

**$A_1$ - $T_2$  splitting for substitutional nitrogen in diamond**

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The reason for which extended Hückel theory leads to an inverted order for the  $A_1$  and  $T_2$  levels of substitutional nitrogen in diamond is discussed in some detail. This situation is shown to originate from an overestimation of the interactions involving "s" states, which also leads to a bad description of the conduction band. The reduction of the corresponding parameters leads to a normal ordering  $E_{A_1} < E_{T_2}$  which agrees with the local-density calculations. This finding has implications for the existence of Jahn-Teller distortions which are discussed.

**I. INTRODUCTION**

There is experimental evidence for a trigonal Jahn-Teller distortion near the substitutional nitrogen defect in diamond.<sup>1,2</sup> One success of extended Hückel theory (EHT) was its ability to explain that situation quite naturally.<sup>3,4</sup> A  $T_2$  bound state was predicted within the band gap at about 2 eV from the bottom of the conduction band. As this state is populated with the extra donor electron, the ground state is orbitally degenerate. The system must then experience a Jahn-Teller distortion which was found to be strong, since the  $T_2$  state corresponds to a deep level.

This situation is completely opposite to what is obtained for shallow donors where the symmetrical  $A_1$  state is lower and is followed by a  $T_2$  state with much smaller binding energy. Furthermore, it is not in agreement with recent results of local density Green's-functions calculations<sup>5</sup> which also find the conventional ordering ( $E_{A_1} < E_{T_2}$ ) for the bound states. In this Communication we show the reason for which EHT fails to give the correct ordering of the states and how this is related to the shape of the conduction band. We also examine how this modifies the conclusions relative to the existence of Jahn-Teller distortions.

**II. ORDERING OF LEVELS IN THE UNDISTORTED CASE**

We view the formation of the substitutional nitrogen defect as the creation of a vacancy plus its replacement by the nitrogen atom. The electronic structure of this defect is then described by the coupling of the s and p states of the nitrogen atom with the electronic states at the vacancy. The dominant part of this coupling will be with the vacancy  $A_1$  and  $T_2$  states built mainly from the dangling bonds. (The  $T_2$  state is found in EHT at about -7 eV, and the  $A_1$  state gives a resonance near the top of the valence

band, i.e., at about -10 eV; the gap extends from about 1 to -9 eV in Messmer and Watkins calculation.<sup>3,4</sup>)

To discuss the origin of the substitutional nitrogen bound states in EHT we then diagonalize the  $2 \times 2$  matrices

$$\begin{bmatrix} E_{sN} - E & \beta_s - ES_s \\ \beta_s - ES_s & E_{A_1} - E \end{bmatrix} \quad (1)$$

for the  $A_1$  state, and

$$\begin{bmatrix} E_{pN} - E & \beta_p - ES_p \\ \beta_p - ES_p & E_{T_2} - E \end{bmatrix} \quad (2)$$

for the  $T_2$  state. The matrix of Eq. (1) describes the coupling of the nitrogen s state of energy  $E_{sN}$  with the  $A_1$  vacancy bound state. The parameters  $\beta_s$  and  $S_s$  are the corresponding coupling matrix element and overlap (since the states are not orthogonal). Similar notations are used in Eq. (2). The coupling to more delocalized conduction- and valence-band states is ignored.

To evaluate the coupling parameters we have to know the vacancy bound-states wave functions  $\psi_{A_1}$  and  $\psi_{T_2}$ . We view them as the corresponding combinations of the pure  $sp^3$  dangling bonds times a reduction factor  $\sqrt{p}$  plus a more delocalized part times  $\sqrt{1-p}$  [ $p$  represents the weight of the dangling bonds in the vacancy states  $\psi_{A_1}$  and  $\psi_{T_2}$  and is of order 50% (Refs. 3 and 4)]. We can thus write

$$\beta_s = 2 \left( \frac{p}{1 + 3pS_d} \right)^{1/2} \beta_s^0 \quad (3)$$

and

$$\beta_p = \frac{2}{\sqrt{3}} \left( \frac{p}{1 - pS_d} \right)^{1/2} \beta_p^0 \quad (4)$$

where  $S_d$  is the overlap between the  $sp^3$  dangling bonds. The parameter  $\beta_s^0$  represents the interaction between the nitrogen  $s$  state and one  $sp^3$  dangling bond. The parameter  $\beta_p^0$  is the interaction between a  $p$  nitrogen state along one bond with the  $sp^3$  orbital along the same bond.

