low compared to the first excited state (${}^4T_1$ about 4 eV above) we can expect this level still to be the fundamental one in silicon. If we assume that the integrals involved in the distortion problem do not vary too much we can extrapolate our results to the case of silicon. With this hypothesis we find, in agreement with Watkins, that V^+ has symmetry axes along the $<100>$ directions. In Table II we see that in the Hartree-Fock approximation the difference in energy between tetragonal configurations is about 0.04 eV. We can assume that the height of the potential barrier of reorientation between tetragonal distortions is smaller or at most equal to this value. We then find good agreement with the value deduced by Watkins from experimental measurements (0.02 eV).

The ground state of V^- is nondegenerate (${}^4A_2$) so there is no distortion for this level. However, as we have mentioned before, in a more accurate model where the whole crystal is taken into account such a level with high-spin multiplicity is probably less stabilized than in the molecular model of Coulson and Kearsley. If we then study the first excited state ${}^2T_1$ (about 1 eV higher in the molecular model) we find that it favors a trigonal distortion but we have no experimental data to check this calculation.

CONCLUSION

To analyze the Jahn-Teller effect for a single vacancy in diamond we started from a molecular model proposed by Coulson and Kearsley to determine its electronic structure. In their study the 3, 4, or 5 electrons of the vacancy are in states built from sp^3 hybrid orbitals centered on the four nearest neighbors of the missing atom.

To treat the Jahn-Teller distortions we have proposed a "rigid LCAO model" in which the atomic orbitals rigidly follow the nuclei in the deformation; the formal calculations required by this study are similar to those we should use in the first-order perturbation treatment. We have found that there was no contribution of the one-center integrals so that we obtain reasonable results when compared to experimental data.

However, it would be necessary to find a more elaborate model of the electronic structure for the vacancy and to see its influence on the results of the Jahn-Teller effect calculated in this model. Actually the numerical values can be greatly affected when we take better account of the crystal. It would be worth trying another method and applying the Green's function method to the study of the electronic structure and the Jahn-Teller effect for vacancies in diamondlike covalent solids.

We also notice that it would be interesting to apply the present study to the case of other systems whose electronic structure has been determined from LCAO wave functions and to compare the results with those of the perturbation method and with the experimental data.

APPENDIX A

Let us give the essential steps of the calculation in the "rigid LCAO model" where we are concerned with integrals such as

$$\left(\frac{\partial}{\partial Q_s}\langle\alpha|V_{\beta 1}|\alpha\rangle\right)_0,\qquad \left(\frac{\partial}{\partial Q_s}\langle\alpha|H_1|\beta\rangle\right)_0, \tag{A1}$$

and

$$\left(\frac{\partial}{\partial Q_s}\int \alpha(1)\beta(2)\frac{1}{r_{12}}\gamma(1)\delta(2)d\tau_1 d\tau_2\right)_0;$$

the last will be denoted $(\partial/\partial Q_s\langle\alpha\beta|\gamma\delta\rangle)_0$. All these integrals are one-, two-, three-, and four-center integrals. By using Mulliken's approximation[17] we can reduce them into two-center integrals. This circumstance allows us to simplify the calculations. The integrals I_1, I_2, I_3 can be expressed in the general form

$$I=\left[\frac{\partial}{\partial Q_s}\Big(\sum_{\alpha\neq\beta} f_{\alpha\beta}\Big)\right]_0, \tag{A2}$$

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[16] T. Yamaguchi, J. Phys. Soc. Japan **18**, 368 (1963).

