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Simulation of vibrations in hydrogenated diamond-like nanofilms

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Abstract. The paper calculates the phonon spectrum of diamane [1] in the framework of the Hamilton formalism. The geometric model of diamane is represented as a two-layer graphene, but each C-atom has sp^3 hybridization of external electronic orbitals. The carbon atoms of one of the grapheme sublattices are covalently bound to the atoms of the second graphene layer, and the outer hydrogen atoms are covalently connected to the atoms of the second sublattice. A diamane unit cell contains two carbon atoms from a graphene unit cell and one hydrogen atom. When constructing the model, the curvature of the graphene plane was taken into account as a result of the addition of hydrogen atoms to it and the change in the hybridization of the external electronic orbitals of carbon atoms from sp^2 to sp^3. The interaction between hydrogen atoms was not taken into account.

Keywords: diamane, phonon spectrum, dispersion equation

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Материалы конференции
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Моделирование колебаний в гидрированных алмазоподобных нанопленках

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Аннотация. Был проведен расчет фононного спектра гидрированного двухслойного графена [1]. При построении модели была учтена деформация графеновой плоскости в результате присоединения к ней атомов водорода и изменение гибридизации внешних электронных орбиталей атомов углерода.

Ключевые слова: диаман, фононный спектр, дисперсионное уравнение

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Introduction

Numerous works have been devoted to the study of carbon-based nanoscale materials [2] and it is due to their unique properties and the possibility of application in various fields of science and technology. Graphene, predicted theoretically more than half a century ago and obtained experimentally in 2005 [3] has high conductivity, thermal conductivity,

hydrophobicity, and so on. Therefore, various modifications based on graphene itself [4], graphane [5], bigraphene with possible impurities [6, 7], diamane [8] also attract the attention of scientists. The relevance of this study is also due to the fact that oscillatory processes in crystal lattices can affect the kinetics of electron transfer [9, 10]. All of the above suggests that the study of the vibrational properties of hydrogenated diamond-like nanofilms is topical.

Investigation of the diamane vibrational properties

The calculation phonon spectrum of the diamane was carried out on the basis of a combination of the classical and quantum approaches. The consideration is based on the Hamiltonian approach, but the parameters of the model Hamiltonian were obtained using quantum chemical calculations [11]. The elementary cell of the diamane (Fig. 1) contains three atoms (two carbon atoms and one hydrogen atom). The letters *A*, *B* denote the carbon atoms of the graphene sublattices, and the letters C denote the hydrogen atoms located above and below the graphene layer, respectively (Fig. 2). Here Δ_1, Δ_2 are the translation vectors of the crystal lattice. The parameters of the geometric model are presented below for the diamane *ABAB* packaging:

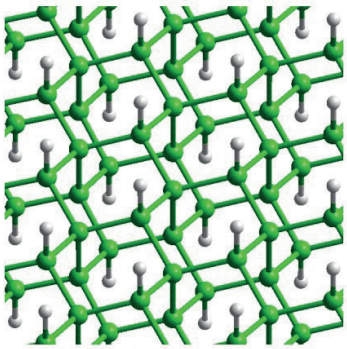

Fig. 1. The diamane structure

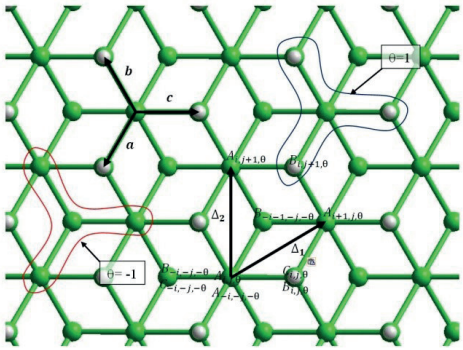

Fig. 2. Geometric model of the diamane

$$\frac{\boldsymbol{a}}{a_1}=\left(-\frac{1}{2}\sin\delta,-\frac{\sqrt{3}}{2}\sin\delta,\cos\delta\right),$$

$$\frac{\boldsymbol{b}}{a_1}=\left(-\frac{1}{2}\sin\delta,\frac{\sqrt{3}}{2}\sin\delta,\cos\delta\right),$$

