with lower power being required for the forward transition. Since the finished unit, which had a heat sink, usually could stand power dissipation of more than a few watts without noticeable change, the effect is not likely to involve heating, melting, or crystallization of materials involved. Since the above-described fabrication process for GaAs crystals of more than 10^{18} cm^{-3} donors provides nearly normal p-n junctions with

In-Zn alloy, we do not think any oxide layers are involved in the observed effect.

[5] C. T. Sah, R. N. Noyce, and W. Shockley, Proc. IEEE 45, 1228 (1957).

[6] N. Holonyak, Jr., D. L. Keune, R. D. Burnham, and C. B. Duke, Phys. Rev. Lett. 24, 589 (1970).

[7] See, for instance, G. W. Ludwig and H. H. Woodbury, Solid State Phys. 13, 223 (1962).

LINEAR COMBINATION OF ATOMIC ORBITAL-MOLECULAR ORBITAL TREATMENT OF THE DEEP DEFECT LEVEL IN A SEMICONDUCTOR: NITROGEN IN DIAMOND

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A deep defect level in a semiconductor is simulated by a large cluster of host atoms surrounding the defect. The electronic states of the entire system are then computed by linear combination of atomic orbital-molecular orbital techniques. The nitrogen donor in diamond is treated as an example. A large Jahn-Teller distortion is predicted which forces the donor state down close to the valence band, in good agreement with experiment. The calculated donor wave function agrees with EPR and electron-nuclear double resonence results.

The effective-mass treatment of Kohn and Luttinger[1] has been highly successful in describing the electronic structure of shallow impurity states in semiconductors. However, this approach has not been successful for defect states which are located more than ~0.1 eV from the band edges. A satisfactory theoretical treatment of the deeper levels has not been given and poses one of the central unsolved theoretical challenges in solid-state physics.

In this Letter we describe a possible approach to the problem using molecular-orbital (MO) techniques. We consider a large molecule made up of the defect and a sufficient number of host-atom neighbor shells surrounding it to constitute a small "crystal." The electronic states of the entire system are then computed by using an approximate linear combination of atomic orbital-molecular orbital (LCAO-MO) method on a high-speed electronic computer.

As a model calculation, we consider the 35-carbon-atom diamond lattice shown in Fig. 1. For the present calculation extended Huckel theory[2] (EHT), which is a simple one-electron molecular-orbital treatment, has been used. The EHT method may be characterized briefly as follows:

(1) The MO's, φ_i, are represented as $\varphi_i = \sum_\nu c_{\nu i}\chi_\nu$, where χ_ν is an atomic orbital.

(2) The solution of the secular equations $\sum_\nu (H_{\mu\nu} - E_i S_{\mu\nu})c_{\nu i} = 0$ yields the MO energies E_i and the MO coefficients $c_{\nu i}$. $S_{\mu\nu}$ are the overlap matrix elements, and $H_{\mu\nu}$ the matrix elements of an effective one-electron Hamiltonian H.

(3) $H_{\mu\nu} = \frac{1}{2}K(H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu}$, $H_{\mu\mu} = -I_\mu$, where the I_μ are taken as the empirical atomic ionization energies.

The atomic orbitals are taken to be one 2s and three 2p Slater orbitals on each carbon atom (orbital exponent, 1.625); the I_μ used are 19.44

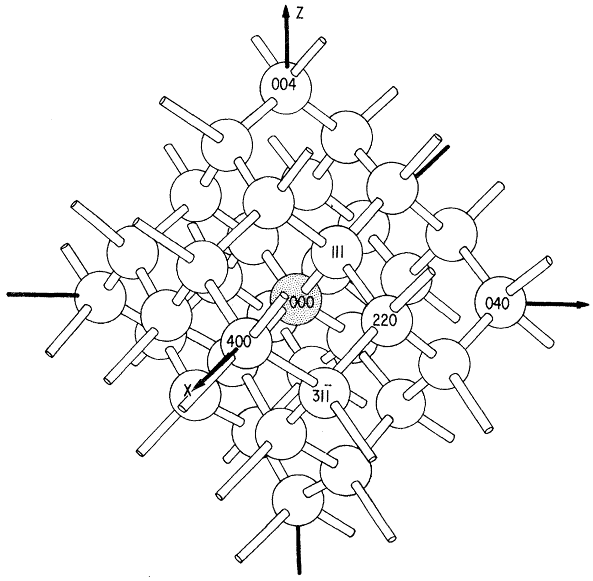

FIG. 1. The 35-atom cluster used for the LCAO-MO calculations.

and 10.67 eV for the 2*s* and 2*p* orbitals, respectively.[3] The value of $K=1.75$ is used in the expression for $H_{\mu\nu}$.[2] It will be shown below, by comparing the calculation of the 35-carbon-atom system with a calculation of the system when the central atom is replaced by a defect, that electronic levels associated with the defect can be identified and LCAO-MO wave functions for the localized states obtained.