[17] In this approximation we write, for instance,

$$\langle\beta|V_{\alpha 1}|\gamma\rangle=\lambda[\langle\beta|V_{\alpha 1}|\beta\rangle+\langle\gamma|V_{\alpha 1}|\gamma\rangle]$$

and

$$\langle\alpha\beta|\gamma\delta\rangle=\lambda^2[\langle\alpha\alpha|\gamma\gamma\rangle+\langle\alpha\alpha|\delta\delta\rangle+\langle\beta\beta|\gamma\gamma\rangle+\langle\beta\beta|\delta\delta\rangle],$$

with

$$\lambda=8.2797\times 10^{-2}.$$

where $f_{\alpha\beta}$ depends only on the distance between atoms α and β since the integrals considered in the problem involve two atoms α and β. The only coordinates which are of interest to us are

$$Q_2=\frac{1}{2\sqrt{2}}(-Y_A+Y_B+Y_C-Y_D-Z_A+Z_B-Z_C+Z_D),$$

$$Q_4=\frac{1}{2\sqrt{2}}(Y_A-Y_B+Y_C-Y_D-Z_A+Z_B+Z_C-Z_D). \tag{A3}$$

For these two coordinates we obtain

$$\left[\frac{\partial}{\partial Q_2}(\sum_{\alpha\neq\beta} f_{\alpha\beta})\right]_0=\tfrac{1}{2}(f_{AC}'-f_{AD}'-f_{BC}'+f_{BD}'),$$

$$\left[\frac{\partial}{\partial Q_4}(\sum_{\alpha\neq\beta} f_{\alpha\beta})\right]_0=(-f_{AB}'+f_{CD}'). \tag{A4}$$

In these relations $f_{\alpha\beta}$ is a function of the internuclear distance $R_{\alpha\beta}$. We are concerned with the derivatives

$$\left[\frac{d}{dR_{\alpha\beta}}f_{\alpha\beta}(R_{\alpha\beta})\right]_{R_{\alpha\beta}=R_{\alpha\beta}{}^0}, \tag{A5}$$

$R_{\alpha\beta}{}^0$ being the internuclear distance for the nuclei in their perfect crystal positions. As we have

$$R_{\alpha\beta}{}^0=R=2.54\text{ Å},$$

we can write (A5) in the simplified form

$$\frac{d}{dR}[f_{\alpha\beta}(R)]=f_{\alpha\beta}'. \tag{A6}$$

The only task to do now is to determine the different functions $f_{\alpha\beta}$ in each case. As we noted at the end of the Sec. II, we must consider matrix elements of $1/r_{ij}$ in the Hartree-Fock case. We then separate the Hartree problem from the Hartree-Fock one.

1. Hartree Case

As in the perturbation treatment [see (B11)], the matrix elements of one-electron operators to be calculated are

$$\left(\frac{\partial}{\partial Q_2}\langle t_y|H_1|t_y\rangle\right)_0,$$

$$\left(\frac{\partial}{\partial Q_4}\langle t_y|H_1|t_z\rangle\right)_0, \tag{A7}$$

$$\left(\frac{\partial}{\partial Q_4}\langle v|H_1|t_x\rangle\right)_0.$$

We introduce the quantities $\theta_{\alpha\beta}$ and $\Gamma_{\alpha\beta}$ defined by

$$\theta_{\alpha\beta}=\langle\alpha|-\Delta/2+V_{\alpha1}+V_{\beta1}|\beta\rangle,$$

$$\Gamma_{\alpha\beta}=\langle\beta|V_{\alpha1}|\beta\rangle. \tag{A8}$$

In order to simplify the calculations we have determined

$$\theta'=\theta_{AB}'+\theta_{CD}'$$

and

$$\Gamma'=\Gamma_{AB}'+\Gamma_{CD}'. \tag{A9}$$

All the quantities $\theta_{\alpha\beta}'$ being equal, we have from (A4) and (4)

$$\left(\frac{\partial}{\partial Q_2}\langle t_y|H_1|t_y\rangle\right)_0=\tfrac{1}{2}(-\theta'+4\lambda\Gamma'),$$

$$\left(\frac{\partial}{\partial Q_4}\langle t_y|H_1|t_z\rangle\right)_0=\tfrac{1}{2}(-\theta'+\Gamma'), \tag{A10}$$

$$\left(\frac{\partial}{\partial Q_4}\langle v|H_1|t_x\rangle\right)_0=\tfrac{1}{2}(-\theta'-\Gamma').$$