$$\frac{\boldsymbol{c}}{a_1}=\left(\sin\delta,0,\cos\delta\right),$$

$$\frac{\boldsymbol{d_1}}{a_2}=\left(0,0,1\right),\ \frac{\boldsymbol{d_2}}{b_0}=\left(0,0,1\right),$$

$$\frac{\boldsymbol{\Delta}_1}{a_1}=\frac{\boldsymbol{c}-\boldsymbol{a}}{a_1}=\left(\frac{3}{2}\sin\delta,\frac{\sqrt{3}}{2}\sin\delta,0\right),\ \frac{\boldsymbol{\Delta}_2}{a_1}=\frac{\boldsymbol{b}-\boldsymbol{a}}{a_1}=\left(0,\sqrt{3}\sin\delta,0\right).$$

where δ is the angle formed by the *z*-axis with each of the vectors $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$.

The radius vectors of the sublattices nodes *A*, *B*, *C* in equilibrium can be represented as:

$$\boldsymbol{r}^A_{0,0,1}=\frac{\boldsymbol{d_1}}{2},\boldsymbol{r}^B_{0,0,1}=\boldsymbol{r}^A_{0,0,1}+\boldsymbol{c}=\frac{\boldsymbol{d_1}}{2}+\boldsymbol{c},$$

$$\boldsymbol{r}^A_{i,j,\theta}=\theta\left(\boldsymbol{r}^A_{0,0,1}+i\boldsymbol{\Delta}_1+j\boldsymbol{\Delta}_2\right),\ \boldsymbol{r}^B_{i,j,\theta}=\theta\left(\boldsymbol{r}^B_{0,0,1}+i\boldsymbol{\Delta}_1+j\boldsymbol{\Delta}_2\right),$$

$$\boldsymbol{r}^C_{i,j,\theta}=\boldsymbol{r}^B_{i,j,\theta}+\theta\boldsymbol{d}=\theta\left(\boldsymbol{r}^B_{0,0,1}+i\boldsymbol{\Delta}_1+j\boldsymbol{\Delta}_2+\boldsymbol{d}_2\right),$$

where the vectors Δ_s are the basis translation vectors of the layers of the diamane $s = 1,2$; $\theta = \pm 1$. Detailed description of the parameter θ is shown in Figure 3.

We write the system Hamiltonian in the harmonic approximation, while taking into account the interaction of each of the atoms only with the nearest neighbors:

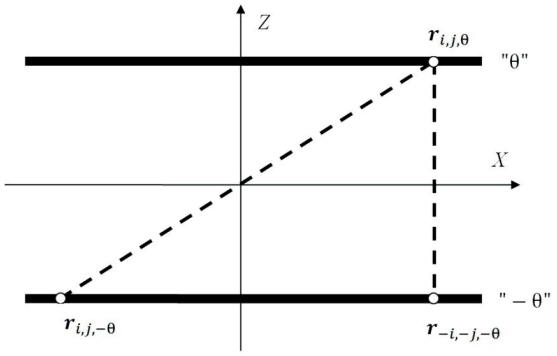

Fig. 3. Indefinite layer symmetry

$$H = \frac{1}{2m_1}\sum_{i,j,\theta}\left(\boldsymbol{p}^{A}_{i,j,\theta}{}^{2} + \boldsymbol{p}^{B}_{i,j,\theta}{}^{2}\right) + \frac{1}{2m_2}\sum_{i,j,\theta}\boldsymbol{p}^{C}_{i,j,\theta}{}^{2} +$$

$$\frac{k_1}{4}\sum_{i,j,\theta}\left(2\left(\boldsymbol{r}^{A}_{i,j,\theta} - \boldsymbol{r}^{B}_{i,j,\theta}\right)^2 + \left(\boldsymbol{r}^{A}_{i,j,\theta} - \boldsymbol{r}^{B}_{i-1,j,\theta}\right)^2 + \left(\boldsymbol{r}^{A}_{i,j,\theta} - \boldsymbol{r}^{B}_{i-1,j+1,\theta}\right)^2 + \left(\boldsymbol{r}^{A}_{i+1,j,\theta} - \boldsymbol{r}^{B}_{i,j,\theta}\right)^2 + \left(\boldsymbol{r}^{A}_{i+1,j-1,\theta} - \boldsymbol{r}^{B}_{i,j,\theta}\right)^2\right) + \quad (1)$$

$$+\frac{k_2}{4}\sum_{i,j,\theta}\left(\boldsymbol{r}^{A}_{i,j,\theta} - \boldsymbol{r}^{A}_{-i,-j,-\theta}\right)^2 + \frac{k_3}{2}\sum_{i,j,\theta}\left(\boldsymbol{r}^{B}_{i,j,\theta} - \boldsymbol{r}^{C}_{i,j,\theta}\right)^2.$$

