

Electronic structure of fcc carbon

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We report first-principles calculations of the electronic structure for carbon in the fcc structure with the experimentally observed lattice parameter. The calculated orbital population shows that the chemical bond in fcc carbon is close to the s^2p^2 bonding with a small s - p hybridization. We find that, in contrast to graphite and diamond, fcc carbon exhibits metallic behavior with an electronic density of states at the Fermi level of 0.5 states/eV-atom.

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New crystalline phases of a given material are interesting because they correspond to a different bonding arrangement and new properties can be expected. The face-centered-cubic (fcc) crystal structure does not appear on the usual pressure-temperature phase diagram of carbon [1]. However, the observation of fcc carbon (fcc-C) in nanoparticles and thin films has been reported [2–7]. Palatnik et al. [2] were the first to report the observation of the fcc phase of carbon, which was obtained from low temperature annealing of an amorphous carbon film with simultaneous bombardment of argon ions. After that process, syngle-crystal inclusions of ~ 100 Å in size with a lattice constant of 3.57 Å and metallic character were observed [2, 3]. Carbon with the fcc crystal structure has also been observed at the core of carbon particles produced by plasma-chemical synthesis [4]. More recently, it was shown that a thin film of fcc carbon is formed on a diamond surface as a result of treatment in a hydrogen plasma [5–7]. The crystal lattice parameter of fcc carbon in thin films was determined by high-resolution transmission electron microscopy to be 3.563 Å [6, 7]. These reports on the existence of carbon thin films and nanoparticles with the fcc structure has stimulated us to study the electronic properties of fcc carbon.

The electronic density of states (DOS) of fcc-C have been studied theoretically by means of the empirical tight-binding method [5]. The tight-binding calculation for the DOS indicates that metallic behavior can be expected for fcc carbon. However, the value of the DOS at the Fermi level as well as the analysis of the electronic

structure was not reported [5]. Thus, first-principles calculations appear to be essential to evaluate the electronic properties of fcc-C since, to the best of our knowledge, accurate calculations of the electronic structure for fcc-C have not been reported previously.

In this letter, we report a study of the electronic structure of carbon in the fcc structure performed by means of first-principles calculations. We present results for the charge density, band structure, Fermi surface, and density of states. From the analysis of the chemical bond and the electronic band structure, we find that fcc-C has a chemical bond very close to an s^2p^2 bonding and exhibits metallic behavior. The DOS at the Fermi level is 0.5 states/eV-atom and the main contribution is coming from p -states.

The calculations were done within the Generalized Gradient Approximation (GGA) to the Density Functional Theory (DFT). The electronic structure of carbon with the fcc structure was determined self-consistently using the pseudopotentials LCAO method [8, 9] as implemented in the SIESTA code [8–10]. The carbon pseudopotential was generated according to the procedure of Troullier and Martins [11] from the atomic configuration [He] $2s^2 2p^2$. The core radii for the s and p orbitals were 1.5, a.u., and 1.25 a.u. for the d and f orbitals. For the expansion of the wave functions we employed a double- ζ plus polarization basis [10]. The basis for the s and p orbitals was slightly excited (270 meV) in order to limit the range of the pseudoatomic basis orbitals [12]. For the exchange-correlation potential we used the GGA as parametrized by Perdew, Burke and Ernzerhof [13]. In order to obtain the potential energy we used a grid in real space which was obtained using a mesh cutoff of 250 Ry. Integrals in k -space were performed in a finite, uniform grid of the Brillouin zone.

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loun zone. The fineness of this grid was controlled by a k -grid cutoff, a real space radius which plays a role equivalent to the plane wave cutoff of the real-space grid [14]. For the present calculation the k -grid cutoff was 130 Å, generating 562482 k -points in the First Brillouin zone. Self-consistency was assumed when the difference between the two density matrix belonging to successive iterations was less than 10^{-4} . The calculation was performed at the experimental lattice parameter for fcc carbon as obtained from high resolution electron microscopy ($a = 3.563$ Å) [5].

