On the possibility of a double-well potential formation in diamond-like amorphous carbon

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A microscopic model, which describes specific features of the electronic spectrum of various allotropes of amorphous carbon as being responsible for their structure peculiarities, is presented. It is shown that the formation of a double-well potential is a possible driving force for this behavior.

71.23.Cq and 61.43.Dq

Amorphous carbon (a-C) and hydrogenated amorphous carbon (a-C:H) attract attention not only due to their intriguing physical properties but also from the point of view of their numerous application. Despite a large body of theoretical and experimental research, the basic question of the interrelationship of a-C atomic structure and its electronic properties remains to be answered. The matter is that carbon has several allotropic forms in contrast to other materials belonging to the fourth group such as, e.g., Si and Ge characterized by tetrahedral fourfold sites (sp^3). Carbon can adopt three different bonding configurations: sp^3, sp^2, and sp^1. In the sp^3 configuration, each of the carbon’s four electrons is assigned to a tetrahedrally directed sp^3 hybrid orbital, which forms a strong σ bond with an adjacent atom. Such a configuration is peculiar, i.e., to diamond and corresponds to a dielectric state with a wide energy gap of 5.5 eV. At a carbon sp^2 site, three of the four electrons are assigned to the trigonally directed sp^2 hybrids, which form σ bonds, with the fourth electron belonging to the p_π(p_π) orbital orthogonal to the σ bonding plane. This configuration is inherent to graphite, which is a good conductor along its basal plane.

It is well known that Si and Ge atoms hold their tetrahedral coordination in amorphous a-Si and a-Ge exhibiting a slight distortion in the bond angle with respect to the value characteristic of a crystal. By contrast, there is abundant evidence that amorphous a-C with the optical gap of 0.4 – 0.7 eV is predominantly sp^2 bonded. \(^{1-3}\) This is not particularly surprising, since graphite is precisely the allotrope of carbon which is stable. This clearly demonstrates the importance of π-states in a-C as they are responsible for the weakest inter-layer bonds closest to the Fermi level on the energy scale. Thus, they seem to affect the upper valence- and conduction-band states to a great extent. There is a slight band overlap (\(^\sim\) 0.04 eV) in graphite with non-distorted π states. As a consequence, majority of theoretical models predict existence of only few sp^3 bonded atoms in a-C. The necessity to consider the contribution both from distorted 5- and 7-element rings \(^{11}\) and from twofold carbon atoms \(^{12}\) was suggested in some theoretical models.

In the following we would like to discuss in more details a few models where the electronic as well as structural properties of amorphous carbon received primary emphasis. Beeman et al. \(^{6}\) considered three model random networks of a-C with differing percentages of threefold- and fourfold-coordinated atoms. The best agreement between theory and experimental data on the radial distribution function was realized within the model with 9% fourfold coordinated atoms. Comparison of calculated and experimental Raman scattering and vibrational density-of-states spectra also suggests that the structure of amorphous carbon is composed of three-coordinated planar regions and occasional four-coordinated atoms which allow the plane orientation changes.

