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Study of the New Two-Dimensional Compound CoC

K. V. Larionov[a, b], Z. I. Popov[a], M. A. Vysotin[c, d], D. G. Kvashnin[a, e], and P. B. Sorokin[a, b, e], *

[a] *National University of Science and Technology MISiS, Moscow, 119049 Russia*

[b] *Technological Institute for Superhard and Novel Carbon Materials, Troitsk, Moscow, 108840 Russia*

[c] *Kirensky Institute of Physics, Federal Research Center KSC, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*

[d] *Siberian Federal University, Krasnoyarsk, 660041 Russia*

[e] *Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, 119334 Russia*

*e-mail: pbsorokin@misis.ru

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A novel quasi-two-dimensional monolayer structure with orthorhombic symmetry based on cobalt carbide, *o*-CoC, has been considered. This structure supplements a recently discovered family of quasi-two-dimensional compounds based on transition metals. The dynamic stability of a monolayer has been demonstrated. Its mechanical and electronic characteristics have been studied.

INTRODUCTION

Rapid development of the field of two-dimensional materials after the discovery of graphene [1] has already resulted in the synthesis of more than a hundred different atomically thin films [2]. Only some of them, e.g., graphene and *h*-BN, are uncorrugated atomically thin monolayers. However, monolayer structures were supplemented in several recent works with a novel family of binary compounds of transition metals with oxygen or carbon. The first indication of the novel family of two-dimensional structures was obtained in [3], where the observation of two-dimensional iron in a graphene pore was reported. That study was almost immediately criticized in a number of theoretical works, where it was assumed that not pure two-dimensional iron was obtained in that experiment (which seems unusual because of the nondirectional character of a metallic bond), but its compound with carbon [4, 5] or oxygen [6]. Subsequent reports on obtaining two-dimensional copper oxide [7, 8] supported this hypothesis. Both described compounds have an atomically thin flat structure and an extraordinary (for two-dimensional films) tetragonal symmetry of the lattice. It can be suggested that the novel family of monolayer films is not limited to two representatives, which requires a systematic search for novel binary compounds based on transition metals.

In this work, we study the possibility of forming a two-dimensional atomically thin cobalt carbide film. We consider different configurations of atomic geometry and find that the ground state of the two-dimensional layer has the orthorhombic symmetry with the structure significantly different from previously considered films. Both hexagonal and tetragonal structures of CoC are unstable. It is shown that atoms in the predicted stable structure tend to remain in a single plane. We study the mechanical and electronic properties of the novel nanostructure and show that the longitudinal stiffness of the proposed two-dimensional film is slightly smaller than that of graphene and the film itself has metallic properties, which is fairly rare for two-dimensional nanostructures.

METHOD OF STUDY

The atomic structure and electronic and mechanical properties of two-dimensional CoC were calculated using the density functional theory method [9] with augmented plane waves under periodic boundary conditions in the generalized gradient approximation in the Perdew−Burke−Ernzerhof parameterization [10] implemented in the VASP code [11−13]. The cut-off energy of plane waves was taken to be 500 eV. To ensure a sufficient accuracy for the optimization of the electronic structure, we took a set of $16 \times 16 \times 1$ *k*-points in the first Brillouin zone according to the Monkhorst−Pack scheme [14]. The geometry was optimized until the forces acting on each atom became less than 10^{-3} eV/Å. To exclude the interaction of neighboring periodic cells, the length of the translation vector normal to the structure plane was chosen to be 15 Å.