θ' and Γ' are two-center integrals and to calculate them it is necessary to use spheroidal coordinates centered on the two atoms in question. We also need the detailed form of the potential energy which turns out to be

$$V_{\alpha1}=-\left(\tfrac{4}{3}\delta^3r^2+4\delta^2r+6\delta+\frac{4}{r}\right)\times\exp(-2\delta r)-\int\frac{[\alpha(2)]^2}{r_{12}}d\tau_2. \tag{A11}$$

In this expression r is the distance between electron 1 and the atom α and r_{12} the distance between electrons 1 and 2. Another interesting form for $V_{\alpha1}$ is

$$V_{\alpha1}=f_1(r)+\frac{f_2(r)}{r}(-x\epsilon_x+y\epsilon_y-z\epsilon_z)+\frac{f_3(r)}{r}(-xy\epsilon_x\epsilon_y+x_z\epsilon_x\epsilon_z-yz\epsilon_y\epsilon_z), \tag{A12}$$

where $r^2=(x^2+y^2+z^2)$. In (A12), ϵ_x, ϵ_y, ϵ_z take the values ±1 and are determined from

$$\alpha=\tfrac{1}{2}(\alpha_s+\epsilon_x\alpha_x+\epsilon_y\alpha_y+\epsilon_z\alpha_z), \tag{A13}$$

where α_s, α_x, α_y, α_z are the Slater's $2s$ and $2p$ atomic orbitals defined by

$$\alpha_s=(\delta^5/3\pi)^{1/2}\exp(-\delta r_\alpha)r_\alpha,$$

$$\alpha_x=(\delta^5/\pi)^{1/2}\exp(-\delta r_\alpha)x_\alpha, \tag{A14}$$

and δ is the effective nuclear charge. The values of f_1,

f_2, f_3 are easily deduced from (A11):

$$f_1=-\left(\delta^3r^2+3\delta^2r+\tfrac{9}{2}\delta+\frac{3}{r}\right)\exp(-2\delta r)-\frac{1}{r},$$

$$f_2=\frac{1}{\sqrt{3}}\left[-\left(\frac{\delta^3r^2}{2}+\tfrac{3}{2}\delta^2r+\tfrac{5}{2}\delta+\frac{5}{2r}+\frac{5}{4\delta r^2}\right)\times\exp(-2\delta r)+\frac{5}{4\delta r^2}\right], \quad \text{(A15)}$$

$$f_3=\left(\frac{\delta^3r^2}{2}+\tfrac{3}{2}\delta^2r+3\delta+\frac{9}{2r}+\frac{9}{2\delta r^2}+\frac{9}{4\delta^2r^3}\right)\times\exp(-2\delta r)-\frac{9}{4\delta^2r^3}.$$

To determine Γ' we have used the form (A11) of $V_{\alpha 1}$ which is more interesting in this case. For θ' we have performed the calculations by analytical methods with the form (A12) and we have expressed all the results in terms of integrals like

$$I_{m,n}(f,g)=\int_{\lambda=1}^{\infty}\int_{\mu=-1}^{+1}(\lambda+\mu)^{m+1}(\lambda-\mu)^{n+1}f\left(\frac{1+\lambda\mu}{\lambda+\mu}\right)g\left(\frac{1-\lambda\mu}{\lambda-\mu}\right)\times\exp(-2\nu\lambda-\nu\mu)d\lambda d\mu, \quad \text{(A16)}$$

$$J_{m,n}(f,g)=\int_{\lambda=1}^{\infty}\int_{\mu=-1}^{+1}(\lambda+\mu)^{m+1}(\lambda-\mu)^{n+1}f\left(\frac{1+\lambda\mu}{\lambda+\mu}\right)g\left(\frac{1-\lambda\mu}{\lambda-\mu}\right)\times\exp(-\nu\lambda)d\lambda d\mu,$$

where $\nu=\delta R$. By derivation with respect to R we obtain

$$\frac{d}{dR}I_{m,n}=\delta\frac{d}{d\nu}I_{m,n}=\delta(-\tfrac{3}{2}I_{m+1,n}+J_{m,n+1}),$$
$$\frac{d}{dR}J_{m,n}=\delta\frac{d}{d\nu}J_{m,n}=-\frac{\delta}{2}(J_{m+1,n}+J_{m,n+1}). \quad \text{(A17)}$$

