

Study of the Surface States of Diamond and Graphite by a Simple MO-LCAO Method

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The surface states of diamond and two-dimensional graphite are investigated on the assumption that the delimitation of the crystal causes no perturbation within the elementary cells of the finite crystal. In both cases a plane perpendicular to the bond between a selected pair of carbon atoms is taken as the delimiting plane. The molecular orbitals are assumed in the form of a linear combination of sp^3 or sp^2 hybrids. In the case of graphite, molecular orbitals that are linear combinations of $2p_z$ orbitals, whose interaction with sp^2 hybrids is neglected, are further considered. It appears that in the case of diamond there exists a band of energies pertaining to Shockley surface states in the gap between the valence and conductivity bands. The number of atoms in this band equals the number of atoms in the surface. From a discussion of the pertinent

wave functions, it follows that these states are an expression of unsaturated bonds of the surface carbon atoms. The electron density on the hybrids projecting from the surface is essentially greater than the density on the other hybrids of the surface atoms. Further bands of surface states exist in the region of energies allowed for the volume valence and the conductivity states. In graphite, a quite analogous behavior is shown by those surface states whose wave functions are linear combinations of sp^2 orbitals. Surface states whose wave functions are linear combinations of p_z orbitals are a manifestation of unsaturated double bonds of surface atoms having only two neighbors. The analogy between these Shockley states and the nonbonding states of odd alternant aromatic hydrocarbons is pointed out.

THE hitherto published papers on surface states set out, with few exceptions,^{1,2} from simple models which could not even in rough approximation define the properties of any actually existing substance.

In the present paper the surface states of diamond and graphite are investigated. Since the question of the existence of these states and their character is of primary interest, we believe that it is permissible to use relatively rough models, which might be considered unsuitable for treating other problems. If the results are to contribute to a better understanding of the processes on a pure surface of these substances, it is desirable that they admit of interpretation in terms of the bonding conditions in the surface. Such an interpretation is considerably facilitated by employing the MO-LCAO method, which is widely utilized in theoretical chemistry.

In a recent paper³ we have dealt with a model in which a one-electron wave function is considered to be a linear combination of s and p_x orbitals situated in the lattice points of a cubic lattice (Goodwin-Artmann model^{4,5}). It was found that the Shockley surface states⁶ in such a crystal, delimited by a plane perpendicular to the x axis, correspond to unsaturated valences projecting from the surface. A generalization of the finding that the Shockley surface states are, in the framework of the band theory, an expression of the specific bonding conditions in the surface⁷ leads us to the assumption that states of this character must exist in graphite and diamond, too.

Indeed, Baldock¹ found in his investigation of a very simple model of two-dimensional graphite that by

delimiting a two-dimensional crystal by a straight line perpendicular to the direction of one type of bonds we obtain Shockley states. Baldock considered only the nearest interaction between the p_z orbitals situated in the lattice points of the lattice of two-dimensional graphite, and set out from a discussion of expressions for the energy states of finite graphite strips. It is not without interest to find out whether this conclusion remains valid even when a somewhat more complicated model is used, taking into consideration the interaction between next-nearest p_z orbitals. In the framework of a one-electron approximation, not considering the interaction between p_z orbitals and sp^2 hybrids in graphite, it is necessary, of course, to consider also surface states arising by breaking of $\pi\sigma$ bonds. Although the justification of this approximation becomes still more doubtful for the problem of surface states than for volume states, we think it useful to show the properties of the Shockley states arising in this way.

SURFACE STATES OF DIAMOND

The one-electron wave function describing the state of the bonding electron in diamond is considered in the form of a linear combination of equivalent sp^3 hybrids of atomic orbitals of carbon which are situated in the lattice points of the diamond lattice. We consider as not negligible in the approximation employed only the interaction between hybrids pertaining to the same carbon atom and the interaction between hybrids pertaining to adjacent carbon atoms and exhibiting their maximum amplitude in the direction of the line connecting the pair of atoms considered. The resonance integrals defining the first or second interaction shall be denoted by γ' or γ , respectively. The other interactions are neglected, so that we obtain a model which is a direct generalization of the Hall diamond model⁸ and at the

¹ G. R. Baldock, Proc. Cambridge Phil. Soc. 48, 457 (1952).

² H. Statz, Z. Naturforsch. 5a, 534 (1950).

³ J. Koutecký and M. Tomášek, J. Phys. Chem. Solids (to be published).

⁴ E. T. Goodwin, Proc. Cambridge Phil. Soc. 35, 232 (1939).

⁵ K. Artmann, Z. Physik 131, 244 (1952).

⁶ W. Shockley, Phys. Rev. 56, 317 (1939).

⁷ J. Koutecký, J. Phys. Chem. Solids (to be published).