In Fig.1 we show the calculated valence charge density at the (001) plane of fcc-C, where the steps in the

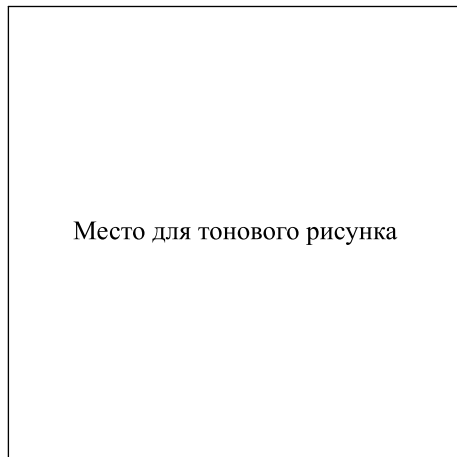


Fig.1. Charge density map for fcc carbon projected in the (001) plane

charge density plot correspond to 0.02 electrons/Å³. We can see that the charge distribution is strongly spherical around the core and mostly homogeneous in the interstitial region, which are features characteristic of a metallic bonding. The electronic configuration of carbon is [He]2s²2p², therefore the valence band consists of s - p -like bands and is relatively simple. The calculated band structure is presented in Fig.2, where the origin in energy is at the Fermi level (E_F). The first band covering the energy range from -14 to -6 eV below the Fermi level shows a minimum at the Γ -point. This band has a strong s -character and exhibits parabolic behavior around Γ . A second set of bands consists of three bands with p -character. It is interesting to note that the p -bands are separated from the s -band by an energy gap. The s - p gap extends from -5.1 to -5.9 eV below the Fermi level. Two p -bands cross the Fermi level, indicating that fcc carbon is a metal. This result is in qualitative agreement with the observations of electrical conductivity in fcc-C reported by Palatnik et al. [2] and Jarkov et al. [15].

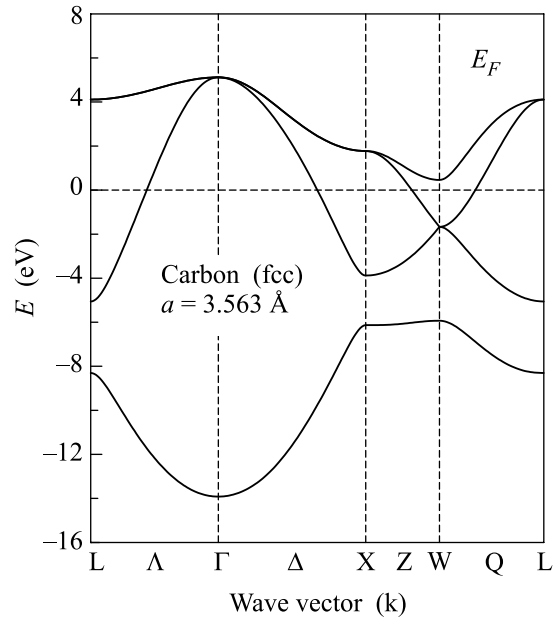


Fig.2. Electronic band structure for fcc carbon at the experimental lattice parameter ($a = 3.563$ Å)

The Fermi surface properties are of special importance in metal physics, since they are related to the transport coefficients as well as to the optical properties. In order to gain insight on the transport properties of fcc-C, we have analyzed the Fermi surface [16]. In Fig.3, we show the surface of constant energy resulting from the two bands crossing the Fermi level in Fig.2. The first Fermi surface (Fig.3a) corresponding to the band centered at Γ (see Fig.2) is a closed surface with hole character. In contrast, the second Fermi surface (see Fig.3b) which corresponds to the band centered at the edges of the first Brillouin zone, form a multiply connected surface. Hence the Fermi surface of fcc-C is highly anisotropic and both kind of charge carriers, “holes” and “electrons”, are present. Therefore, rather complex galvanometric properties are expected for fcc-C, since the charge carrier orbits on the Fermi surface are not all of a single carrier type.

The calculated electronic density of states (DOS) is shown in Fig.4, where the origin in energy is at E_F . The top panel corresponds to the total DOS, the middle and lower panel correspond to the s and p partial contributions, respectively. As was mentioned above, fcc-C presents metallic behavior. In particular, we found that the density of states at the Fermi level is 0.5 states/eV-atom and that the main contribution comes from the p states (89%). The lower energy states correspond mainly to s -states, and are separated from the high energy p -states by a gap of 0.8 eV. The s -states have only a small overlap with the p -states, indicating a small s - p