First, consider the calculation for the 35-carbon-atom system. The energies of the 140 MO's which result are shown in Fig. 2(a). It is apparent that the model contains enough atoms so that the "band structure" associated with the solid is beginning to emerge. In particular, we see that the bonding MO's are grouped into what can be identified as the valence band; then there is a forbidden gap followed by a conduction band consisting of the antibonding orbitals.

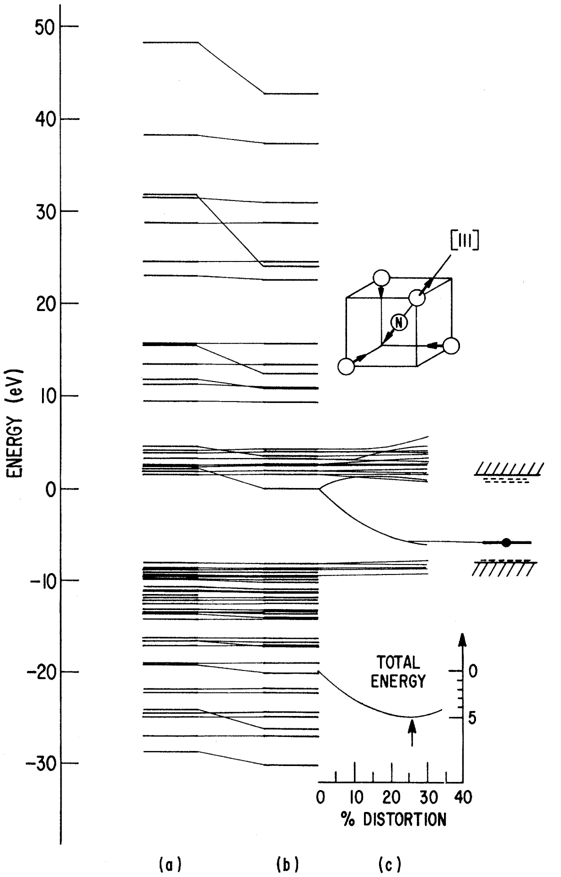

FIG. 2. (a) The energies of the one electron MO's for the 35-carbon-atom "diamond." (b) The energies with nitrogen as the central atom, no lattice relaxation. (c) Effect of Jahn-Teller distortion. The total energy has a minimum when the amplitude of the normalized distortion mode (shown in inset) is ~26 % of the nearest-neighbor distance. The distortion causes a lowering of the donor level to $\sim E_V+2.2$ eV.

As a check on the model, the energy levels of Fig. 2 can be compared with the known properties of the band structure of diamond. The band gap of Fig. 2(a) is 9.5 eV while the observed indirect gap value is 5.5 eV.[4] (Part of this discrepancy can be attributed to the finite size of the model solid.) The width of the valence band in the figure is 20.7 eV, which agrees rather well with the band-structure-calculation value, 22.5 eV.[5] We conclude therefore that this model does indeed represent a reasonable starting point for the defect calculations. Treatments more sophisticated than the simple EHT method and which use a larger basis set would obviously be more realistic. However, all involve considerably more complexity in the calculation. The encouraging feature is that this very simple treatment appears to provide a rather reasonable description.

A further feature of the model is that it describes elastic restoring forces.[6] The total energy of the system is given by $E_{\mathrm{tot}}=\sum_i n_i E_i$, where n_i is the occupation number of *i*th MO. By distorting the lattice and recalculating the total energy, approximate elastic constants may be determined.[7] For our 35-carbon model, we calculate $C_{11}=8.58$, $C_{12}=2.67$, and $C_{44}=5.00$ (10^{12} dyn/cm^2). These compare remarkably well with the experimental values for diamond[8] of 10.76, 1.25, and 5.67, respectively. This feature is important because it allows us to investigate lattice relaxations around the defect.

In Fig. 2(b) we show the one-electron energies for the case in which the central atom is replaced by nitrogen (Slater exponent 1.95, ionization potentials 25.58 and 13.19 eV for the 2*s* and 2*p* orbitals, respectively[2]). We note that a triply degenerate MO has been pulled down from the conduction band into the forbidden gap. Its energy is $E_c-1.5$ eV and we identify this as the nitrogen donor state.

