SUBSTITUTIONAL STRUCTURES STABLE AGAINST THE FORMATION OF ANTIPHASE BOUNDARIES IN GRAPHENE DOPED WITH METAL. KINETICS OF LONG-RANGE ORDER

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Introduction

The crystal lattice of graphene (Fig. 1) is a two-dimensional 'honeycomb' structure of C atoms (so-called 'two-dimensional carbon') located at the vertexes of regular hexagons [1, 2]. Graphene doping with metal (*Me*) atoms may improve some of its physical properties for a wider range of applications. Such a doping changes particularly the electrical conductivity as well as the band structure strongly dependent on atomic order. Study of such effects becomes topical since graphene is not only the hardest material but also the best conductor [3].

Model

Let us consider all possible stably-ordered substitutional structures of *Me* atoms doped in graphene lattice (in ordered C–*Me* solution) with superstructural stoichiometries: C_3Me, C_7Me, C*Me*. Probability-distribution functions for these (super)structures are determined by the method of static concentration waves [4, 5].

Interatomic interactions in C–*Me* lattice can be taken into consideration by means of the 'mixing' energies (or the 'interchange' energies) [4, 5]:

$$w_{pq}(\mathbf{R}-\mathbf{R}') \equiv W_{pq}^{CC}(\mathbf{R}-\mathbf{R}') + W_{pq}^{MeMe}(\mathbf{R}-\mathbf{R}') - -2W_{pq}^{CMe}(\mathbf{R}-\mathbf{R}'). \quad (1)$$

Here, p and q number the of sublattices, where corresponding atoms can be distributed; $W_{pq}^{CC}(\mathbf{R}-\mathbf{R}')$, $W_{pq}^{MeMe}(\mathbf{R}-\mathbf{R}')$, $W_{pq}^{CMe}(\mathbf{R}-\mathbf{R}')$ are the pair-wise interaction energies of C–C, *Me*–*Me*, C–*Me* pairs of atoms, respectively, located at the sites of p-th and q-th (p, q = 1, 2) sublattices within the unit cells with 'origins' ('zero' sites) at sites $\mathbf{R}$ and $\mathbf{R}'$.

For a statistical-thermodynamic description of the arbitrary-range interatomic-interactions (i.e. in all co-ordination shells), it is conveniently to apply the Fourier transformations for the elements of the 'mixing'-energies' matrixes [4, 5],

$$\left\| \tilde{w}_{pq}(\mathbf{k}) \right\| \equiv \begin{pmatrix} \tilde{w}_{11}(\mathbf{k}) & \tilde{w}_{12}(\mathbf{k}) \\ \tilde{w}_{12}^{*}(\mathbf{k}) & \tilde{w}_{11}(\mathbf{k}) \end{pmatrix}, \quad (2)$$

$$\tilde{w}_{pq}(\mathbf{k}) \equiv \sum\nolimits_{\mathbf{R}} w_{pq}(\mathbf{R}-\mathbf{R}') \exp(-i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')).$$

Here, $\mathbf{k}$ is a wave vector in a two-dimensional reciprocal space (Fig. 2), which 'generates' corresponding (super)structure; $\tilde{w}_{12}^{*}(\mathbf{k})$ is a complex conjugate to $\tilde{w}_{12}(\mathbf{k})$. Writing Hermitian matrix (2), the symmetry relations, $\tilde{w}_{11}(\mathbf{k}) = \tilde{w}_{22}(\mathbf{k})$ and $\tilde{w}_{21}(\mathbf{k}) = \tilde{w}_{12}^{*}(\mathbf{k})$, are also taken into account.

