First-principle calculation of SP³ hybridization and bonding in diamond-structure semiconductor crystals

Garba Babaji,
Department of Physics,
Bayero University,
P. M. B. 3011, Kano, Nigeria

Abstract

The electronic charge density due to the sp³ hybridized orbitals electrons in the diamond-structure semiconductor crystals has been calculated for the k = 0 state. This charge density represents the electronic distribution in the direct lattice of the crystals. Normally, the charge density in a condensed matter such as crystals is obtained from extremely complicated functions. However, in this work, the charge density is calculated from first-principles. The basic inputs are the lattice constant of the crystal and the atomic number of the atom. To obtain the required expression for the hybrids, we must choose some orientation for the tetrahedral bonds with respect to the Cartesian axes. The most convenient orientation chosen is to inscribe the tetrahedron in a cube whose edges are parallel to the Cartesian axes as shown in Figure 3.1. The tetrahedral bonds point towards the corners of a unit cube. The centre of the cube is the origin of the coordinates. The charge density is calculated along the four tetrahedral bonds and the [100], [010], and [001] directions. The density along the bonds directions is found to be the same. Also, the density along the [100], [010], and [001] directions are the same at equal distances from the center of the Wigner-Seitz cell (which is the origin of coordinate axes employed). In general, the density rises from zero at the center of a cell to a certain maximum value and then drops down as the distance is further increased. The results obtained also explain the known hardness of carbon (diamond).

1.0 Introduction

It is a well known fact [9] and [22] that the one-electron wave function for the jth electron in a crystal, $\Psi_j(\mathbf{k},\mathbf{r})$ at the point **r** is given by the Bloch theorem as

$$\Psi_j(\lambda,k,r) = \exp(ik \bullet r)u_{\lambda k}(r) \qquad (1.1)$$

where λ is the energy eigenvalue, *k* is the wave vector, and u is the Bloch function. The Bloch function is required to have the full translational symmetry of the lattice, i.e

e-mail address: garbababaji@yahoo.com
Telephone: +234-07025120635

$$u_{\lambda,k}(r) = u_{\lambda,k}(r+R), \tag{1.2}$$

for any direct lattice point vector *R*. The probability function for the electrons in a spatial region of volume $d\Omega$ is given by $|\Psi_{n,k}(r)|^2 d\Omega$ for the electrons in valence band n and state *k*. When many *k*-states are considered, a charge density can be described. In particular, the charge density for each valence band can be written as

$$\rho_n(r) = \sum_k c|\Psi_{n,k}(r)|^2, \tag{1.3}$$

where the summation is over all states in the Brillouin zone for a given band n. The total charge density for a semiconductor can be obtained by adding the charge densities from all the valence bands. i.e.

$$\rho(r) = \sum_n \rho_n(r), \tag{1.4}$$

where the sum is over all occupied bands. The function $\rho_n(r)$ yields information about the properties of individual bands and can be used to determine the role of each band in the bonding nature of the crystal. The total charge density $\rho(r)$ represents the electronic distribution in a direct lattice. It has been shown experimentally in [4] and theoretically in [8] that $\rho(r)$ clearly demonstrates the peaking of the charge density in the covalent bond halfway between the atoms in *C, Si, Ge*, and gray-*Sn*.

Normally, the charge density in a condensed matter such as crystals is obtained from extremely complicated functions. However, in this work, the sp^3 electrons charge density in the diamond-structure semiconductor crystals for the state *k* = 0 is calculated from first-principles. The basic inputs are the lattice constant of the crystal and the atomic number of the atom. It is assumed here that the Bloch functions in the crystal will not very seriously differ from the wave functions in the atomic system; in fact even in practical and accurate calculations in solids, the atomic orbitals are used as a first approximation [5]. Therefore, the sp^3 normalized Slater orbitals, were used to represent the various Bloch functions, u$_j$.

It should be noted that for the state k = 0, $\exp(ik \bullet r) = 1$. Therefore, the one-electron wave function in a crystal reduces to $\Psi = u$, and the electronic charge density is simply given by $|u|^2$.

