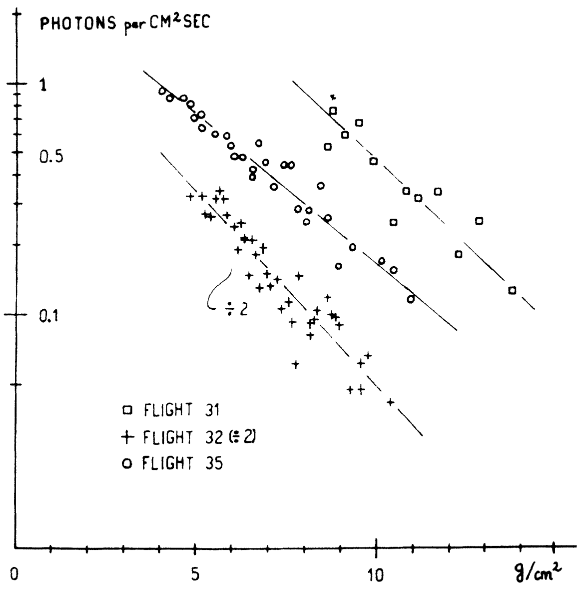

FIG. 3. Additional x-ray flux in the 20- to 60-keV interval, for flights Nos. 31, 32, and 35.

(solid lines in Fig. 2). A geometrical factor of 7.13 cm^2 was used. Apparently, flight No. 31 showed the strongest effect, although it reached only 8.7 g/cm^2 atmospheric depth. Only the knowledge of the energy spectrum of the additional flux will enable us to decide whether the differences between the three flights are due to a geographic dependence or to small differences in the channel widths. The mean absorption length for the additional flux is 3.0 ± 0.5 g/cm^2.

In summary, there seems to be no doubt about the existence of an additional flux of low-energy x rays in the region of the South American anomaly, detectable above 30-km altitude. We suggest that this x-ray flux enhancement originates in electron bremsstrahlung. These electrons might precipitate from the inner radiation belt, or from the remainder of the "Starfish" fission electron belt. A more detailed interpretation of data in order to estimate the precipitating electron flux and spectrum is under progress.

The fact that secondary effects of the electron precipitation in the South American anomaly can be detected at balloon altitudes makes it possible to study in a rather simple way the behavior of electrons trapped in low L shells as a function of time.

We are grateful to the Servicio de Hidrografía Naval for providing facilities at the oceanographic ship "Comodoro Laserre." The cooperation of Captain H. Gómez Beret and the officers and crew of the ship is greatly appreciated. We are also indebted to T. Rehbock, A. Kogan, and C. Ferro Fontán for their help during flight preparation and data evaluation.

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*Work supported in part by the Consejo Nacional de Investigaciones Científicas y Técnicas and The Ford Foundation.

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SURFACE STATES ON THE (111) SURFACE OF DIAMOND

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(Received 24 February 1964)

A calculation of the surface states on the (111) surface of the diamond crystal has been made, based on the linear combination of band orbitals (LCBO) model. The interaction integrals between the localized orbitals have been evaulated in the same approximation used in the *a priori* LCBO volume-state calculation of Cohan, Pugh, and Tredgold,[1] so that the surface-state spectrum fits consistently into the volume-state energy bands of that model.

The volume-state calculation was based on an expansion in terms of eight tetrahedrally directed bonding and antibonding orbitals $\phi_1{}^b$ to $\phi_4{}^b$, $\phi_1{}^a$ to $\phi_4{}^a$, made up from Slater 2s and 2p atomic orbitals orthogonalized to the 1s functions. The orbitals directed along the bond between the nearest-neighbor atoms 0 and 1 are

$$\phi_1{}^b = A_b[s_0 + s_1 + \sqrt{3}(p_{01} + p_{10})],$$
$$\phi_1{}^a = A_a[s_0 - s_1 + \sqrt{3}(p_{01} - p_{10})], \tag{1}$$