⁸ G. G. Hall, Phil. Mag. 43, 338 (1952); Phys. Rev. 90, 317 (1953).

same time permits description of the conductivity band.⁹ The model considered is so simple that the calculation of the energy of the volume states leads to explicit expressions, a feature which is advantageous in the application of a method in which we set out from the characteristics of these states when studying the properties of surface states.¹⁰

Since two atoms are contained in an elementary cell of diamond, we considered altogether eight kinds of equivalent orbitals. The wave function describing the state of an electron in an infinite crystal will have the form

$$\psi_{j;\xi_1,\xi_2,\xi_3} = \sum_{m_1,m_2,m_3} \sum_{p=1}^8 c_{j,p}(\xi_1,\xi_2,\xi_3) e^{i(m_1\xi_1+m_2\xi_2+m_3\xi_3)} \times \varphi_p(r-m_1a_1-m_2a_2-m_3a_3), \quad (1)$$

where ξ_i are quantum numbers coordinating the wave function to a certain irreducible representation of a translation group, j denotes the remaining quantum number ($j=1\cdots 8$), $\varphi_p(r)$ are equivalent orbitals ($p=1\cdots 8$), a_i are elementary translations of the diamond lattice, and m_i are integers. If we take the value of the Coulomb integral of the sp^3 hybrid as zero level of the energy, the secular determinant has the form

$$\Delta = |D| = \begin{vmatrix} -W & \gamma' & \gamma' & \gamma' & 0 & 0 & 0 & \gamma e^{i\xi_3} \\ \gamma' & -W & \gamma' & \gamma' & 0 & 0 & \gamma e^{i\xi_2} & 0 \\ \gamma' & \gamma' & -W & \gamma' & 0 & \gamma e^{i\xi_1} & 0 & 0 \\ \gamma' & \gamma' & \gamma' & -W & \gamma & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma & -W & \gamma' & \gamma' & \gamma' \\ 0 & 0 & \gamma e^{-i\xi_1} & 0 & \gamma' & -W & \gamma' & \gamma' \\ 0 & \gamma e^{-i\xi_2} & 0 & 0 & \gamma' & \gamma' & -W & \gamma' \\ \gamma e^{-i\xi_3} & 0 & 0 & 0 & \gamma' & \gamma' & \gamma' & -W \end{vmatrix} = 0. \quad (2)$$

For further calculation, it is advantageous to take into consideration also another form of this secular equation:

$$\Gamma = |C| = |D| = 0, \quad (3)$$

where the elements of the matrix $C = (c_{ij})$ are connected with the elements of the matrix $D = (d_{ij})$ as follows:

$$\begin{aligned} i=1, 2, 3: & \quad c_{ij} = d_{ij} - d_{i4}, \\ i=4, 5: & \quad c_{ij} = d_{ij}, \\ i=6, 7, 8: & \quad c_{ij} = d_{ij} - d_{i5}. \end{aligned} \quad (4)$$

We introduce a new variable by the relation

$$x = W + \gamma'. \quad (5)$$

As energy unit we select the value of the resonance integral γ . The secular equation (2) has two double roots, independent of the quantum numbers ξ_i :

$$x_{1-4} = \pm 1. \quad (6)$$

Four further roots of Eq. (2) are

$$x_{5-8} = 2\gamma' \pm [1 + \gamma'(4\gamma' \pm |A|)]^{\frac{1}{2}}, \quad (7)$$

where

$$A = 1 + \sum_{i=1}^3 e^{i\xi_i}. \quad (8)$$

For small values of γ' in comparison to unity (i.e., to γ), the root on the right side of Eq. (7) can be expanded, whereby we obtain the expression derived by Hall.⁸

Now we delimit the crystal by a plane perpendicular to the elementary translation a_3 and bisecting the line connecting two neighboring atoms. In order to obtain a model of a finite crystal, it is sufficient to assume that

the zero density of the electrons is in the sp^3 hybrids $\varphi_1(r-m_1a_1-m_2a_2)$, having their maximum amplitude in the direction of the translation a_3 and pertaining to elementary cells characterized by the condition $m_3=0$ in a cyclic crystal, which according to the Born-von Kármán conditions represents an infinite crystal. Since we consider, as already mentioned, only the interaction between two orbitals pertaining to neighboring atoms, we thus obtain actually zero probability for the transition of the electron over the given delimiting plane.