Using (3) and (4) we can calculate  $\beta_s$  and  $\beta_p$  from standard EHT theory.<sup>3,4</sup> As we look for states near  $E \approx 0$  eV we first drop  $ES_s$  and  $ES_p$  in Eqs. (1) and (2). We find that  $\beta_s^0 = -28$  eV,  $\beta_p^0 = -20.16$  eV, and  $S_d = 0.15$  (we also have  $E_{sN} = -25.6$  eV and  $E_{pN} = -13.2$  eV). We can thus calculate the anti-bonding solutions of Eqs. (1) and (2) which lead to the  $A_1$  and  $T_2$  solutions of interest. These are given in Table I for  $p = 1$  and 0.5. In both cases the  $A_1$  and  $T_2$  states are in inverted order (i.e.,  $E_{A_1} > E_{T_2}$ ) and, as expected, for  $p = 0.5$  we find a value for  $E_{T_2}$  equal to  $-1$  eV, not far from Messmer and Watkins's value of  $-1.5$  eV (inclusion of the  $ES_p$  contribution gives  $-1.4$  eV). This shows that we get an essentially correct description of the  $T_2$  bound state predicted by EHT theory. This simplified description also allows us to understand why there is inverted order of the levels: This is simply because of the fact that the term  $\beta_s$  is overestimated as compared to  $\beta_p$ , in such a way that the antibonding  $A_1$  component is raised over the  $T_2$  one.

That this is really the case can be judged from the value of the ratio  $\beta_s/\beta_p \approx 2$ . The origin of this comes from the values of  $\beta_{ss}$ ,  $\beta_{s\sigma}$ , and  $\beta_{\sigma\sigma}$  (in the notations of Slater and Koster<sup>6</sup>) which correspond to  $\beta_{ss}/\beta_{\sigma\sigma} \approx 1.8$  and  $\beta_{s\sigma}/\beta_{\sigma\sigma} \approx 1.4$ . This is much too high when compared to the values determined from empirical tight-binding fits where these ratios are of order unity or less.<sup>7-9</sup> To improve one should probably reduce  $\beta_s$  by a factor of 2 which would give the usual ordering for the  $A_1$  and  $T_2$  level. To be more precise on that point, it is interesting to relate this to the detailed shape of the conduction band. EHT predicts a correct valence band but a completely wrong conduction band,<sup>10</sup> the  $\Gamma_2'$ , antibonding pure  $s$  state being much too high in energy. This is related to the overestimated value of  $\beta_{ss}$  and Messmer has

TABLE I.  $A_1$  and  $T_2$  energies in normal extended Hückel theory.

$p$ (eV)	1	0.5
$E_{A_1}$	+6.7	+1.7
$E_{T_2}$	+2.9	-1

TABLE II.  $A_1$  and  $T_2$  energies in extended Hückel theory with contracted  $s$  orbitals.

$p$ (eV)	1	0.5
$E_{A_1}$	+1.8	-1.9
$E_{T_2}$	+2	-1.6

corrected this by using contracted Slater  $s$  functions (the argument in the exponential being increased by 25%). This gave a great improvement on the band structure, the conduction band being much better and the valence band remaining practically unaltered.

We can estimate the corrections brought by such a modification. The vacancy states will remain practically unaltered (the main coupling occurs between the  $sp^3$  dangling bonds and the valence band). The correction results from changes in  $\beta_s$  and  $\beta_p$  which are multiplied by reducing factors, respectively, equal to 0.6 and 0.85. Inserting these values into the equations for the  $A_1$  and  $T_2$  states now gives the values of Table II. Clearly, in both cases, the normal order is restored, and we obtain two bound states for  $p = 0.5$ . Our estimation is certainly approximate but clearly shows that the  $A_1$ - $T_2$  splitting is closely related to a correct description of the conduction band (this is also trivially the case for shallow donors).

Our conclusion is thus that the  $A_1$  state is likely to be lower than the  $T_2$  state, as was recently found in self-consistent local density plus pseudopotential calculations.<sup>5</sup>

### III. POSSIBILITY OF JAHN-TELLER DISTORTIONS

If we accept the fact that  $E_{A_1} < E_{T_2}$  the excess donor electron goes into the  $A_1$  state and there is in principle no Jahn-Teller distortion, since the ground state is nondegenerate. This conclusion is opposite to the experimental evidence. However, there are still possibilities for distortions which we can obtain by treating the couple of levels  $A_1$  and  $T_2$  together. For this we consider one trigonal distortion corresponding to a normal displacement  $Q$  (one possibility is pictured on Fig. 1) such that the system has  $C_{3v}$  symmetry along the  $\langle 111 \rangle$  axis. For zero distortion we take the origin of energies on the  $A_1$  level,  $E_{T_2}$  being at an energy  $\Delta$  above. There will be linear electron-phonon coupling in  $Q$  within the manifold of the four electronic states of the  $A_1$  and  $T_2$  levels. The corresponding matrix can be reduced by symmetry into

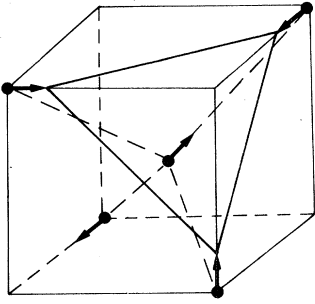


FIG. 1. Trigonal distortion near the nitrogen substitutional atom in diamond.