Here m_1, m_2 are the masses of carbon and hydrogen atoms, respectively, k_1, k_2, k_3 are coupling constant (see Table 1), $r_{i,j,\theta}$ are the radius vectors of atoms, $p_{i,j,\theta}$ are the atoms moments.

Table 1

Atomic geometry of the diamane

	C_A–C_B	C_A–C_A	C_B–H
a, Å	1.53	1.52	1.1
k, *N/m*	408	405	453

Obtaining the dispersion equation

Using the Hamiltonian system, we write down the equations of atoms motion. We find the first derivative with respect to the coordinate of each of the elementary cell and substitute it into the expression $m_1\ddot{\boldsymbol{r}}_{i,j} = -\dfrac{\partial H}{\partial \boldsymbol{r}_{i,j}}$. Let us introduce a small displacement from the equilibrium position: $\boldsymbol{r}_{i,j,\theta} \to \boldsymbol{r}_{i,j,\theta} + \tilde{\boldsymbol{r}}_{i,j,\theta}$.

As a result we get:

$$\begin{cases} m_1\ddot{\tilde{\boldsymbol{r}}}^{A}_{i,j,\theta} = -k_1\left(3\tilde{\boldsymbol{r}}^{A}_{i,j,\theta} - \tilde{\boldsymbol{r}}^{B}_{i,j,\theta} - \tilde{\boldsymbol{r}}^{B}_{i-1,j,\theta} - \tilde{\boldsymbol{r}}^{B}_{i-1,j+1,\theta}\right) - k_2\left(\tilde{\boldsymbol{r}}^{A}_{i,j,\theta} - \tilde{\boldsymbol{r}}^{A}_{-i,-j,-\theta}\right), \\ m_1\ddot{\tilde{\boldsymbol{r}}}^{B}_{i,j,\theta} = -k_1\left(3\tilde{\boldsymbol{r}}^{B}_{i,j,\theta} - \tilde{\boldsymbol{r}}^{A}_{i,j,\theta} - \tilde{\boldsymbol{r}}^{A}_{i+1,j,\theta} - \tilde{\boldsymbol{r}}^{B}_{i+1,j-1,\theta}\right) - k_3\left(\tilde{\boldsymbol{r}}^{B}_{i,j,\theta} - \tilde{\boldsymbol{r}}^{C}_{i,j,\theta}\right), \\ m_2\ddot{\tilde{\boldsymbol{r}}}^{C}_{i,j,\theta} = -k_3\left(\tilde{\boldsymbol{r}}^{C}_{i,j,\theta} - \tilde{\boldsymbol{r}}^{B}_{i,j,\theta}\right). \end{cases} \quad (2)$$

Substituting the radius vectors with the functions describing the harmonic waves propagating along the graphane sheet we obtained:

$$\begin{cases} \tilde{\boldsymbol{r}}^{A}_{i,j,\theta} = \boldsymbol{A}\exp\{-i\omega t + i\boldsymbol{k}\boldsymbol{r}^{A}_{i,j,\theta}\}, \\ \tilde{\boldsymbol{r}}^{B}_{i,j,\theta} = \boldsymbol{B}\exp\{-i\omega t + i\boldsymbol{k}\boldsymbol{r}^{B}_{i,j,\theta}\}, \\ \tilde{\boldsymbol{r}}^{C}_{i,j,\theta} = \boldsymbol{C}\exp\{-i\omega t + i\boldsymbol{k}\boldsymbol{r}^{C}_{i,j,\theta}\}, \end{cases} \quad (3)$$

where k is the wave vector, ω is the cyclic frequency of the propagating wave; A, B, C are the vibration amplitudes of the corresponding atoms. We obtain a homogeneous system of linear algebraic equations with respect to the oscillation amplitudes.