2. 0 The normalized slater orbitals

There are many ways of obtaining the one-electron function for an electron in an atomic system. For example, they can be obtained numerically with the Hartree-Fock method [6] or analytically with Roothan's Self-eonsistent-Field (SCF) method [1]. However, the usefulness of functions simpler than the Hartree-Fock functions were recognized long ago, [10] and [18]. They both made use of a single exponential function to describe an atomic orbital. In this work, the one-electron function for an electron in an atomic system is represented by the Slater atomic orbital for multi-electron atoms and ions, given by [13] as

$$\Phi_n(r, \theta, \varphi) = A r^{n^*-1} \exp\left(\frac{-Z_{eff} r}{n^*}\right) Y_{l,m}(\theta, \varphi), \tag{2.1}$$

where *n* is the principal quantum number, *n** is the effective principal quantum number, *A* is a normalization constant, and Z$_{eff}$ is the effective nuclear charge. The effective nuclear charge is given by

$$Z_{eff} = Z - \sigma,$$
(2.2)

where σ is the screening constant.

The radial part of the Slater orbital, R is given by

$$R_n(r) = Ar^b \exp(-t \times r),$$
(2.3)

where

$$b = n^* - 1, \quad \text{and} \quad t = \frac{Z_{eff}}{n^*}.$$
(2.4)

To calculate $R(r)$, n^* and σ must be known. There are several rules proposed for the calculation of these quantities and the interested reader is referred to the work of [17]. These rules were used to calculate n^*, σ, and z_{eff} and then the various radial factors $R(r)$ in α — tin. However, in the case of C, Si and Ge the various $R(r)$ were calculated using the values Z_{eff} reported by [2].

3.0   Normalized wave function for sp^3 orbital

In its ground state, carbon atom has the $1s$ and $2s$ orbitals filled and only two electrons in the three $2p$ orbitals i.e. configuration of $1s^2 2s^2 2p^2$. Therefore, it might be expected to be divalent and form bonds through the 2p orbitals, at 90° to one another. But in nearly all its compounds carbon is tetravalent. In order to account for the tetravalent bond formation, we must assume that the state of carbon which is forming the bonds is one having the electron configuration $1s^2 2s^1 2p^3$, for then the $2s$ and the three $2p$ electrons are all available for bond formation. Let the normalized ground state orbitals be represented by the letters s, p, d, *ect*, and the hybridized state be represented by *SP*. Considering sp hybridization, the general expression for a normalized hybrid wave function is given in [5] as

$$SP = \alpha_1 s + \alpha_2 p,$$
(3.1)

where $\alpha_1^2 + \alpha_2^2 = 1$. Its fractional s and p characters are α_1^2 and α_2^2 respectively and it is called an $s^{\alpha_1^2} p^{\alpha_2^2}$ or $sp^{(\alpha_2/\alpha_1)^2}$ hybrid. Reversing the process, we see that an sp^x hybrid has a normalized wave function

$$SP^x = (1+x)^{-1/2} \left(s + \sqrt{x} p \right),$$
(3.2)

where x may be any positive number.

Since the *s* orbitals are spherically symmetrical, the directions in which these hybrids orbitals point are the same as the directions of the *p* orbitals [14]. As the three *p* orbitals (p_x, p_y, and p_z) have angular variation like unit vectors in the *x*-, *y*-, and *z*-directions respectively, we can always find the component of a *p* orbital pointing in a specified direction by the normal rules of vector algebra. If we are interested in the direction of the unit vector (a,b,c) then the value (i.e. magnitude) of the *p* orbitals along this direction, $p(a,b,c)$ is given by the wave function
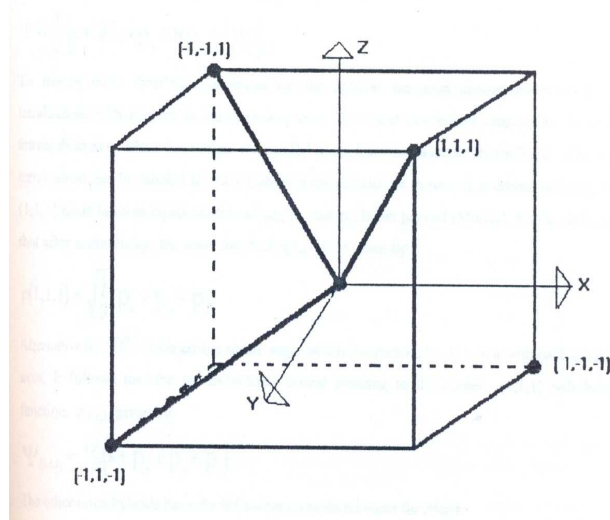
$$p(a,b,c) = ap_x + bp_y + cp_z.$$
(3.3)