We have tabulated all the integrals of this kind by using the tables of Kotani, Amemiya and Simose.[9] We finally obtain the numerical values

$$\left(\frac{\partial}{\partial Q_2}\langle t_y|H_1|t_y\rangle\right)_0=-47\,502\times10^{-6}\delta^2,$$
$$\left(\frac{\partial}{\partial Q_4}\langle t_y|H_1|t_z\rangle\right)_0=-24\,868\times10^{-6}\delta^2, \quad \text{(A18)}$$
$$\left(\frac{\partial}{\partial Q_4}\langle v|H_1|t_x\rangle\right)_0=-92\,552\times10^{-6}\delta^2.$$

2. Hartree-Fock Case

We now have to deal with terms like $(\partial/\partial Q_s\langle\alpha\beta|\gamma\delta\rangle)_0$ defined in (A1). As we can reduce them by Mulliken's approximation in two-center integrals the general calculation of (A2)–(A4) still holds for them. The whole problem involves the following integrals in units of $10^{-6}\delta^2$:

$$\begin{array}{lll}
\langle vv|yy\rangle_2=13\,742, & \langle vv|vx\rangle_4=43\,240, & \langle xx|yz\rangle_4=-3631,\\
\langle vy|vy\rangle_2=24\,473, & \langle vv|yz\rangle_4=-216, & \langle yy|yz\rangle_4=8724,\\
\langle vy|xz\rangle_2=-3815, & \langle vx|xx\rangle_4=29\,408, & \langle xy|xz\rangle_4=7414,\\
\langle xx|yy\rangle_2=6178, & \langle vx|yy\rangle_4=1924, & \\
\langle yy|yy\rangle_2=19\,920, & \langle vy|vz\rangle_4=12\,622, & \\
\langle xz|xz\rangle_2=655, & \langle vy|xy\rangle_4=-5706. &
\end{array} \quad \text{(A19)}$$

These terms add to those determined in the Hartree case.

In the case of V^+, V^0, and V^- and for each considered electronic level we have to calculate matrix elements of Slater determinants. We have used Löwdin's method[18–20] in the case of orthonormal determinantal wave functions. The decomposition is in terms of the integrals (A19).

The numerical calculations will not be detailed here. The decomposition of the terms (A19) into integrals like

$$\left(\frac{\partial}{\partial Q_s}\langle\alpha\beta|\gamma\delta\rangle\right)_0 \quad \text{(A20)}$$

is straightforward but lengthy. After that we obtain only three types of integrals:

$$\langle\alpha\alpha|\beta\beta\rangle',\quad\langle\alpha\beta|\alpha\beta\rangle',\quad\langle\alpha\alpha|\alpha\beta\rangle', \quad \text{(A21)}$$

where we use the same notation as in (A4). Let us give briefly the method of calculation for each one.

The terms like $\langle\alpha\alpha|\beta\beta\rangle'$ have been calculated by using the $D_{\alpha\beta\gamma\delta}$ of Kotani, Amemiya, and Simose[8] and of Von Hermann and Kopineck.[9] A similar method holds

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[18] P. O. Löwdin, Phys. Rev. **97**, 1474, 1490 (1955).

[19] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1963).