On the other hand, calculation of the electronic density-of-states function by O’Reilly et al. \(^{11}\) carried out in the framework of Beeman’s model proved the absence of a gap at Fermi level. Based on this fact Robertson \(^{8}\) concluded that a-C possesses a higher degree of sp^3 site ordering than it was assumed in Ref. \(^{6}\). The electronic structure of a-C was investigated by Robertson and O’Reilly \(^{8}\). They performed a simulation of a number of model structures with different sp^2 – sp^3 site ratio. This approach has led to the cluster model that claimed sp^2 and sp^1 site segregation, with sp^2 graphit clusters being embedded into sp^3-bounded matrix. The gap \(E_g\) of planar clusters varies with number of 6-fold aromatic rings \(M\) as \(E_g \propto 6/\sqrt{M}\). The typical \(E_g \sim 0.5\) eV was found to be consistent with clusters of about 15 Å in diameter. That cluster approach was generally accepted for some years and was considered to be a good starting point for the experimental data analysis. But recently
Robertson [7] demonstrated that the cluster model [4] presupposes much more order and existence of large number of clusters than can exist in a-C and a-C:H which are essentially disordered due to an ion bombardment during deposition. In the context of cluster model it is further difficult to explain the well-known experimental results on the optical gap opening in completely sp²-coordinated carbon (both in graphite and in glassy-carbon) which is caused by an ion beam exposure [3]. Compagnini et al. [11] observed the saturation effect in the sp² – sp³ configuration ratio with the exposure dosage growth, with the essential prevailing of sp²-type configurations. It seems reasonable to suppose that the cluster size is to decrease down to a single aromatic ring at intensive bombarding. It was actually shown in Ref. [7] that disorder greatly reduce the probability of clustering, with single 6-fold distorted rings becoming the most probable configuration. The local density-of-states function was calculated for different types of ring distortion, taking σ – π mixing due to out-of-plane distortion of the ring into account. It was shown that the typical value of $E_g \sim 1$ eV, which is characteristic for amorphous carbon, can be obtained for a single 6-fold ring with a “chair” distortion. The role of a ring distortion was also discussed by Lee et al. [12].

In this paper we propose a microscopic model in the framework of which we managed to associate the properties of sp² electronic configuration inherent to the stable carbon state with the local potential relief peculiarities of a-C.

Let us first summarize the bonding possibilities of a carbon atom placing the primary emphasis on the interrelation between the local crystalline structure and the electronic band peculiarities. As graphite is the stable allotrope of carbon, many disordered forms of carbon have structures based on its lattice. The key feature of the electronic structure of amorphous carbon is that it possesses a narrow optical gap of 0.4 – 0.7 eV [3], which is in contrast to the slight band overlap in graphite and the 5.5 eV band gap of diamond. Now let us suppose that some carbon atoms of graphite are allowed to displace perpendicular to the σ bonding plane of graphite structure. As a matter of fact, by doing so we change the local symmetry of bonding and introduce the sp³-type features into the sp² hybridization [11]. In the absence of a long-range order the energy fluctuation leading to the above mentioned distortion seems to be more probable. The microscopic mechanisms that can be responsible for the stabilization of such a distortion are well-known in the theory of ferroelectric and superionic states. In accordance with the vibronic mechanism [13,14], the ferroelectric distortion originates from the lattice instability due to the strong interaction between the dipole moment of virtual interband electronic transition and some transverse optical phonon. Such an interaction results in a phonon softening, with the phonon frequency approaching zero at the transition point.

The other possible mechanism suggests a strong hybridization of electronic states of different symmetry at the top of the valence band [17,19]. The escape of an electron from one of these states leaves a hole. Incomplete screening (for symmetry reasons) of the hole results in the appearance of an effective electron-hole dipole. The interaction of this dipole with a transverse optical phonon can give rise to the formation of a local potential minimum additional to the lattice site, i.e., to the double-well (DW). The essential energy overlap of σ-type and π-type states within the valence band, which takes place in the amorphous carbon, allows us to believe the latter mechanism to be more suitable for this system. The spacing of potential minima of a double-well was found to be [18]

$$\delta \sim f_{exc} \left[ \frac{2}{M_i \omega^2 A} \right]^{1/2}, \quad (1)$$

where

$$A = \frac{1}{N} \sum_q |\gamma_q|^2 \omega_q$$

is the eigenenergy shift due to the electron-hole-phonon coupling. $M_i$ is the effective ionic mass, $N$ is the total number of ions, $\omega$ is the characteristic phonon frequency ($\hbar = 1$), $\gamma_q$ is the electron-hole pair – TO phonon coupling constant, and $f_{exc}$ is the expectation value for the operator of number of electron-hole excitations. The evaluation of the lattice deformation energy yields [13]

$$A \sim \frac{V^2}{M_i \omega^2 a^2}, \quad (2)$$

at low ($T \ll T_D$) and

$$A \sim 2 \frac{V^2}{\omega} \frac{T}{M_i \omega^2 a^2},$$

at high ($T \gtrsim T_D$) temperatures ($k_B = 1$). Here $T_D$ is the Debye temperature, $a$ is the bond length, and $V$ is the characteristic potential felt by an electron-hole pair ($V \sim E_g$).