Thus an sp^x hybrid along this direction has the wave function

$$SP^x(a,b,c) = (1+x)^{-1/2} \left\{ s + \sqrt{x} \left(ap_x + bp_y + cp_z \right) \right\}.$$
(3.4)

In sp^3 hybridized orbital, $x = 3$, (3.4) becomes

$$SP^3(a,b,c) = \frac{1}{2} \left\{ s + \sqrt{3} \left(ap_x + bp_y + cp_z \right) \right\}.$$
(3.5)

Figure 3.1: Tetrahedral bonds pointing towards the corners of a unit cube. the center of the cube is the origin of the coordinates.

To obtain more detail expression for the hybrids, we must choose some orientation for the tetrahedron with respect to the Cartesian axes. The most convenient orientation is to inscribe the tetrahedron in a cube whose edges are parallel to the Cartesian axes as shown in Figure 3.1. The corners of the tetrahedron can be labeled by their Cartesian coordinates as shown. A p orbital pointing to the corner (1,1,1) must have an equal mixture of p_x, p_y, and p_z. It can be proved [14] that after normalizing, the wave function $p(1,1,1)$ is given by

$$p(1,1,1) = \sqrt{1/3}\left(p_x + p_y + p_z\right). \tag{3.6}$$

Alternatively, $1/3^{0.5}$ is the cosine of the angle which the vector makes with each of the coordinate axes. It follows that the sp³ hybridized orbital pointing to the corner (1,1,1) will have the wave function $SP^3{}_{(1,1,1)}$ which is given by

$$SP^3{}_{(1,1,1)} = 1/2\left(s + p_x + p_y + p_z\right). \tag{3.7}$$

The normalized wave functions of the other three hybrids are

$$SP^3{}_{(-1,-1,-1)} = 1/2\left(s + p_x - p_y - p_z\right), \tag{3.8}$$

$$SP^3{}_{(-1,1,-1)} = 1/2\left(s - p_x + p_y - p_z\right), \tag{3.9}$$

$$SP^3{}_{(-1,-1,1)} = 1/2\left(s - p_x - p_y + p_z\right). \tag{3.10}$$

The charge density of the sp³ orbitals electrons along the bond direction is given by

$$\rho(r) = \left|\Psi_{(a,b,c)}(r)\right|^2, \tag{3.11}$$

where $\Psi \equiv SP^3$, and is given by equations (3.7) to (3.10).

4.0   Computational procedure
An outline of the computational procedure is as follows:
(i)   Slater rules were used to calculate n* and σ and then the various radial factors $R(r)$ in α—tin. However, in the case of *C, Si* and *Ge* the various $R(r)$ were calculated using the values Z_{eff} reported by [2]. The author could not find in the literature a reliable Z_{eff} for α—tin; therefore, it

becomes imperative for it to be evaluated using Slater rules.

 (ii)   The radial part of the Slater orbital, (2.3) is then formed for each atomic species.

(iii)   The expressions for the real spherical harmonics given in appendix *A* of [11] were used to evaluate the angular part of the Slater orbital, $Y_{l,m}(\theta,\varphi)$ along the [001], [010], and [100] directions.

(iv)   The Slater orbitals, $\Phi_n(r,\theta,\varphi)$ (i.e. Eq. [2.1]) were then setup along the directions [001], [010], and [100] directions.

(v)   A direction is chosen and then
  (a)   The normalized sp^3 orbitals for the chosen direction calculated by use of (3.4).
  (b)   Finally, the charge density is evaluated from (3.11).