[20] M. Lannoo, Thèse de 3ème Cycle, Orsay, 1966 (unpublished).

for $\langle\alpha\beta|\alpha\beta\rangle'$ in terms of the $C_{\alpha\beta\gamma\delta}$ for which we had to extrapolate the values from $\nu=7$ to $\nu=7.6$. Finally for $\langle\alpha\alpha|\alpha\beta\rangle'$ we have used the integrals $I_{m,n}$ and $J_{m,n}$ defined in (A16).

The symmetrical term Q_3: Let us now detail the calculation of (37). We have defined $F_{\alpha\beta}$ as the repulsion energy between atoms α and β, i.e., the sum of four terms:

(i) The exact repulsion between α and β, which is $16/R_{\alpha\beta}$;
(ii) an attractive term between atom α and the three electrons engaged in the three sp_3 orbitals centered on nucleus β and pointing outside the cube of Fig. 1;
(iii) the same term between atom β and the three electrons around α;
(iv) the repulsion between those electrons.

We can easily show that such terms do not appear in the calculation of the distortion. Actually we have

$$Q_3=\frac{1}{2\sqrt{3}}(X_A-Y_A+Z_A+X_B+Y_B-Z_B-X_C+Y_C+Z_C-X_D-Y_D-Z_D),\qquad\text{(A22)}$$

and as we have for I the form (A2) we obtain for the $F_{\alpha\beta}$ a contribution of the form

$$(F_{AB}'+F_{AC}'+F_{AD}'+F_{BC}'+F_{BD}'+F_{CD}').\qquad\text{(A23)}$$

As the $\Gamma_{\alpha\beta}'$ have the same form, this reduces to

$$6F_{AB}'.\qquad\text{(A24)}$$

However, in the distortion terms we obtain (A4) instead of (A23) and these expressions identically vanish.

We now can notice an important fact in the frequency determination. Up to now we considered only terms like

$$\tfrac{1}{2}M\omega_s^2Q_s^2,\qquad\text{(A25)}$$

where ω_s would be deduced from the force constants. However, there are second-order terms in Q_s^2 which can give an important contribution to this crystal elastic term. For this reason we have taken the value

$$\omega_A=\omega_E$$

instead of

$$\omega_A=\omega_E/2,$$

which we obtain by using the same model as in (32).

This remark remains valid for ω_E and ω_T and as we expect a positive contribution of the second-order terms, the energy lowerings we have found in Sec. II would be reduced. But, to be consistent, in such a model it would be necessary to study all the second-order terms like Q_rQ_s.

APPENDIX B

We recall here the essential steps of the determination of the Jahn-Teller effect when using the perturbation theory. As in (9) the electronic Hamiltonian can be expanded in a series of the Q_s:

$$H=H^0+\sum_s\left(\frac{\partial H}{\partial Q_s}\right)_0 Q_s.\qquad\text{(B1)}$$

The second term in (B1) can be studied by perturbation theory. For a degenerate electronic level with basis functions ψ_i^0 and ψ_j^0 the matrix elements of the perturbation are given by

$$\sum_s Q_s\langle\psi_i^0|\left(\frac{\partial H}{\partial Q_s}\right)_0|\psi_j^0\rangle,\qquad\text{(B2)}$$

while in the "rigid LCAO model" we had to study (11):

$$\sum_s Q_s\left(\frac{\partial}{\partial Q_s}\langle\psi_i|H|\psi_j\rangle\right)_0.\qquad\text{(B3)}$$

The symmetry properties of these two terms being identical the formalism is the same. To transpose the results it is sufficient to take new definitions for the integrals I_1, I_2, I_3 [Eqs. (17) and (22)]:

$$\begin{aligned}I_1&=\langle\psi_1^0|\left(\frac{\partial H}{\partial Q_2}\right)_0|\psi_2^0\rangle,\\ I_2&=\sqrt{3}\left[\langle\psi_2^0|\left(\frac{\partial H}{\partial Q_2}\right)_0|\psi_2^0\rangle-\langle\psi_3^0|\left(\frac{\partial H}{\partial Q_2}\right)_0|\psi_3^0\rangle\right],\qquad\text{(B4)}\\ I_3&=\langle\psi_2^0|\left(\frac{\partial H}{\partial Q_4}\right)_0|\psi_3^0\rangle.\end{aligned}$$

With these expressions all the conclusions of Sec. II are valid.