The one-electron wave function in the finite crystal we assume in the form

$$\psi_{j;\xi_1,\xi_2} = \sum_{m_3=1}^N \sum_{p=1}^8 d_{j;pm_3}(\xi_1,\xi_2) \varphi_p(r-m_3a_3), \quad (9)$$

where

$$\begin{aligned} \varphi_p(r-m_3a_3) &= \frac{1}{N} \sum_{m_1,m_2} e^{i(m_1\xi_1+m_2\xi_2)} \\ &\times \varphi_p(r-m_1a_1-m_2a_2-m_3a_3). \end{aligned} \quad (10)$$

For the expansion coefficients, the following equations may be written down^{10,11}:

$$d_{j;pm_3} = -L_{pm_3;10} d_{j;81}, \quad (11a)$$

$$d_{j;10} = 0 = -L_{10;10} d_{j;81}. \quad (11b)$$

In Eqs. (11) and in the succeeding text we no longer indicate the dependence on ξ_1 and ξ_2 . The magnitude $L_{pm_3;10}$ is, for an infinite crystal ($N \rightarrow \infty$), defined as follows^{10,11}:

$$L_{pm_3;10} = \frac{1}{2\pi} \int_0^{2\pi} \sum_{i=1}^8 \frac{\tilde{c}_{j1} c_{jp}}{(x-x_j)} e^{im_3\xi_3} d\xi_3, \quad (12a)$$

⁹ J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

¹⁰ J. Koutecký, Phys. Rev. **108**, 13 (1957).

¹¹ J. Koutecký and A. Fingerland, Doklady Akad. Nauk S.S.S.R. **125**, 841 (1959).

or¹²

$$L_{pm_3;10} = \frac{(-1)^{m_3}}{2\pi} \int_0^{2\pi} \sum_{j=1}^8 \frac{\Delta_{1p} e^{im_3 \xi_3}}{\Delta} d\xi_3. \quad (12b)$$

Δ_{rp} denotes the determinant which arises by omitting the p th column and the r th row from the determinant Δ . From Eq. (11b) immediately follows the relation defining the energy of the surface states in the form

$$\Delta_{11} \equiv \Gamma_{11} = 0, \quad (13)$$

i.e.,

$$(x^2 - 1)[(x^2 - 3\gamma'x - 1)(x^3 - 4\gamma'x^2 - x + \gamma') - \gamma'^2 x |a|^2] = 0, \quad (14)$$

where

$$a = |a| e^{i\varphi} = 1 + e^{-i\xi_1} + e^{-i\xi_2}. \quad (15)$$

The roots $x = \pm 1$ are of no significance for our case as they correspond to volume states. From Eq. (11a) for $p=8$, $m_3=1$ we obtain a relation from which can be derived, besides the expression for the energy of surface states, also the condition for their existence:

$$\frac{1}{2\pi} \int_0^{2\pi} \frac{\Gamma_{18}}{\Gamma} e^{i\xi_3} d\xi_3 = 1. \quad (16)$$

Since from Eq. (13) there follows

$$\Gamma_{18;18} = -\frac{\gamma'}{\gamma' + W} \Gamma_{18;15}, \quad (17)$$

the relations

$$\begin{aligned} (\Gamma)_{\Gamma_{11}=0} &= \gamma'(\gamma' + W)\Gamma_{18;48} - \gamma'^2 \Gamma_{18;45} + \frac{\gamma'}{\gamma' + W} \Gamma_{18;15} \\ &\quad - \gamma' [e^{-i\xi_3} \bar{\Gamma}_{18;58} + e^{i\xi_3} \Gamma_{18;58}], \\ (\Gamma_{18})_{\Gamma_{11}=0} e^{i\xi_3} &= -\frac{\gamma'}{\gamma' + W} \Gamma_{18;15} + \gamma' \Gamma_{18;58} e^{i\xi_3}, \end{aligned} \quad (18)$$

also hold, where the symbols $\Gamma_{pr;st}$ denote the determinants which arise from the determinant Γ by omitting the p th and r th rows and the s th and t th columns. The determinants in Eqs. (18) are easily calculated, eliminating from each of them the factor $(x^2 - 1)$.

If we define

$$z = e^{i(\varphi + \xi_3)}, \quad (19)$$

and carry out the integration indicated in Eq. (16) in the known way along the unit circle in the complex plane, this relation passes into the condition

$$z_2 = \frac{1}{x|a|\gamma'} [x^2 - 3\gamma'x - 1], \quad (20)$$

where

$$z_1 = \frac{1}{|a|\gamma'} [(x - \gamma')(x^2 - 1) - 3\gamma'x]. \quad (21)$$

The magnitudes z_1, z_2 must satisfy the relation

$$z_1 z_2 = 1, \quad (22)$$

$$|z_1|^2 < 1. \quad (23)$$

The condition (22) is obviously equivalent to Eq. (14), while the second condition is the condition for the existence of surface states.