5.0   Results and discussion

The bonding electrons charge density is calculated along the four tetrahedral bonds and the [100], [010], and [001] directions. The density along the bond directions is found to be the same. Also, the density along the [100], [010], and [001] directions are the same at equal distances from the centre of the Wigner-Seitz cell (which is the origin of coordinate axes employed), therefore, only the charge densities along the bond and [001] directions are presented.
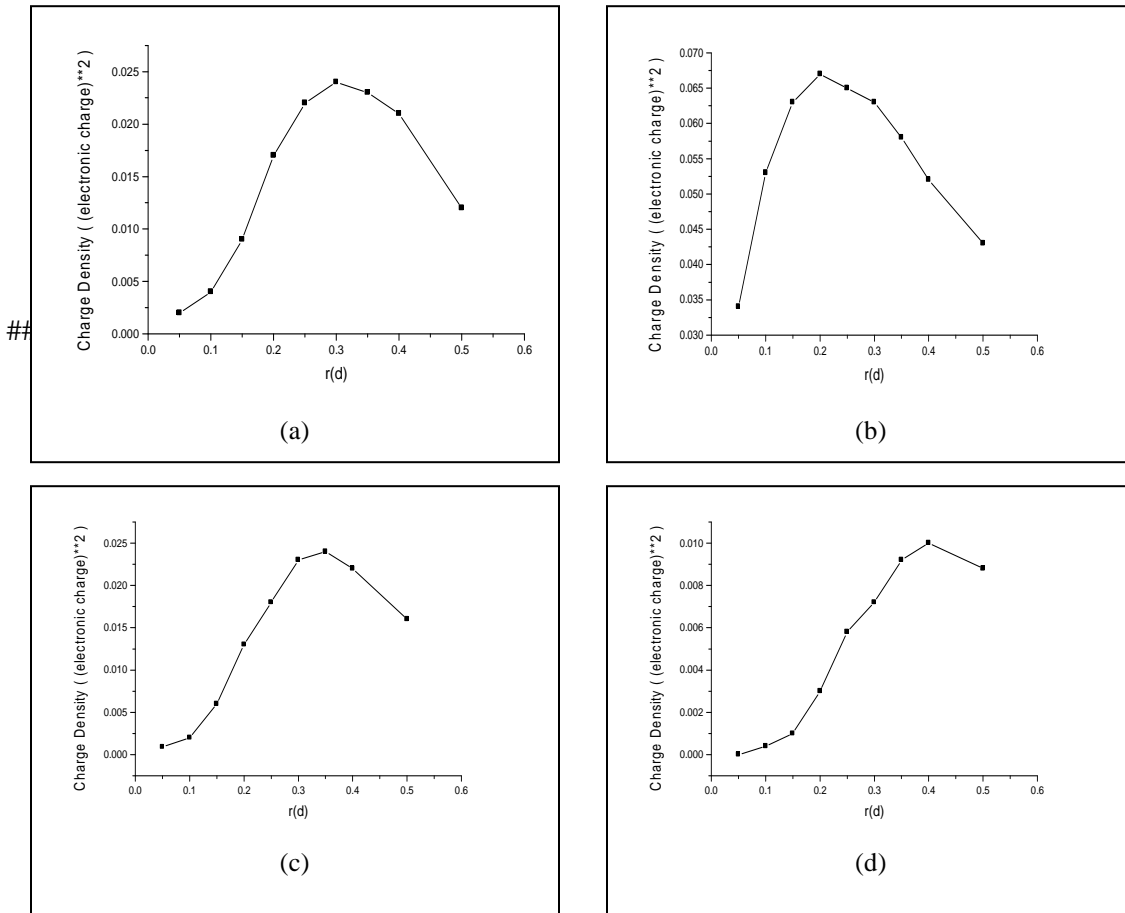