We introduce the following notation:

$$\omega_1^2 = \frac{k_1}{m_1},\ \omega_2^2 = \frac{k_2}{m_1},\ \omega_3^2 = \frac{k_3}{m_1},\ \omega_4^2 = \frac{k_3}{m_2},$$

$$\mu = 1 + 8\cos\left(\frac{\boldsymbol{k}\left(\Delta_1 - \Delta_2\right)}{2}\right)\cos\left(\frac{\boldsymbol{k}\Delta_1}{2}\right)\cos\left(\frac{\boldsymbol{k}\Delta_2}{2}\right).$$

This system will have non-trivial solutions if the determinant of the main matrix see (4) of the system is equal to zero. Thus, we obtain a dispersion equation for the phonon spectrum of diamane. This equation is a third-degree equation with respect to the square of the frequency:

$$\begin{vmatrix} \omega^2 - 3\omega_1^2 - \omega_2^2\left(1 - e^{-i\theta\boldsymbol{k}\boldsymbol{d}_1}\right) & \omega_1^2\left(e^{i\theta\boldsymbol{k}\boldsymbol{c}} + e^{i\theta\boldsymbol{k}(\boldsymbol{c}-\Delta_1)} + e^{i\theta\boldsymbol{k}(\boldsymbol{c}-\Delta_1+\Delta_2)}\right) & 0 \\ \omega_1^2\left(e^{i\theta\boldsymbol{k}\boldsymbol{c}} + e^{i\theta\boldsymbol{k}(\boldsymbol{c}-\Delta_1)} + e^{i\theta\boldsymbol{k}(\boldsymbol{c}-\Delta_1+\Delta_2)}\right) & \omega^2 - 3\omega_1^2 - \omega_3^2 & \omega_3^2 e^{i\theta\boldsymbol{k}\boldsymbol{d}_2} \\ 0 & \omega_4^2 e^{-i\theta\boldsymbol{k}\boldsymbol{d}_2} & \omega^2 - \omega_4^2 \end{vmatrix} = 0. \quad (4)$$

Using the technique described in [12], the dispersion equation for the phonon spectrum of the diamane was obtained. It has two independent equations:

$$\begin{gathered} \omega^6 - \omega^4\left(6\omega_1^2 + \left(\omega_2^2 \pm \omega_2^2\right) + \omega_3^2 + \omega_4^2\right) + \\ + \omega^2\left(3\omega_1^2\left(3\omega_1^2 + \omega_3^2 + 2\omega_4^2\right) - \left(\pm\omega_2^2 - \omega_2^2\right)\left(3\omega_1^2 + \omega_3^2 + \omega_4^2\right) - \omega_1^4\mu\right) + \\ \pm 3\omega_1^2\omega_2^2\omega_4^2 + 3\omega_1^2\omega_3^2\omega_4^2 + \omega_2^2\omega_3^2\omega_4^2\left(1 \pm 2\right) + \omega_1^4\omega_4^2\mu = 0. \end{gathered} \quad (5)$$

In a simpler form, these equations are:

$$\alpha_1\left(\omega^2\right)^3 + \alpha_2\left(\omega^2\right)^2 + \alpha_3\omega^2 + \alpha_4 = 0. \quad (6)$$

where the coefficients α_i, $i = 1 \div 4$ are different form depending on the choice of sign in the original equation, ω_1, ω_2, ω_3, ω_4 are parameters defined as the ratio of the bond stiffness between atoms to the mass of one of the atoms (see (5)).

The solution for such equations can be obtained analytically. For the solution, it is necessary to take into account the size of the film, and therefore, boundary conditions will be imposed on the wave number. As a result, the Hamiltonian system was compiled and the equations of motion of the diamane atoms were written.

Conclusion

Thus, we obtain a set of two equations of the third degree with respect to the frequency square. The equations are simple due to the choice of a unit cell of three atoms of one layer and the introduction of a coordinate system that takes into account the odd symmetry of the layers (Fig. 3).

As a result of solving the dispersion equation, a diamane phonon spectrum consisting of acoustic and optical modes will be obtained. By the inclination angle of the acoustic mode, it is possible to calculate the sound speed in this medium. The maximum energy of the optical modes will make it possible to estimate the Debye diamane temperature.

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