where A_b and A_a are normalization constants. The Hartree-Fock Hamiltonian, $\mathcal{H}$, is set up and the volume states at any point in the zone can then be expressed in terms of the interaction integrals $\langle\phi_m{}^x(\vec{r})|\mathcal{H}|\phi_n{}^y(\vec{r}-\vec{R}_j)\rangle$, where $m, n = 1, \cdots, 4$ and $x, y = a$ or b. There were thirteen distinct interaction integrals of this type involved in the volume-state calculation where interactions with all bonds up to parallel third neighbors were included. The above expressions were expanded in terms of diatomic molecular integrals, using various approximations, and computed. The very large amount of algebraic manipulation involved in the expansion was dealt with by a 7090 Fortran program (see reference 1)

The (111) surface of diamond intersects at right angles one set of the tetrahedral bonds and in the present model the orbitals for the layer of bonds intersected by the surface are replaced by the hybrid functions, $\frac{1}{4}(s_0 + \sqrt{3}p_{01})$, directed along the broken bonds from the surface atoms, the positions of the atoms being unchanged. I.e., the surface bonding arrangements are represented as a system of "dangling hybrids." In fact, of course, under most conditions the surface will be more complicated than this. In particular, it appears that under some circumstances a superlattice is present which gives rise to half-integral order diffraction beams (Farnsworth, Marsh, and Toots[2]). Possible configurations for surfaces of this symmetry have been proposed by Haneman[3] and Lander, Gobeli, and Morrison.[4] However, it seems worthwhile trying to elucidate the theoretical properties of the simplest possible surface structure first. In the zeroth approximation of no interaction between the neighboring orbitals, the hybrid would be a state occupied by one electron, each of the bonding orbitals being doubly occupied and the antibonding orbitals empty. The configuration at the surface is not therefore a closed-shell structure.

The interaction integrals $\langle\phi_m{}^x(\vec{r})|\mathcal{H}|\phi_n(\vec{r}-\vec{R}_j)\rangle$ for orbitals near the surface differ, of course, from those for orbitals in the bulk of the crystal, and the fundamental principle of this work is that they should be calculated a priori in the same approximation as was used for the interactions in the bulk. In a method where the Hamiltonian is constructed from the contributions of electrons in localized orbitals, the termination of the crystal in itself produces a large change in the potential in the cells near the surface. (For instance, in the last layer of cells half the adjacent cells, which would have contributed to the potential in the bulk, are missing.) This is in contrast to methods in which a fixed periodic potential is assumed, when a termination of the lattice leaves the potential up to the point of termination unchanged. The largest contributions to the matrix elements near the surface still come, therefore, from electrons in closed shells, and the matrix elements are changed chiefly owing to the absence of other electrons in closed shells. The contribution of the electron "in the hybrid" only gives rise to a small part of this effect, and the rather crude method to be used in evaluating its contribution is therefore more tolerable. In fact, the closed-shell Hartree-Fock Hamiltonian was used, the contribution of the electron in the hybrid being represented by a term

$$\tfrac{1}{2}(2J_{\text{hybrid}} - K_{\text{hybrid}}), \tag{2}$$

where J and K are the Coulomb and exchange operators.

The interaction integrals can be expanded in terms of diatomic integrals in the same approximation as in the volume-state calculation using a modified version of the 7090 Fortran program previously mentioned. Because of the asymmetry introduced by the surface, there are now 33 parameters to be computed.

If we let $\vec{k}^S$ be a wave vector parallel to the surface, where there is still translational symmetry, states near the surface may be classified according to the value of their $\vec{k}^S$ vector and expanded in terms of the functions

$$\chi_{ml}(\vec{k}^S, \vec{r}) = \sum_j \exp(i\vec{k}^S \cdot \vec{R}_j{}^S)\phi_m(\vec{r} - \vec{R}_j - \vec{R}_1), \tag{3}$$

where $\vec{R}_j{}^S$ is vector of the space lattice parallel to the surface and $\vec{R}_1$ is a vector in some other direction. The suffix l then specifies a layer of cells parallel to the surface. Each function χ_{ml} is therefore localized at a particular layer but is a Bloch-type function in directions parallel to the surface. There are eight such functions for each layer except the first where there are seven, the hybrid function replacing one pair of bonding and antibonding orbitals.