Figure 5.1. Variation of bonding electrons charge density with distance from the center of the wigner-seitz cell of diamond-structure semiconductor crystals along the bonding direction. (a) carbon, (b) silicon, (c) germanium, and (d) α-tin
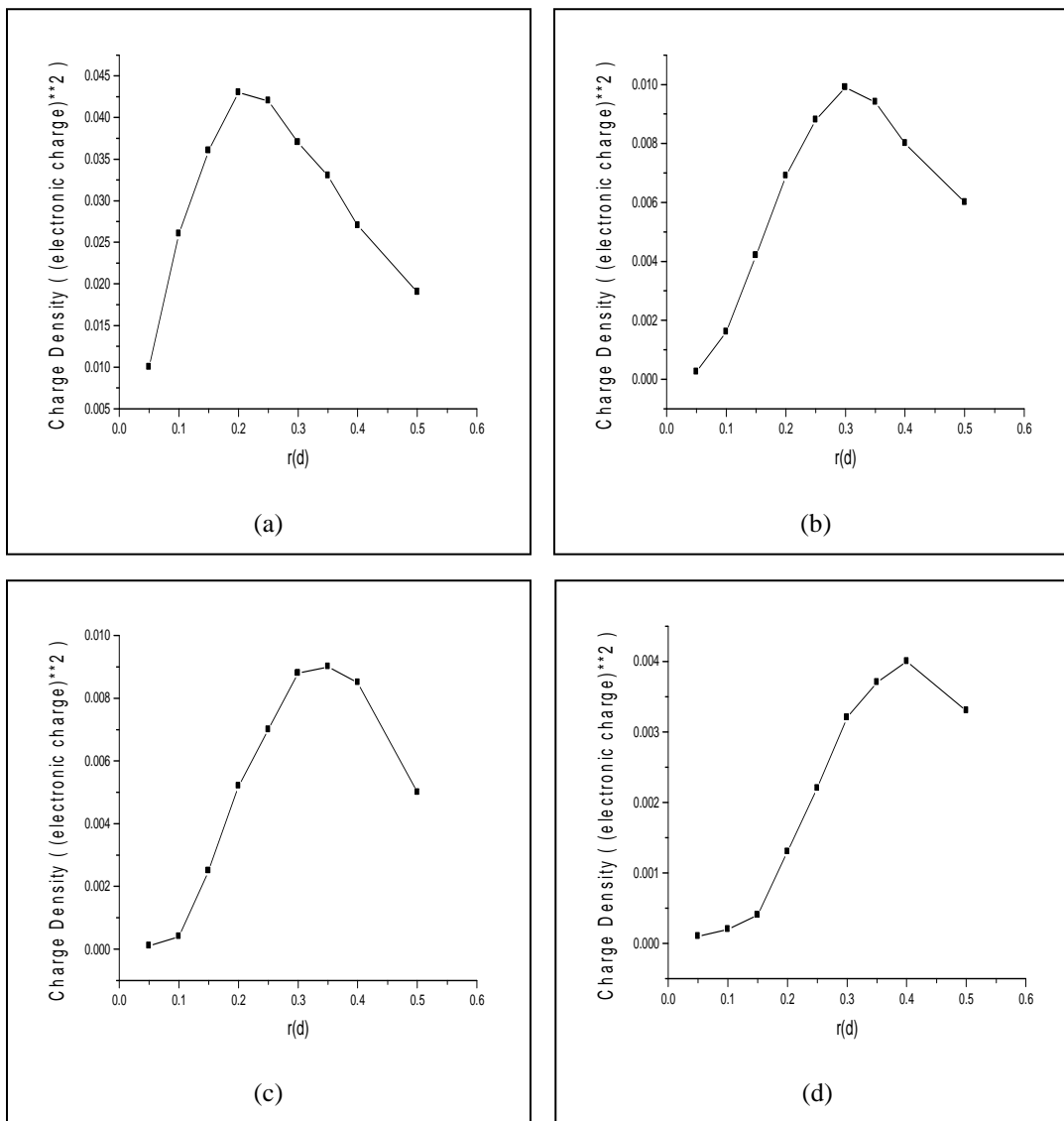
Figure 5.2. Variation of bonding electrons charge density with distance from the center of the wigner-seitz cell of diamond-structure semiconductor crystals along the [001] direction. (a) carbon, (b) silicon, (c) germanium, and (d) α-tin.