If we set

$$f_1(x) = |a|^2 z_1 z_2, \quad (24)$$

$$f_2(x) = |a|^2 |z_1|^2,$$

the necessary and sufficient condition for the existence of surface states of the energy x reads as follows:

$$f_2(x) < f_1(x) < 9. \quad (25)$$

Of interest for a discussion of the energy spectra of the surface states are those points for which the equation $f_1(x) = f_2(x)$ holds. These are first of all the points $u_1 < u_2 < u_3$, in which both functions equal zero, because

$$x^3 - 4\gamma'x^2 - x + \gamma' = 0 \quad (26)$$

applies. In addition, $f_1(x) = f_2(x) = 9$ holds for $x = \pm 1$. Finally, for

$$x = v_{1,2} = 2\gamma' \pm (1 + 4\gamma'^2)^{1/2}, \quad (27)$$

$$f_1(v_i) = f_2(v_i) = 1.$$

Moreover, let us note that the relations $f_1(y_i) = 9 \neq f_2(y_i)$ hold for the roots $y_1 < y_2 < y_3$ of the equation

$$x^3 - 7\gamma'x^2 + x(12\gamma'^2 - 1) + \gamma' = 0. \quad (28)$$

For purposes of illustration, Fig. 1 represents the functions $f_1(x)$ and $f_2(x)$ and the intervals of the permissible energies of surface states for $\gamma' = 0.25$. This value seems to be probable, according both to the evaluation of respective integrals,^{13,14} and to the results of the application of the semiempirical method to unsaturated hydrocarbons.¹⁵ Figure 2 shows the intervals of the allowed energies of surface states for a number of values of this

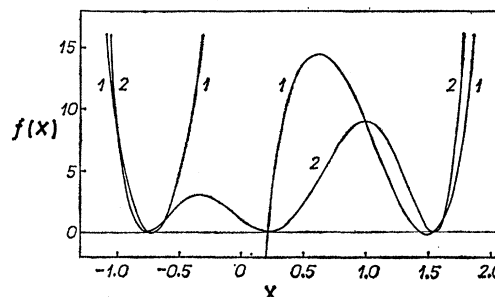


FIG. 1. The diagram of functions $f_1(x)$ (curve 1) and $f_2(x)$ (curve 2) for $\gamma' = 0.25$. The allowed energy intervals of surface states of diamond in γ units can be obtained from this graph by means of the inequality (25).

¹² K. Fukui, Ch. Nagata, T. Yonezawa, H. Kato, and K. Morokuma, J. Chem. Phys. **31**, 287 (1959).

¹³ G. E. Kimball, J. Chem. Phys. **3**, 560 (1935).

¹⁴ G. G. Hall, Proc. Roy. Soc. (London) **A205**, 541 (1951).

¹⁵ G. Sandorfy, Can. J. Chem. **33**, 1337 (1955).

parameter. From the graph it is immediately apparent that we obtain four bands of allowed energies of surface states, of which one (I_2) lies for not too great γ' ($\gamma' < 0.331$) in the gap between the valence and the conductivity band in the neighborhood of the energy $W=0$. For $\gamma' > 0.3311$, the upper limit of the band of the surface states I_2 lies above the lower limit of the conductivity band of the volume states. For $\gamma' = 0.5$, the conductivity and valence bands contact each other, and the interval I_2 is completely contained in the conductivity band. For $\gamma' > 0$, one further band (I_1) lies in the intervals of the energies allowed for the volume valence states, and two (I_3, I_4) in the intervals of the energies allowed for the volume conductivity states. The number of states in the band of the surface states I_2 equals the number of surface atoms. It is evident from Fig. 1 that the intervals of the energies x for which surface states are allowed are delimited by the following points:

$$I_1 \equiv (u_3, v_2), \quad I_2 \equiv (u_2, \min[1, y_2]), \\ I_3 \equiv (v_1, y_1), \quad I_4 \equiv (-1, u_1).$$

One boundary point of the interval I_1 or interval I_3 therefore is the point v_2 or v_1 , respectively. By comparing the relation (27) with Eq. (7) for $A=0$, we find that the intervals I_1 and I_3 have one of their boundaries at the point where the bands of the surface states contact each other. The boundary point of the interval I_4 is a degenerated level of the volume states, given by Eq. (6) with the negative sign on the right side.

By means of the relations (11a) and (12b) we can calculate the coefficients $d_{j;pm_3}$. From Eq. (13) it follows that for an arbitrary m_3 ,

$$d_{j;1m_3} = 0. \quad (29)$$

In the interval I_2 , which lies in the neighborhood of $W=0$, we can easily estimate the ratio of the coefficients for the hybrids φ_k ($k=5-7$) to the coefficients for the

hybrid φ_8 , there applies

$$k=5-7: |d_{j;k1}/d_{j;81}|^2 \sim \gamma'^4. \quad (30)$$

From Eqs. (29) and (30) it is evident that the surface states whose energy lies in the interval I_2 can be interpreted as unsaturated valences of surface atoms. The wave function describing these states exhibits a high electron density on the sp^3 hybrids of the surface atoms projecting from the surface and a low density on the remaining three hybrids of these atoms.