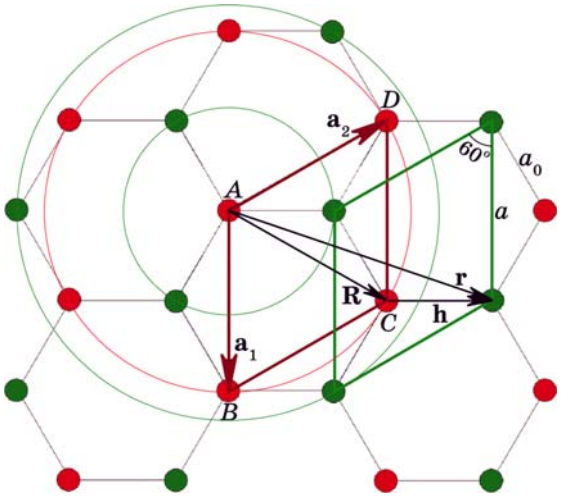

Fig. 1. The lattice of graphene. *ABCD*—primitive unit cell, $\mathbf{a}_1$ and $\mathbf{a}_2$—basis translation vectors of the lattice, a—its translation parameter, a_0—distance between the nearest neighbour sites. Circles denote the first three co-ordination shells with respect to the origin (at the site *A*) of the oblique co-ordinates.

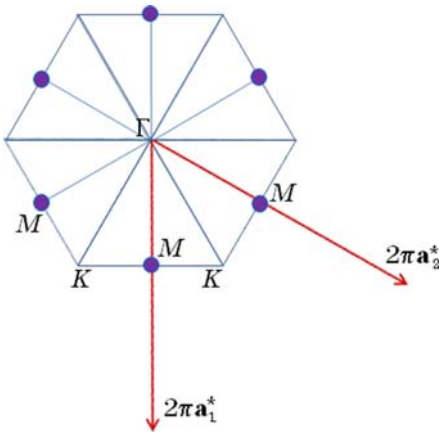

Fig. 2. The first Brillouin zone of the reciprocal space of graphene lattice (Γ, *M*, *K*—its high-symmetry points); $\mathbf{a}_1^*$, $\mathbf{a}_2^*$—fundamental translation vectors of the reciprocal lattice.

The ‘mixing’ energies and corresponding eigenvalues of the matrix (2),

$$\lambda_1(\mathbf{k}) = \tilde{w}_{11}(\mathbf{k}) + \left|\tilde{w}_{12}(\mathbf{k})\right|, \quad \lambda_2(\mathbf{k}) = \tilde{w}_{11}(\mathbf{k}) - \left|\tilde{w}_{12}(\mathbf{k})\right|,$$

entering into expressions for the configurational free energy obtained within the self-consistent field approximation [4, 5] define the statistical thermodynamics of graphene-based structures.

Results

Expressing eigenvalues of the matrix (2) in terms of the ‘mixing’ energies w_1, w_2, w_3, etc. inside the 1-st, 2-nd, 3-rd, etc., co-ordination shells, respectively, one can reveal unpredictability of some ordered structures (of C_2Me and C_5Me type) ‘generated’ by the star of wave vector corresponding to K point (see Fig. 2) at nonzero temperatures (at least, with short-range interatomic interactions).

The regions for allowable energy parameters, w_2/w_1 and w_3/w_1, providing stability (against the antiphase shifts) of the corresponding ordered states are presented in Fig. 3. For instant, the M region (in Fig. 3) ‘indicates’ the tendency of a C–Me system to form a state of order concerned with the M-point wave-vector star (see also Fig. 2).