Let us now detail the perturbation. We can write

$$\left(\frac{\partial H}{\partial Q_s}\right)_0=\sum_i\left(\frac{\partial V_i}{\partial Q_s}\right)_0,\qquad\text{(B5)}$$

$\sum_i V_i$ being the potential energy defined in Sec. I. By putting

$$G_{is}=\left(\frac{\partial V_i}{\partial Q_s}\right)_0,\quad \eta_s=\sum_i G_{is},\qquad\text{(B6)}$$

the perturbation term [Eqs. (B1) and (B5)] can be written

$$\sum_s\eta_sQ_s.\qquad\text{(B7)}$$

The problem requires the determination of integrals such as

$$\langle\psi_i^0|\eta_s|\psi_j^0\rangle.\qquad\text{(B8)}$$

As the η_s are sums of one-electron operators, the integrals (B8) break down, both in the Hartree and Hartree-Fock approximation, into one-electron integrals such as

$$\langle v^0(1)|G_{1s}|v^0(1)\rangle,\quad \langle v^0(1)|G_{1s}|t_i^0(1)\rangle,$$
$$\langle t_i^0(1)|G_{1s}|t_j^0(1)\rangle;\quad i=x,\,y,\,z. \tag{B9}$$

1. Simplification of the Integrals (B9)

By definition the wave vectors v^0, t_x^0, t_y^0, t_z^0 do form bases for the irreducible representations of T_D. From (B6) it is also easy to show that the quantities G_{1s} transform in the same manner as do the Q_s. We can conclude from Fig. 4 that

$$G_{11},\, G_{12}\ \text{ belong to }\ E,$$
$$G_{14},\, G_{15},\, G_{16}\ \text{ belong to }\ T_2, \tag{B10}$$

Thus it is easy to show by symmetry considerations that I_1, I_2, I_3 can be reduced to the following terms only:

$$\langle t_y^0|G_{12}|t_y^0\rangle\ \text{ noted }\ \langle yy\rangle,$$
$$\langle t_y^0|G_{14}|t_z^0\rangle\ \text{ noted }\ \langle yz\rangle, \tag{B11}$$
$$\langle v^0|G_{14}|t_x^0\rangle\ \text{ noted }\ \langle vx\rangle.$$

To determine the G_{1s} we write

$$\frac{\partial V_1}{\partial Q_s}=\sum_\alpha \frac{\partial V_1}{\partial X_\alpha}\frac{\partial X_\alpha}{\partial Q_s}+\frac{\partial V_1}{\partial Y_\alpha}\frac{\partial Y_\alpha}{\partial Q_s}+\frac{\partial V_1}{\partial Z_\alpha}\frac{\partial Z_\alpha}{\partial Q_s}. \tag{B12}$$

As the transformation between the Q_s and the X_α is orthogonal,

$$\partial X_\alpha/\partial Q_s=\partial Q_s/\partial X_\alpha. \tag{B13}$$

We also have

$$V_1=\sum_\alpha V_{\alpha 1},\quad \alpha=A,\,B,\,C,\,D.$$

Thus we obtain with (B12) and (B13)

$$G_{1s}=\sum_\alpha\left[\left(\frac{\partial V_{\alpha1}}{\partial X_\alpha}\right)_0\frac{\partial Q_s}{\partial X_\alpha}+\left(\frac{\partial V_{\alpha1}}{\partial Y_\alpha}\right)_0\frac{\partial Q_s}{\partial Y_\alpha}+\left(\frac{\partial V_{\alpha1}}{\partial Z_\alpha}\right)_0\frac{\partial Q_s}{\partial Z_\alpha}\right] \tag{B14}$$
$$=\sum_\alpha G_{1s\alpha}.$$