SURFACE STATES OF GRAPHITE, CAUSED BY BREAKING OF THE π BONDS

Within the framework of an approximation in which the interaction between p_z orbitals and sp^2 hybrids is neglected, let us first pay attention to the one-electron wave function produced by a linear combination of the p_z orbitals of the carbon atoms of the graphite lattice. We make the same assumptions as Wallace¹⁶ (compare also other papers¹⁷⁻²¹), whose model of two-dimensional graphite is interesting, first of all for the reason that it considers also the interaction between carbon atoms which are not nearest neighbors.

If we consider only the interaction between the nearest adjacent p_z orbitals, the problem of the surface states in two-dimensional graphite can be solved in a quite trivial way. It must be pointed out that a semi-infinite crystal of two-dimensional graphite (as far as double bonds are concerned) may be considered formally as an alternant hydrocarbon.²² It is known that on odd hydrocarbons of this type there exist nonbonding states with the energy

$$W=0 \quad (31)$$

if we select the scale of energies so that the zero level equals the Coulomb integral of the p_z orbital of carbon.

Let us consider a straight line determined by the direction of one of the elementary translations a_1 of the graphite lattice. This straight line is perpendicular to the line connecting two atoms (compare Fig. 3) and delimits the surface of the crystal in which the carbon atoms bound to two neighbors alternate with atoms bound to three nearest neighbors. In Fig. 3 we have starred the surface atoms of the first kind and this starring is further performed consistently. The coefficients in the wave function of orbitals pertaining to non-starred atoms shall be assumed to equal zero. Then there must hold

$$l_{j;m_1,m_2}^* + l_{j;m_1+1,m_2}^* + l_{j;m_1,m_2+1}^* = 0, \quad (32)$$

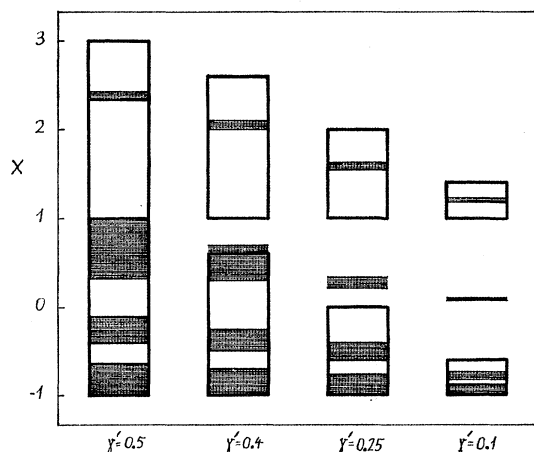


FIG. 2. Intervals of allowed energies of volume and surface states of diamond in γ units. The surface-state intervals are shaded.

¹⁶ P. R. Wallace, Phys. Rev. **71**, 622 (1947); **72**, 258 (1947).

¹⁷ C. A. Coulson, Nature **159**, 265 (1947).

¹⁸ C. A. Coulson and R. Taylor, Proc. Phys. Soc. (London) **A65**, 815 (1952).

¹⁹ J. Barriol and J. Metzger, J. chim. phys. **47**, 432 (1950).

²⁰ W. M. Lomer, Proc. Roy. Soc. (London) **A227**, 330 (1955).

²¹ C. A. Coulson and G. I. Rushbrooke, Proc. Cambridge Phil. Soc. **36**, 193 (1940).

²² H. C. Longuet-Higgins, J. Chem. Phys. **18**, 265 (1950).

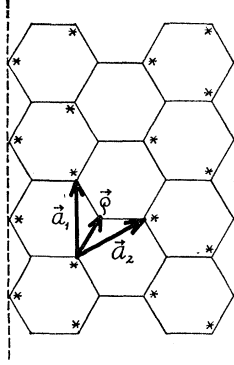


FIG. 3. Schematic representation of a planar graphite crystal. In the picture are shown the straight line $m_2=0$, which limits the crystal, and the elementary translations a_1 , a_2 as well as the translation ρ by means of which we pass from the starred to the non-starred position.

where $l_{j;m_1,m_2}^*$ is the coefficient in the j th molecular orbital at the p_z orbital of the starred atom lying in the cell characterized by the translation $m_1 a_1 + m_2 a_2$. In order to preserve periodicity in the direction of the elementary translation a_1 , the coefficients must satisfy

$$l_{j;m_1+1,m_2}^* = l_{j;m_1,m_2}^* e^{i\xi_1}, \quad (33)$$

so that from the requirement

$$|l_{j;m_1,m_2+1}^* / l_{j;m_1,m_2}^*|^2 < 1 \quad (34)$$

follows the condition of existence of the surface states with the energy given by Eq. (31) in the form

$$|1 + e^{i\xi_1}|^2 < 1. \quad (35)$$

Since therefore the magnitude ξ_1 must satisfy the inequality $120^\circ < \xi_1 < 240^\circ$, the number of the surface states equals one third of the number of surface atoms bound to two neighbors.