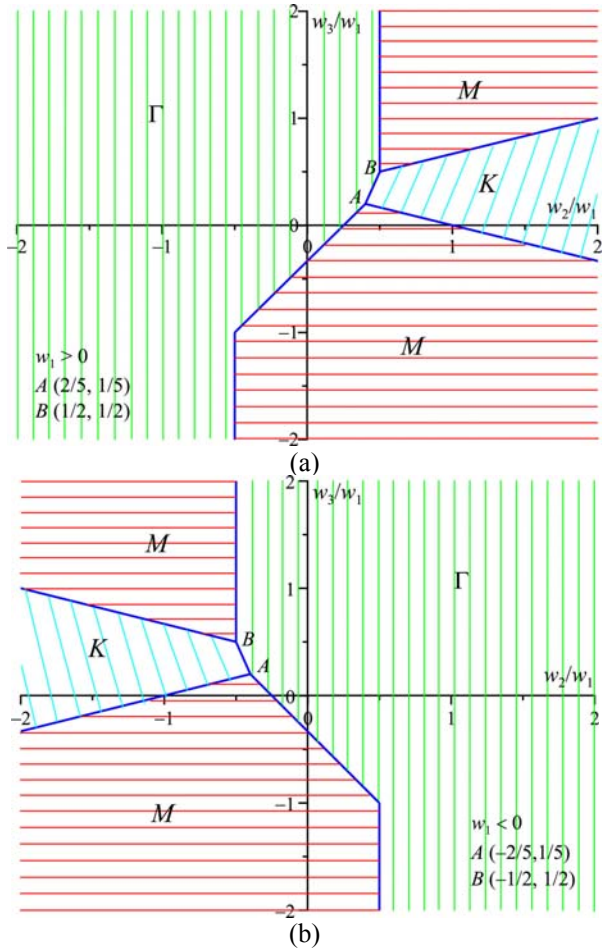

Fig. 3. Energy regions of the stability of ordered graphene-based binary solution states; (a) $w_1 > 0$, (b) $w_1 < 0$.

Atomic-ordering kinetics can be described by the microdiffusion Onsager-type differential equations [4, 5]. Curves in Fig. 4 describe the time dependence of the long-range order parameters $\{\eta_\sigma^{\aleph}\}$ for the structures with CMe, C_7Me, C_3Me stoichiometries at the fixed reduced temperature and ratios between the energy parameters, $\lambda_2(\mathbf{0})$, $\lambda_1(\mathbf{k}^M)$, $\lambda_2(\mathbf{k}^M)$, and, particularly, between w_2/w_1 and w_3/w_1. Inasmuch as the intrasublattice and intersublattice ‘mixing’ energies are competitively different, the kinetics curves for long-range order parameters of the structures described by two or three parameters can be significantly nonmonotonic (Fig. 4b).

References

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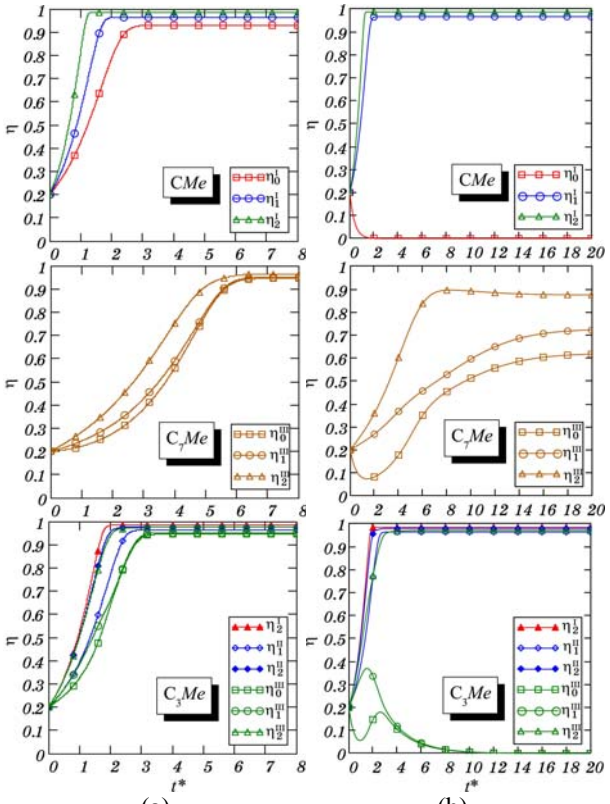

Fig. 4. The reduced-time (t^*) dependence of the long-range order parameters for CMe, C_7Me, C_3Me structures. The reduced temperature $T^* = k_BT/|\lambda_2(\mathbf{k}^M)| = 0.1$ ($\lambda_2(\mathbf{k}^M) < 0$); $\lambda_2(\mathbf{0})/\lambda_2(\mathbf{k}^M) = 5/7$, $\lambda_1(\mathbf{k}^M)/\lambda_2(\mathbf{k}^M) = 5/6$ (that corresponds to $w_2/w_1 = 0.5$, $w_3/w_1 = 0.3$) (a); $\lambda_2(\mathbf{0})/\lambda_2(\mathbf{k}^M) = -5/8$, $\lambda_1(\mathbf{k}^M)/\lambda_2(\mathbf{k}^M) = 5/6$ ($w_2/w_1 = 0.9$, $w_3/w_1 = 0.4$) (b).