As v^0, t_x^0, t_z^0 are linear combinations of a^0, b^0, c^0, d^0 the integrals (B11) break down into

$$\langle\alpha^0|G_{1s\alpha}|\alpha^0\rangle\ \text{ one-center},$$
$$\langle\beta^0|G_{1s\alpha}|\beta^0\rangle\ \text{ and }\ \langle\alpha^0|G_{1s\alpha}|\beta^0\rangle\ \text{ two-center}, \tag{B15}$$
$$\langle\beta^0|G_{1s\alpha}|\gamma^0\rangle\ \text{ three-center}.$$

We use Mulliken's approximation[1] for three-center integrals and write

$$\langle\beta^0|G_{1s\alpha}|\gamma^0\rangle=\lambda(\langle\beta^0|G_{1s\alpha}|\beta^0\rangle+\langle\gamma^0|G_{1s\alpha}|\gamma^0\rangle), \tag{B16}$$

with $\lambda=8.2797\times10^{-2}$. Thus we can write formally for the integrals (B11)

$$\langle yy\rangle=\langle yy\rangle_1+\langle yy\rangle_2+\langle yy\rangle_3, \tag{B17}$$

the same decomposition holding for $\langle yz\rangle$ and $\langle vx\rangle$. In (B17) we define the terms in the following way:

$-\langle yy\rangle_1$ is built from integrals like $\langle\alpha^0|G_{1s\alpha}|\alpha^0\rangle$,

$-\langle yy\rangle_2$ from $\langle\beta^0|G_{1s\alpha}|\beta^0\rangle$,

$-\langle yy\rangle_3$ from $\langle\alpha^0|G_{1s\alpha}|\beta^0\rangle$.

These terms are calculated by different methods.

2. Summary of the Calculations

We now can determine the one-center integrals. As $G_{1s\alpha}$ and $[\alpha(1)]^2$ are functions of the coordinates of electron 1 related to the atom α we take spherical coordinates r_α, θ_α, φ_α around this atom. By integrating first over angles we eliminate a large number of terms. To do this we choose the form (A12) for the potential $V_{\alpha1}$ and calculate the quantities $G_{1s\alpha}$ as combinations of partial derivatives of $V_{\alpha1}$. In this case we obtain analytical results.

The two-center integrals like $\langle\beta^0(1)|G_{1s\alpha}|\beta^0(1)\rangle$ need more elaborate methods. We only give here the essential features of the calculation. We can write

$$\langle\beta^0|G_{1s\alpha}|\beta^0\rangle=\frac{\partial Q_s}{\partial X_\alpha}\left[\frac{\partial}{\partial X_\alpha}\langle\beta^0|V_{\alpha1}|\beta^0\rangle\right]_{X_\alpha=0}+\frac{\partial Q_s}{\partial Y_\alpha}\left[\frac{\partial}{\partial Y_\alpha}\langle\beta^0|V_{\alpha1}|\beta^0\rangle\right]_{Y_\alpha=0}+\frac{\partial Q_s}{\partial Z_\alpha}\left[\frac{\partial}{\partial Z_\alpha}\langle\beta^0|V_{\alpha1}|\beta^0\rangle\right]_{Z_\alpha=0}. \tag{B18}$$

These terms involve the quantities

$$\Gamma_{\alpha\beta}(R_{\alpha\beta})=\langle\beta^0|V_{\alpha1}|\beta^0\rangle, \tag{B19}$$

where $R_{\alpha\beta}$ is the distance between atoms α and β. If we denote by $R_{\alpha\beta}^0$ this distance when α and β are in their perfect-crystal positions with

$$R_{\alpha\beta}^0=[(X_{\alpha\beta}^0)^2+(Y_{\alpha\beta}^0)^2+(Z_{\alpha\beta}^0)^2]^{1/2}=R, \tag{B20}$$

we can finally write in a more interesting way

$$\langle\beta^0|G_{1s\alpha}|\beta^0\rangle=\left(\frac{\partial Q_s}{\partial X_\alpha}X_{\alpha\beta}^0+\frac{\partial Q_s}{\partial Y_\alpha}Y_{\alpha\beta}^0+\frac{\partial Q_s}{\partial Z_\alpha}Z_{\alpha\beta}^0\right)\frac{1}{R}\frac{d}{dR}\Gamma_{\alpha\beta}(R). \tag{B21}$$