Now we are going to show that the principal results of this elementary analysis of the problem of Shockley states in the graphite model considered, which are in accordance with Baldock's conclusions, remain valid also in the Wallace model.

We write the wave function in the form

$$\psi_{\xi_1} = \sum_{m_2=-1}^{\infty} [d_{m_2}^* u_{\xi_1}(r - m_2 a_2) + d_{m_2} u_{\xi_1}(r - m_2 a_2 - \rho)], \quad (36)$$

where we have defined

$$u_{\xi_1}(r - m_2 a_2) = \frac{1}{\sqrt{N}} \sum_{m_1} e^{im_1 \xi_1} \varphi_z(r - m_1 a_1 - m_2 a_2); \quad (37)$$

$\varphi_z(r)$ denotes the p_z orbital and ρ the translation by which we obtain, from the starred position, the non-starred position in the same elementary cell.

By the standard variation procedure we obtain for the coefficients of the wave functions (36) the following system of equations:

$$\begin{aligned} W d_1^* + \beta' \bar{b} d_2^* - \beta \bar{b} d_0 &= 0, \\ W d_1 + \beta b d_1^* + \beta d_2^* + \beta' \bar{b} d_1 &= 0, \end{aligned} \quad (38a)$$

$m_2 > 1$:

$$\begin{aligned} W d_{m_2}^* + \beta' \bar{b} d_{m_2+1}^* + \beta' b d_{m_2-1}^* \\ + \beta \bar{b} d_{m_2} + \beta d_{m_2-1} &= 0, \\ W d_{m_2} + \beta b d_{m_2}^* + \beta d_{m_2+1}^* + \beta' \bar{b} d_{m_2+1} \\ + \beta' b d_{m_2-1} &= 0, \end{aligned} \quad (38b)$$

where we have set

$$b = |b| e^{i\omega} = 1 + e^{i\xi_1}. \quad (39)$$

β denotes the resonance integral between the nearest neighboring p_z orbitals, and β' the analogous integral between next-nearest orbitals.

Now we introduce the following linear combinations:

$$\begin{aligned} \chi_{s,m_2}(r; \xi_1) &= \frac{e^{im_2\omega}}{\sqrt{2}} [u_{\xi_1}(r - m_2 a_2) + e^{i\omega} u_{\xi_1}(r - m_2 a_2 - \rho)], \\ \chi_{p,m_2}(r; \xi_1) &= \frac{e^{im_2\omega}}{\sqrt{2}} [-u_{\xi_1}(r - m_2 a_2) + e^{i\omega} u_{\xi_1}(r - m_2 a_2 - \rho)]. \end{aligned} \quad (40)$$

The wave function (36) can be expressed by means of the orbitals, defined by the relations (40), in the form

$$\psi_{\xi_1} = \sum_{\mu=s,p} \sum_{m_2} D_{\mu,m_2}(\xi_1) \chi_{\mu,m_2}(r; \xi_1), \quad (41)$$

where the coefficients $D_{\mu,m_2}(\xi_1)$ satisfy the system of equations

$$\sum_{\mu=s,p} \sum_{m_2} D_{\mu,m_2} [E_{\mu m_2; m_2'} - W \delta_{\mu\mu'} \delta_{m_2 m_2'}] = 0. \quad (42)$$

The magnitudes $E_{\mu m_2; m_2'}$ are defined, as obviously follows from the transformation (40), by the expressions

$$\begin{aligned} E_{sm_2; sm_2'} &= -\beta |b| \delta_{m_2 m_2'} \\ &\quad - (\tfrac{1}{2}\beta + |b| \beta') (\delta_{m_2, m_2'+1} + \delta_{m_2, m_2'-1}), \\ E_{pm_2; pm_2'} &= \beta |b| \delta_{m_2 m_2'} \\ &\quad + (\tfrac{1}{2}\beta - |b| \beta') (\delta_{m_2, m_2'+1} + \delta_{m_2, m_2'-1}), \\ E_{sm_2; pm_2'} &= -E_{pm_2; sm_2'} = \tfrac{1}{2}\beta (\delta_{m_2, m_2'-1} - \delta_{m_2, m_2'+1}), \end{aligned} \quad (43)$$

where $\delta_{i,j}$ is Kronecker's delta. If we write

$$\begin{aligned} \gamma_s &= \tfrac{1}{2}\beta + \beta' |b|, \quad \gamma_p = \tfrac{1}{2}\beta - \beta' |b|, \quad \gamma_{sp} = \tfrac{1}{2}\beta, \\ q &= \tfrac{1}{2}\beta |b|, \quad q_0 = \tfrac{1}{2}(\gamma_s + \gamma_p) = \tfrac{1}{2}\beta, \end{aligned} \quad (44)$$