blocks of the form

$$\begin{array}{cc|cc} 0 & GQ & 0 & 0 \\ GQ & \Delta + IQ & 0 & 0 \\ \hline 0 & 0 & \Delta - \frac{1}{2}IQ & 0 \\ 0 & 0 & 0 & \Delta - \frac{1}{2}IQ \end{array} \quad (5)$$

The terms  $IQ$  and  $-\frac{1}{2}IQ$  correspond to the ordinary Jahn-Teller effect within the  $T_2$  state, while  $GQ$  expresses the interlevel coupling between  $A_1$  and  $T_2$ . The stable situation can be obtained by determining the eigenvalues of Eq. (5), adding a quadratic term  $\frac{1}{2}kQ^2$  and minimizing with respect to  $Q$  for the lower-energy branch. For simplicity we discuss here only two limiting cases, i.e., pure intralevel coupling ( $G=0$ ) and pure interlevel coupling ( $I=0$ ).

#### A. Pure $T_2$ coupling ( $G=0$ )

The matrix is completely diagonal and the stable situation is obtained from the comparison between the two branches

$$E_{A_1} = \frac{1}{2}kQ^2 \quad (6)$$

and

$$E_{T_2} = \Delta + IQ + \frac{1}{2}kQ^2 \quad (7)$$

The first one gives a minimum equal to zero, while the second one gives  $\Delta - I^2/2k$ . Thus the system will experience a static trigonal distortion only if the following condition is satisfied:

$$\Delta < I^2/2k \quad (8)$$

In this case it is energetically favorable to promote an electron from the  $A_1$  to the  $T_2$  state. This costs an energy  $\Delta$  but the system can thus distort with a gain in energy equal to  $I^2/2k$  which can be larger than  $\Delta$ . The final situation is thus qualitatively analogous to what is obtained in the inverted case.

#### B. Pure interlevel coupling ( $I=0$ )

The eigenvalue of (5) corresponding to the lower-energy branch gives

$$E = \frac{1}{2}\Delta - [(\frac{1}{2}\Delta)^2 + G^2Q^2]^{1/2} + \frac{1}{2}kQ^2 \quad (9)$$

This has a minimum for  $Q \neq 0$  at a value

$$Q = [(G/k)^2 - (\Delta/2G)^2]^{1/2} \quad (10)$$

which exists only if the following condition is realized:

$$G^2/k > \frac{1}{2}\Delta \quad (11)$$

i.e., for sufficiently strong interlevel coupling. In this case the minimum energy is given by

$$E_{\min} = -\frac{1}{2}k(G/k - \Delta/2G)^2 \quad (12)$$

In this case, it is the  $A_1$  state which is stabilized by the interlevel coupling. The final state will be an admixture of the  $A_1$  and  $T_2$  states.

In both limits, there is a condition on the strength of the electron-phonon coupling [given by Eq. (8) or Eq. (11)] in order that a stable distortion can exist. This is also true in the general case<sup>11</sup> but the main conclusion of this discussion is that distortions can still exist by virtue of the intralevel and interlevel coupling for the  $A_1$  and  $T_2$  system.

A simple empirical suggestion can be made as regards this distortion. It is well known that the elements of columns  $N > 4$  tend to form systems where each atom is involved in  $(8-N)$  bonds (the so-called  $8-N$  rule<sup>12</sup>).  $8-N$  electrons of each atom are thus engaged in bonds and  $2N-8$  in lone-pair nonbonding states. If such a tendency remains for the corresponding substitutional impurity in zinc-blende systems we can predict very simply the kind of distortion which would occur. For instance, neutral oxygen would form two bonds, which is likely to be true from the evidence in  $\text{SiO}_x$  compounds. As regards neutral  $N$  it would tend to form three stronger bonds with three neighbors and a weaker bond with the fourth one. In such a case the donor electron would go into the weaker antibonding state which would be much like the isolated dangling bond state whose energy is in the lower part of the energy gap. This was effectively the tendency found in EHT calculations, although their conclusions have to be taken with some care, in view of their inverted  $A_1T_2$  order at zero distortion.

#### IV. CONCLUSION

From simple considerations, we have been able to show that the inverted order predicted by EHT for the  $A_1$  and  $T_2$  levels of substitutional nitrogen in diamond was due to an overestimation of the parame-

ters involving the  $s$  states. This is related to the shape of the conduction band which is completely wrong in usual EHT theory, the  $\Gamma'_2$   $s$  antibonding state being much too high in energy. The reduction of these interactions lowers the  $\Gamma'_2$  state and restores the normal order  $E_{A_1} < E_{T_2}$ . This new situation is

less favorable for Jahn-Teller distortions, and the electron lattice interaction must be larger than some threshold value for such distortions to exist. Finally we have presented arguments supporting the idea that the nitrogen tends to form three stronger bonds and a weaker one.

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