The only quantities we must know are the $\Gamma_{\alpha\beta}(R)$ which were determined in Appendix A. The calculations which follow are too extensive to present here, and we only mention that we have used analytical forms for the integrals proposed by Von Hermann and Kopineck.[9]

The other two-center integrals of the form $\langle\alpha^0|G_{1s\alpha}|\beta^0\rangle$ are much more complicated. To determine $G_{1s\alpha}$ from (A12), we must use spheroïdal coordinates centered on nuclei α and β and express all the integrals in terms of elementary ones which we have tabulated. Throughout the whole calculation we have followed the methods of Kotani, Amemiya, and Simose[8] to determine the auxiliary functions. Few of them have been extrapolated from the parameter $\delta R=7$ to 7.6 which is the value for diamond.

3. Numerical Results

We obtain the following values:

$$\begin{aligned}\langle yy\rangle&=-7.739\times10^{-6}\delta^2,\\ \langle yz\rangle&=197\,355\times10^{-6}\delta^2,\\ \langle vx\rangle&=-267\,231\times10^{-6}\delta^2.\end{aligned}\tag{B22}$$

We notice that $\langle yz\rangle$ and $\langle vx\rangle$ have much higher values than $\langle yy\rangle$. This comes from the fact that for the one-center integrals we have

$$\langle yz\rangle_1=-\langle vx\rangle_1\simeq10\langle yy\rangle_1,\tag{B23}$$

while two-center integrals are of the same order of magnitude in each case. We give (Table III) the energy lowering in each case, in the Hartree-Fock approximation with $\omega_E=\omega_T=2.5\times10^{14}$ rad/sec, maximum optical value of the phonon spectrum.

TABLE III. Energy lowering in the perturbation model. We can see that the energy lowering for a trigonal distortion takes on values which are too large in each case.

Center	Electronic level	ΔE tetragonal eV	ΔE trigonal eV
V^+	$^2T_2$	4.10^{-3}	11.5
V^0	^1E	4.10^{-3}	
	$^3T_1$	3.10^{-3}	9.4
V^-	$^2T_1$	7.10^{-4}	1.5

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Electronic Structure and Optical Properties of Hexagonal CdSe, CdS, and ZnS†

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Pseudopotential form factors and band structures are determined for CdSe, CdS, and ZnS. These band structures are then used to analyze the optical data for these crystals. The calculation confirms some earlier identifications of the optical structure in some cases, and causes new interpretations in other cases. In addition, some previously unidentified structure is explained. A calculation of the imaginary part of the dielectric function is given for hexagonal CdSe and ZnS.

I. INTRODUCTION

THE empirical pseudopotential method[1] (EPM) and related methods have been shown to yield accurate band structures for semiconductors,[2] insulators,[3] semimetals,[4] and metals.[5] With this method, the potential used in the secular equation to find the one-electron energy levels and wave functions is determined by a small number of parameters, the pseudopotential form factors. These parameters are obtained from experimental optical data: In the present work, reflectivity taken over a wide range of energy. The potential is appropriate for the states of interest, the valence and conduction band states, and the core states are not solutions of the secular equation.[6] The present work is a straightforward extension of the work of CB to the hexagonal, wurtzite structure semiconductors ZnS, CdS, and CdSe. The pseudopotential form factors obtained for cubic ZnS (zinc blende) in CB are taken over and are used for the calculation of the band structure of hexagonal ZnS (wurtzite). The knowledge gained in the ZnS calculation aids in the calculation of the band structures of hexagonal CdS and CdSe, using the

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