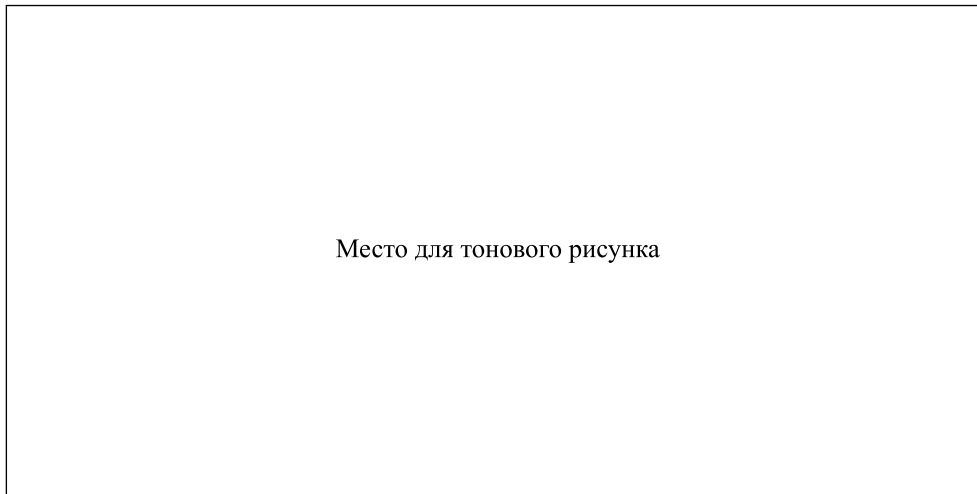


Fig.3. Fermi surface for fcc-C, corresponding to the band centered at Γ (a) and to the band centered at the First Brillouin edges (b)

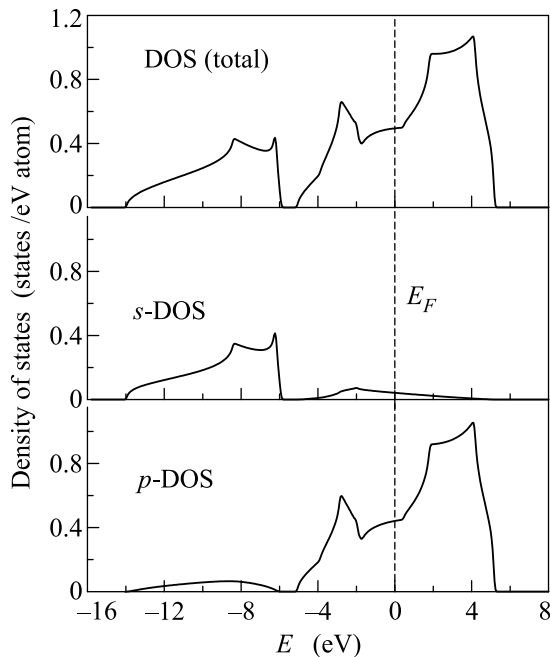


Fig.4. Density of states for fcc carbon at the experimental lattice parameter ($a = 3.563 \text{ \AA}$)

hybridization. The orbital population by symmetry can be obtained by integrating the partial s -DOS and p -DOS up to the Fermi level. From this procedure we find that the number of electrons in the s and p orbitals are 1.98 and 2.02, respectively. There exists a very small charge transfer of 0.02 electrons from the s to the p orbitals. Thus, the chemical bond in fcc-C is close to the s^2p^2 bonding.

From the results presented above, we can see that the electronic structure of fcc-C is different to the well-

known electronic properties of graphite, diamond, and amorphous carbon [17]. Nevertheless, the electronic structure of fcc-C shows a similarity with that of lead (Pb) [18, 19], which is a tetravalent metal like carbon with an fcc ground state. It is interesting to note that in both systems there is an s - p gap below the Fermi level, however in Pb the gap is 3.5 eV [19, 20], which is much larger than for fcc-C (0.8 eV). A small s - p hybridization is also a feature common between fcc-C and Pb but, in contrast to fcc-C, the charge transfer in Pb is from the p to the s orbitals (0.18 electrons) [20]. The Fermi surface for fcc-C has a shape and complexity similar to that of Pb [21]. However, further investigation is necessary to determine the transport properties of fcc carbon, including the superconducting properties as was pointed out by Palatnik et al. [2].

In summary, we have calculated the electronic structure of fcc carbon using a first-principles pseudopotential LCAO method. We find that the electronic structure of fcc carbon is clearly different than those of graphite and diamond. The results show that fcc-C has a chemical bond very close to the s^2p^2 bonding, and is a metal with a DOS at E_F of 0.5 states/eV-atom. The metallic behavior obtained from the present calculations for fcc-C is in agreement with the experimental observation of high electrical conductivity in thin films of carbon with the fcc structure. The Fermi surface of carbon in the fcc structure has a similar complexity as that of Pb(fcc). Thus, metallic fcc carbon is expected to have unique electronic properties.

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