The value of $f_{exc}$ is estimated as [19]

$$f_{exc} \sim \exp \left\{ -\frac{\varepsilon_c - V}{T} \right\},$$

where $\varepsilon_c$ is the characteristic energy of electrons having escaped the valence π and σ states with the hole formation. The evaluation made with the following set of parameters $M_i \approx 2 \times 10^{-23} \text{g}$, $\omega \approx 1300 \text{ cm}^{-1}$, $a = 1.4 \text{ Å}$, and $E_g \approx 0.4 - 0.7 \text{ eV}$ yields, as the first approximation, $f_{exc} \sim 1$ and the ion displacement $\delta \approx 0.2 - 0.35 \text{ Å}$. This finding is in line with the result of calculations presented in Ref. [4], where the optical gap of a-C was calculated,
with the ion out-of-plane displacement value taken as the starting point.

The modification of potential shape with, e.g., temperature increase is mainly due to the DW spacing \( \delta \) growth (Eqs. (1)-(2)) as well as due to the difference in minima depth change which reads as follows [18]

\[
\Delta \varepsilon \simeq \varepsilon_c - \Delta W - A/2,
\]

where

\[
\Delta W = W \left( \begin{array}{cccc}
1 & 1 & 1 \\
1 & 2 & 1 \\
1 & 2 & 1
\end{array} \right) - W \left( \begin{array}{cccc}
1 & 1 & 1 \\
1 & 2 & 1 \\
1 & 2 & 1
\end{array} \right)
\]

is the difference between the one-site \( \pi - \sigma \) electron direct and exchange Coulomb interaction terms [20]. It should be noticed here that the displacement of carbon ion from the basal \( \sigma \)-plane is associated with the distortion of chemical bonds such that the \( z \)-component of \( \sigma \)-like bonds appears to overlap with the \( \pi \) electron state.

The potential evolution is manifested in changes of lattice dynamics. The dispersion equation of the dielectric function includes the DW-associated contribution of the form [21]

\[
e^* \propto \frac{1}{\int \exp \left\{ -\frac{V(x)}{T} \right\} dx} \int \exp \left\{ -\frac{V(x)}{M_\omega^2 - iM_\gamma \omega - \nabla^2 V(x)} \right\} dx,
\]

where \( V(x) \) is of the double-well type.

In order to simulate the potential relief we have to specify some trial function \( V_{tr} \) possessing desired properties. The function

\[
V_{tr} = -T \ln \left[ \exp \left\{ -\frac{V_1}{T} \right\} + \exp \left\{ -\frac{V_2}{T} \right\} \right],
\]

where

\[
V_1 = -E_1 + \frac{1}{2} kx^2,
\]

\[
V_2 = -E_2 + \frac{1}{2} k(x - \delta)^2,
\]

seems to be adequate enough to reproduce the principal features of the true local potential, provided that \( E_1 - E_2 = \Delta \varepsilon \) and \( k = M_\omega \bar{\omega}^2 \). With allowance made for conservation of the number of particles within the elementary cell, which is possible under the condition of neglecting any long-distance diffusion processes, \( \delta, \Delta \varepsilon, \) and \( \bar{\omega} \) parameters completely determine the relief properties. The analysis reveals a new feature of spectrum which appears at [21]

\[
\omega_{eff} \sim \bar{\omega} \sqrt{1 - \frac{M_\omega \bar{\omega}^2 \delta^2}{4T}}
\]
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