The graphs for the variation of density with distance from the centre of the Wigner-Seitz cell are given in Figures. 5.1 and 5.2, and a summary is given in Table 4.1. It should be noted that the charge density is given in units of (electronic charge)^2, while distance is in units of the appropriate nearest neighbour distance, d. In general, the density rises from zero at the centre of the cell to a certain maximum value and the drops down as the distance is further increased.

The maximum density along the bond direction is about 2.5 times the maximum density along the [001] direction in all the crystals investigated. The maximum density in each crystal occurs at the same distance along both the bond direction and the z-axis. In carbon the maximum density occurs at $0.2d$, in silicon at $0.3d$, in germanium at $0.35d$, and at $0.4d$ in α-tin in agreement with the results of [4] and that of [8].

In the crystals investigated, carbon has the smallest Wigner-Seitz cell and α-tin the largest. Since the number of the bonding electrons in all the crystals are the same (four), it is obvious that the charge density will be highest in carbon and smallest in tin as has been found in this work. The higher the bonding electrons charge density the stronger the bond and the harder the crystal. Thus the known hardness of diamond (carbon) has been accounted by the results obtained.

Table 5.1. A comparison of the maximum charge densities along the [100] and the bonding directions.

Crystal	[001] Direction		Bond Direction	
	Max. Density (e^2)	r (d)	Max. Density (e^2)	r (d)
Carbon	0.042469	0.20	0.110068	0.20
Silicon	0.009839	0.30	0.024969	0.30
Germanium	0.009179	0.35	0.023261	0.35
α-Tin	0.003931	0.40	0.010237	0.40

6.0   Conclusion

A first-principle calculation of the sp^3 hybridized orbtital wave functions and charge densities in the diamond-structure semiconductor crystals has been done. The basic input to all calculations are the lattice constant of the crystal and the atomic number of the constituent atom. The bonding electrons charge density for the $k = 0$ state (i.e. the ground state) is calculated along the four tetrahedral bonds and the [100], [010], and [001] directions. The density along the bond directions are the same at equal distances from the centre of the Wigner-Seitz cell. The agreement of the obtained results with those found by others are good, particularly in silicon, germanium, and tin.

References

[1]   Breene, R. G. (1958), Analytic –Wave Function: Atoms with 1s, 2s, and 2p Electrons. *Phys. Rev*. **111**, 1111.
[2]   Clementi, F. and Raimondi, D.L. (1963). Analytical Screening Constant From SCF Functions. *J. Chem. Phys.* **38**, 2686.
[3]   Cohen, M. L. and Chelikowsky, J.R. (1988). *Electronic Structure and Optical Properties of Semiconductors* (Spring-Verlag, New York) Chap. 4.
[4]   Chen, R. , Trucano, P. and R. F. Stewart (1977). *Acta Cryst. Sect. A* **33**, 823.
[5]   Dalton, N. W. and D. E. Schreiber (1972). Charge Density in the Gallium Arsenide Crystal, in *Computational Solid State Physics*, Edited by Franck Herman, Norris W. Dalton, and Thomas R. Kochler (Plenum Press, New York) p. 183.
[6]   Hartree, D. R. (1957). *The Calculation of Atomic Struc*tures (John Wiley, New York) pp. 13-16.
[7]   Hartree, D. R. (1957a). *The Calculation of Atomic Struc*tures (John Wiley, New York) chaps. 2&3.
[8]   Holzwarth, N. A. W. , Louie, S.G. and S. Rabii (1982). Electronic Structure of Third-Stage Lithium Intercalated Graphite, *Phys. Rev. B* **26**, 5382.
[9]   Huag, H. and Stephen W. Koch (1990). *Quantum Theory of the Optical and Electronic Properties of Semiconductors* (World Scientific, New Jersey) p. 31.
[10]   Lowdin, P.O. (1953). Studies of Atomic Self-Consistent Fields 1: Calculations of Slater Functions, *Phys. Rev*. **90**, 120.
[11]   Mcglynn, S. P. , Vanquickenborne, L.G. , Kinoshita, M. and Caroll, D.G. (1972). *Introduction to Applied Quantum Chemistry* (Holt Rinehart and Winston Prees, London) chap. 2.
[12]   Marvin, L. C. (1975). *Introduction to the Quantum Theory of Semiconductors* (John Wiley and Sons, New York) chap. 3.
[13]   Mcweeny, R. (1979). *Coulson's Valence* (Oxford University Press, London) chap. 2.
[14]   Murrell, J. N. , Kettle, S.F.A. and Tedder, J.M. (1977). Valence Theory (John Wiley and Sons, London). Chapt. 5
[15]   Randic, J.A.(1962). Construction of Hybrid Orbitals, *J. Chem. Phys.* , **36**, 3278.
[16]   Slater, J. C. (1934). Electronic Energy Band in Metals, *Phys. Rev.* **45**, 794.
[17]   Slater, J. C. (1955). One-Electron Energies of Atoms, Molecules and Solids *Phys. Rev*. **98**, 1039.
[18]   Slater, J. C. (1951). A Simplification of the Hartree-fock Method, *Phys. Rev*. **81**, 385.
[19]   Walter, J. P , and M. L. Cohen (1971). Electronic Charge Densities in Semiconductors, *Phys. Rev. Lett.* **26**, 17.

[20]   Wigner, E. and F. Seitz (1933). On the Construction of Metallic Sodium I, *Phys. Rev*. 43, 804.
[21]   Wigner, E. and F. Seitz (1934). On the Construction of Metallic Sodium II, *Phys. Rev*. 46, 509.
[22]   Ziman, J. M. (1965). Principles of the Theory of Solids (Cambridge University Press, Cambridge) chapter two.