For the wave function of a state near the surface, we write

$$\psi(k^S, r) = \sum_{m,l} c_{ml} \chi_{ml}(\vec{k}^S, \vec{r}), \qquad (4)$$

and the possible energies of states with surface wave vector $\vec{k}^S$ are given by the eigenvalues of the secular equation

$$|\langle \chi_{nl'}^*(\vec{k}^S, \vec{r}) | \mathcal{H} | \chi_{ml}(\vec{k}^S, \vec{r}) \rangle - E\delta_{mn}\delta_{ll'}| = 0, \qquad (5)$$

since the bond orbitals are assumed orthogonal throughout the calculation. In the case of diamond it is known that near the middle of the gap the surface states would extend over about two or three layers only, and it is therefore simpler to solve Eq. (5) directly rather than to attempt to transform it in the manner of Koutecky[5] using the Koster-Slater[6] method, or by an extension of the method of Goodwin[7]. Using Householder's method[8] and the IBM-7090 Computer, 100×100 matrices can be solved in a few minutes, so that in obtaining the eigenvalues of Eq. (5) near the band edges, up to seven layers were included in the calculation. This corresponds to an $(8\times7)\times(8\times7) = (56\times56)$ Hermitian matrix which for the purposes of computation is equivalent to a (112×112) real symmetric matrix.

The values of $\vec{k}^S$ can be represented in a two-dimensional hexagonal zone, and in Fig. 1 the energy spectrum of the surface states is shown plotted along two lines from the center of this zone, the point O being the center, A being at the midpoint of one of the hexagonal edges, and B being one of the corners. There are no surface states at the center of the zone, but as $\vec{k}^S$ varies from O, surface states split off from the top of the valence band leaving equal numbers of states in the valence and conduction bands. A rough density-of-states curve can be deduced from these results. It indicates that more than 90% of the states lie above the level marked X in the diagram. This shows that for practical purposes the spectrum consists of a narrow band of states lying somewhat below the middle of the gap. Since half the surface states are filled, the Fermi level (in the hypothetical case where band bending is absent) will be within this narrow band probably somewhat below the energy for which the density of states is a maximum. It seems likely that a more refined treatment including magnetic interaction would lead to the band of surface states being completely separate from the valence band even at the center of the zone.

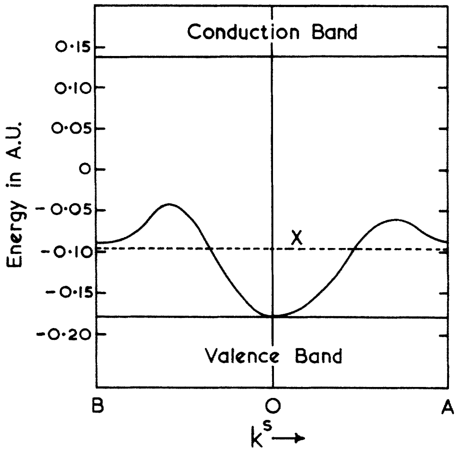

FIG. 1. The surface bands plotted in the two-dimensional hexagonal surface zone along the lines OA, from the center of the zone to the midpoint of one of the edges, and OB from the center to a corner.

One may, therefore, while bearing in mind the inadequacies of the volume-energy band structure on which the calculation is based, tentatively conclude that the "dangling-hybrid" model of the (111) surface of diamond is most likely to lead to a band of surface states in the lower part of the forbidden energy region. The total width of this band is of the order of half the gap width while, owing to the sharply peaked form of the density-of-states function, the effective width is a good deal smaller. The Fermi level in the case of no band bending lies somewhere in the region of high density.

I am very much indebted to Dr. R. H. Tredgold of this department for his constant advice and encouragement in carrying out this work and to Dr. N. V. Cohan of Facultad de Ciencas Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina, for many valuable discussions.

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