It is known from EPR studies[9] that the nitrogen donor is Jahn-Teller distorted in a $\langle 111\rangle$ direction. This is consistent with the degeneracy of the state predicted by our calculation and we can probe this directly by letting the lattice relax. A small $\langle 111\rangle$ displacement of the nitrogen alone and a small trigonal distortion of the four nearest neighbors were imposed and the Jahn-Teller coupling coefficients determined. From this, a combined mode was determined. The total energy and the MO energies near the gap are plotted versus the distortion in Fig. 2(c). We see that a very large Jahn-Teller distortion is predicted. The total Jahn-Teller stabilization energy is ~5.0 eV. As a result of this distortion, the nitrogen donor level drops to within 2.2 eV of the valence-band edge.

Experimentally, the electrical level position for the nitrogen donor has been estimated to be ~1.5 eV from the valence band.[10,11] The reason for its being so deep has been a mystery and indeed has led some to doubt the experimental interpretation. Effective-mass estimates lead to ~$E_c - 0.4$ eV.[12] We believe our calculations demonstrate for the first time why the donor level is so deep. It is the result of a very large Jahn-Teller distortion which can be estimated directly in this type of calculation. The fact that Jahn-Teller effects can be important in determining the electrical level position of a deep level in the gap has previously been pointed out.[13] However, we believe that this is the first quantitative demonstration of this point.

The MO wave function determined for the level can also be compared with experiment via hyperfine interactions observed in EPR[9] and ENDOR[14] studies. Figure 3 shows the calculated MO 2p character along the ⟨111⟩ distortion direction for the nitrogen and the (111) carbon atom as a function of the distortion. The circled points are estimates from the anisotropic part of the observed hyperfine interactions.[15] Also in the figure, the unbalanced p character of the total charge density on the nitrogen atom—determined by summing over all the occupied orbitals—is compared with that estimated from the observed nitrogen quadrupole interaction.[15] A very good fit is indicated at the estimated 26% distortion. We conclude therefore that the wave functions generated by this calculation are realistic.[16] We conclude further that the detailed agreement of Fig. 3 serves as strong support for the magnitude of the distortion predicted by the calculation.

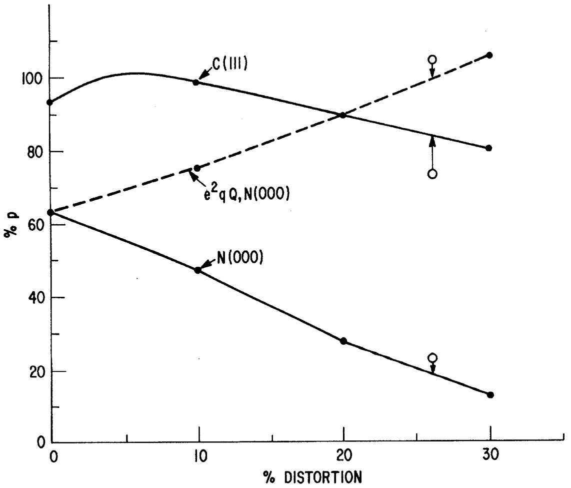

FIG. 3. Solid lines: percentage 2p character on the nitrogen atom (000) and its (111) carbon neighbor for the calculated donor MO versus the amplitude of the Jahn-Teller distortion. Dashed line: percentage unbalanced 2p character of the total electronic charge density on the nitrogen atom. The experimental points were derived from nuclear magnetic dipole and electric quadrupole hyperfine data obtained from EPR and ENDOR studies.

In summary, we have described a possible approach to the problem of the deep defect level using molecular-orbital theory on a large cluster surrounding the defect. In the example considered here we have chosen to use the simplest representation of the MO theory, namely the EHT method. This has proved quite successful for the neutral nitrogen donor level in diamond. Similar calculations have also been performed for the substitutional boron acceptor and for the neutral charge state of the lattice vacancy. Here again the results are encouraging. (These will be reported in subsequent publication.) The success of the EHT method here is related to the uniform charge density over the cluster. For III-V or II-VI type solids, however, or for charged states of defects, one should use a better approximation which would determine the charge distribution self-consistently. There are many ways in which this can be accomplished, but the essential character of the approach used here would be unchanged.

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[1] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 257.

[2] R. Hoffman, J. Chem. Phys. 39, 1397 (1963).

[3] J. A. Pople and G. A. Segal, J. Chem. Phys. 43, 5136 (1965).

[4] C. D. Clark, P. J. Dean, and P. V. Harris, Proc. Roy. Soc., Ser. A 277, 312 (1964).