we see that the relations (43) pass into the first three equations (26) of reference 3. In this way it is shown, of course, that by means of the transformation (40) the problem of the surface electron Shockley states in graphite may be converted into the case of the Goodwin-Artmann model. It is essential for the applicability of the procedure given in reference 3 that the magnitude γ_p is positive, from which follows the condition

$$\beta > 2\beta' |b|. \quad (45)$$

On the assumption that this condition is satisfied, we can immediately write the relations for the energy of the surface electron Shockley states at zero deformation

of the potential within the finite crystal, as well as the pertinent condition for the existence of these states [compare Eqs. (38) and (39) of reference 3]:

$$W = q(\gamma_s - \gamma_p)/q_0 = 2\beta'|b|^2 = 4\beta'(1 + \cos\xi_1), \quad (46)$$

$$|b| \leq 1. \quad (35)$$

Further there holds [compare Eq. (48) in reference 3]

$$\frac{d_{m_2}}{d_{m_2}^*} = e^{i\omega} \left[1 - \left(\frac{\beta + 2\beta'|b|}{\beta - 2\beta'|b|} \right)^{\frac{1}{2}} \right] / \left[1 + \left(\frac{\beta + 2\beta'|b|}{\beta - 2\beta'|b|} \right)^{\frac{1}{2}} \right]. \quad (47)$$

In Wallace's model, the condition for the existence of surface states (35) is therefore maintained, so that here also the number of these states equals one third of the surface atoms connected by bonds to two neighbors. The level of the energy $W=0$ extends into a band given by Eq. (46). The charge density of the π electrons is essentially higher on the starred atoms than on the non-starred atoms. It is evident from these results that the Shockley π -electron surface states correspond to the unsaturated double bonds of the surface atoms, and that in this sense the investigated plane delimiting the graphite crystal behaves as a radical.

It can be easily shown by simple considerations according to Heilbronner²³ that no Shockley surface states exist in a crystal of two-dimensional graphite delimited by straight lines defined by the equations (see Fig. 4)

$$m_1 + \frac{1}{2}m_2 = 0, \quad m_1 + \frac{1}{2}m_2 = N. \quad (48)$$

Now we form the linear combinations of the wave functions in the infinite crystal:

$$\phi_k = \psi_k - \psi_{k'}, \quad (49)$$

where the wave vectors k, k' can be expressed by means of the components in the direction of the mutually

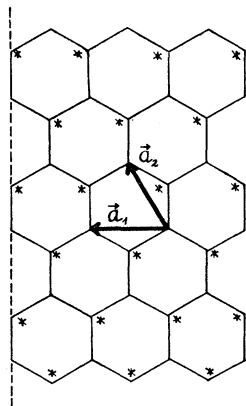


FIG. 4. Schematic representation of a planar graphite crystal. In the picture the limiting straight line is drawn according to the Eq. (48).

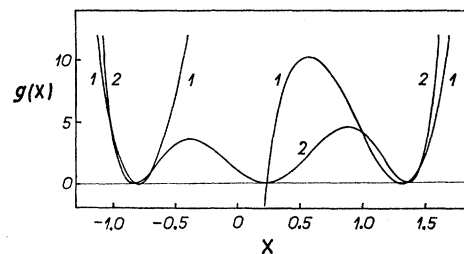


FIG. 5. The diagram of functions $g_1(x)$ (curve 1) and $g_2(x)$ (curve 2) for $\gamma' = 0.25$. The allowed energy intervals of surface states of graphite in γ units can be obtained from this graph by means of the inequality (56).

perpendicular x and y axes, the x axis being perpendicular to the delimiting plane:

$$k = (k_x, k_y), \quad k' = (k_x, -k_y). \quad (50)$$

From the relations derived by Wallace¹⁶ it follows that the function ϕ_k has its zero value in the cells characterized by Eqs. (48). The function ϕ_k therefore represents the solution for a finite two-dimensional crystal delimited by the straight lines defined by Eqs. (48). The number of functions defined by Eq. (49) is here equal to the number of atoms in the crystal. For this reason, in such a crystal no wave functions pertaining to surface states can exist.

SURFACE STATES CAUSED BY BREAKING OF THE σ BONDS IN TWO-DIMENSIONAL GRAPHITE

If we set out from the mentioned assumption that the interaction between the p_z orbitals and the sp^2 hybrids in two-dimensional graphite can be neglected, the wave function for the σ states in the infinite crystal can be written in the form of Eq. (1), in which, however, the index p runs through the values from 1 to 6, and we do not consider the elementary translation a_3 and the pertinent quantum number ξ_3 .