[5] F. Herman, in *Physics of Semiconductors: Proceedings of the Seventh International Conference, Paris, France, 1964*, edited by M. Hulin (Academic, New York, 1964), p. 3.

[6] Although neither the nuclear-nuclear nor electron-electron interactions are explicitly introduced, it can be shown that for the EHT method these two neglected terms approximately cancel each other when the charge is evenly distributed over the system. [See J. Goodisman, J. Amer. Chem. Soc. 91, 6552 (1969)].

[7] The valence band in our model contains 36 more orbitals than the conduction band due to "surface states" (or "dangling" orbitals on the surface atoms; see Fig. 1). In our model the energies of these orbitals are in the valence band and, as such, penetrate well into the bulk. Since it is not possible therefore to distinguish them, the total energy is determined by filling *all* orbitals in the valence band. This must be done in order to fill properly all of the bulk orbitals. In doing this, surface orbitals are also being filled, but we argue that they should not contribute significantly to the elastic forces.

[8] H. J. McSkimin and W. L. Bond, Phys. Rev. 105, 116 (1957). A recent measurement gives $C_{12} = 2.75$ [Markham, unpublished, and reported in *Physical Properties of Diamond,* edited by R. Berman (Oxford Univ., London, 1965), p. 415] giving even better agreement.

[9] W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, Phys. Rev. 115, 1546 (1959).

[10] P. J. Dean, Phys. Rev. 139, A588 (1965).

[11] P. Denham, E. C. Lightowlers, and P. J. Dean, Phys. Rev. 161, 762 (1967).

[12] A. B. Lidiard and A. M. Stoneham, in *Science and Technology of Industrial Diamonds,* edited by J. Burls (Eyre and Spottiswoode, London, 1967), Vol. I, p. 1.

[13] G. D. Watkins, in *Radiation Effects in Semiconductors,* edited by F. Vook (Plenum, New York, 1968), p. 67.

[14] R. J. Cook and D. H. Whiffen, Proc. Roy. Soc., Ser. A 295, 99 (1966).

[15] The details of these estimates will be included in a more complete account to be published later.

[16] The 2*s* character of the MO appears somewhat too low to account for the isotropic hyperfine interaction, particularly for the nitrogen atom. The difficulty here may be our limited basis set—particularly ignoring the 1*s* core.

CORE TRANSITIONS AND DENSITY OF CONDUCTION STATES IN THE III-V SEMICONDUCTORS

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The absorption and reflection spectra of several amorphous and crystalline III-V semiconductors have been measured in the region from 10 to 30 eV where transitions from the outermost *d* levels of the cation cores occur. The use of the continuous spectrum of synchrotron radiation of DESY enabled us to resolve considerable structure in the crystalline samples. This structure can be interpreted as due to structure in the density of conduction states and to the spin-orbit splitting of the core level.

The optical transitions from the valence to the conduction bands of crystalline III-V compounds show a great deal of structure in the energy region below 7 eV. This structure is now quite well understood and has been responsible for the recent advances in our knowledge of the energy bands of these materials.[1] For absorption and reflection spectroscopy above 7 eV, gas-discharge sources with relatively widely spaced lines, which are conventionally used,[2,3] limit the resolution rather drastically. This fact is particularly critical in the region where the first core transitions of the III-V compounds (~20 eV)[3] occur: The hot-cathode argon lamps used have typical separations of about 1 eV between adjacent lines, equal to the expected spin-orbit splitting of the core levels[4] (0.53 eV for Ga, 0.97 eV for In) and to the separation between peaks in the density of conduction states.[5] For this reason we measured the absorption and reflection spectra of the crystalline and the amorphous modifications of GaP, GaAs, GaSb, InP, InAs, and InSb in the 10-30 eV region using as a source the continuous synchrotron radiation of DESY.[6,7] We found, in all cases, considerable structure which can be assigned to structure in the density of conduction states.[5] All the In compounds measured also showed structure which could be correlated with the splitting of the *d* levels of In. This splitting is too small to be observed in most of the Ga compounds.

The samples for reflection measurements were mechanically polished and etched single crystals with flash-evaporated layers; vacuum-deposited layers were used in transmission work. These layers were prepared as either amorphous or crystalline by varying the substrate temperature. The transmission samples were deposited on a KCl-coated microscope slide. They were then floated on water and picked up with a copper mesh. The transmission spectra of crystalline films and the reflection spectra from etched single crystals as well as from crystalline layers showed essentially the same structure. The amorphous layers gave only broad structure similar to that obtained with polished but un-