The secular equation for the infinite crystal then has the form

$$\Delta_{18,18} = 0, \quad (51)$$

if the symbols γ, γ' denote the resonance integrals between the sp^2 hybrids. Putting again $\gamma = 1$, we obtain the solutions

$$x_{1,2} = \pm 1, \quad (52)$$

and

$$x_{3-6} = \gamma' \pm [1 + \gamma'(3\gamma' \pm |B|)]^{\frac{1}{2}}, \quad (53)$$

where the magnitude x is defined by the relation (5) and we have introduced the notation

$$B = 1 + \sum_{j=1}^2 e^{ik_j}. \quad (54)$$

By a procedure quite analogous to the case of the diamond model considered in this paper, we obtain the

²³ E. Heilbronner, *Helv. Chim. Acta* **36**, 921 (1954).

equation for the energy of the surface states for the crystal delimited by the straight line $m_2=0$:

$$g_1(x) = \frac{1}{\gamma'^2 x} (x^2 - 2\gamma'x - 1)(x^3 - 3\gamma'x^2 - x + \gamma') = |b|^2, \quad (55)$$

where the quantity b is defined by Eq. (39).

The condition for the existence of surface states then reads

$$g_2(x) < g_1(x) < 6, \quad (56)$$

if the function $g_2(x)$ is defined as follows:

$$g_2(x) = \frac{1}{\gamma'^2} [x^3 - 3\gamma'x^2 - x + \gamma']^2. \quad (57)$$

With regard to the similarity of the results obtained for the σ bonds of the two-dimensional graphite model with the results for diamond, we give here no detailed discussion of the spectra of the surface states produced by breaking of the σ bonds in graphite. For orientation it will be probably sufficient to refer to Fig. 5 for $\gamma' = 0.25$.

Hall Effect and Resistivity of Ni-Pd Alloys*†

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The two Hall coefficients and the resistivity of Ni-Pd alloys have been measured from 4°K to room temperature using fields up to 3.1 webers/m². The ordinary Hall coefficient is found to decrease in magnitude for small additions of Pd in Ni, but to increase as more Pd is added. It is also found that the ordinary Hall coefficient varies more slowly with composition for these alloys than it does for the Ni-Cu alloys. It is shown that a simple treatment successfully correlates the ordinary Hall coefficient, the resistivity, and the saturation magnetization of these alloys. The results indicate that the parallel half of the d band in pure Ni is not quite full at the absolute zero of temperature, and that the relaxation time is not a function only of the energy for the thermal scattering in these alloys. The extraordinary Hall coefficient is found to obey none of the variously proposed theoretical relations.

INTRODUCTION

IT has been established by a number of experiments that the Hall effect in ferromagnetics obeys a relation of the form

$$Vt/I = R_0(\mu_0 H) + R_1 M, \quad (1)$$

where V is the Hall potential, t the sample thickness, I the sample current, H the magnetic field and M the magnetization. R_0 and R_1 have been called¹ the ordinary and extraordinary Hall coefficients, respectively. The ordinary coefficient R_0 was found to correspond to the Hall coefficient in nonferromagnetic materials.

An analysis of the Ni-Cu² and Ni-Co³ data based upon the free electron relation

$$R_0 = -1/(Nne), \quad (2)$$

where N is the number of atoms per m³, n the number of conduction electrons per atom, and e the magnitude

of the electronic charge in coulombs, gave for n_s , the number of $4s$ electrons per atom, values agreeing only within a factor of two with those deduced from magnetic data. Nor could this discrepancy be explained on the basis of a two band model where conduction occurs in both the $3d$ and $4s$ bands.

A four band model, proposed by Pugh,⁴ has been more successful in explaining the data. In this model, both the $3d$ and $4s$ bands are divided into sub-bands where the spins of the electrons are aligned either parallel or antiparallel to the magnetic field. Applications of this model have usually neglected the conduction in the d band, in which case the expression for the ordinary Hall coefficient reduces to

$$R_0 = (-2/Nn_s e) [1 - 2\lambda/(1+\lambda)^2], \quad (3)$$

where λ is the ratio σ_a/σ_p ; σ is the conductivity and the subscripts a and p refer to the antiparallel and parallel electrons, respectively. In terms of the effective number of conduction electrons per atom, n^* , defined by

$$R_0 = -1/(Nn^* e) \quad (4)$$

this reduces to

$$1/n^* = (2/n_s) [1 - 2\lambda/(1+\lambda)^2]. \quad (5)$$

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² A. I. Schindler and E. M. Pugh, Phys. Rev. **89**, 295 (1953).

³ S. Foner and E. M. Pugh, Phys. Rev. **91**, 20 (1953).

⁴ E. M. Pugh, Phys. Rev. **97**, 647 (1955).