The behavior of the cobalt carbide monolayer was considered in a $2 \times 2 \times 1$ supercell. The classical molecular dynamics simulation at high temperatures
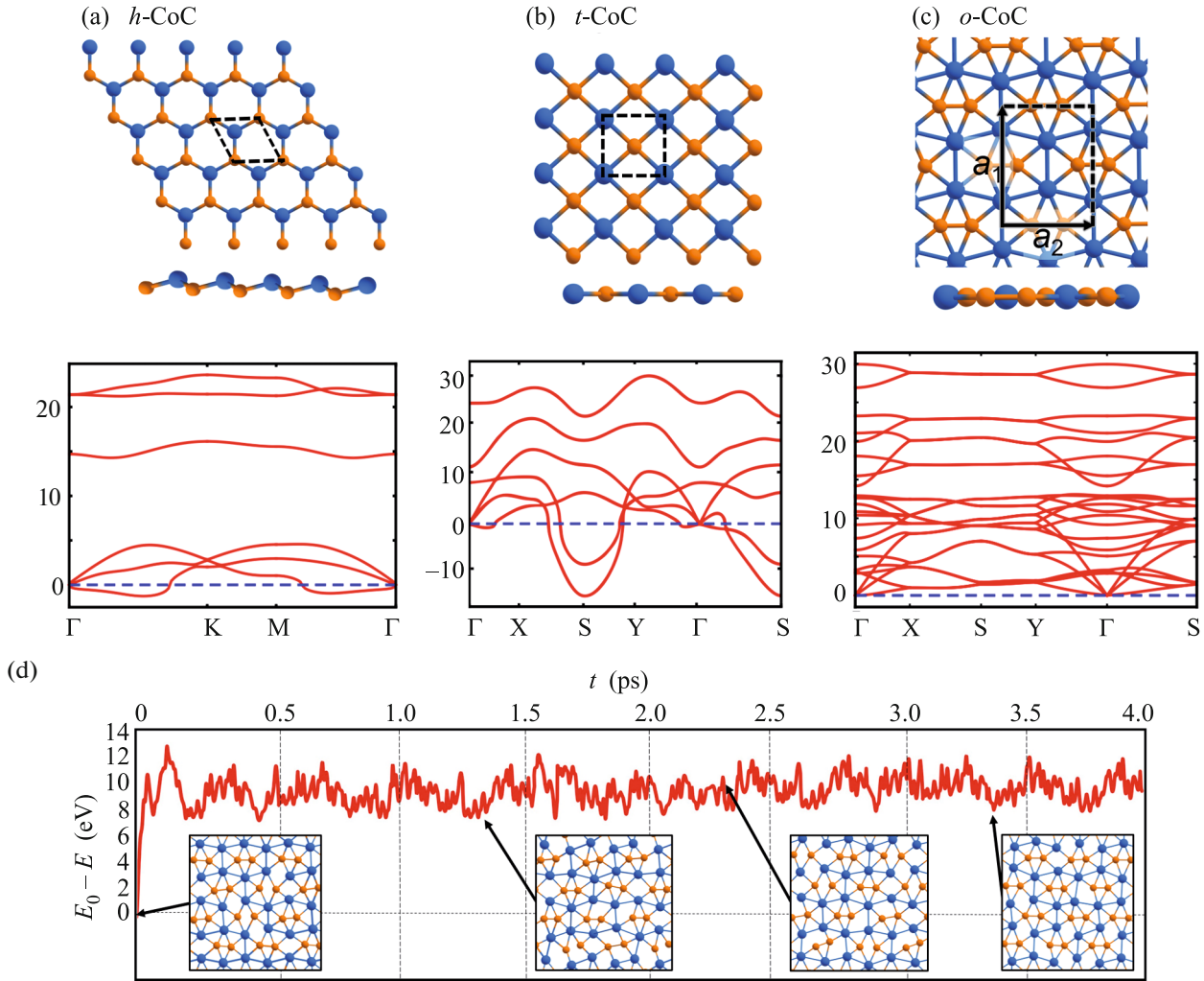
Fig. 1. (Color online) Atomic structures and corresponding phonon spectra for the considered configurations of two-dimensional CoC: (a) *h*-CoC, (b) *t*-CoC, (c) *o*-CoC. Dashed lines show unit cells. The crystal lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are shown for *o*-CoC in panel (c). Cobalt and carbon atoms are shown in blue and orange, respectively. (d) Fluctuation of the potential energy ($2 \times 2 \times 1$ supercell) in the molecular dynamics calculation for 2000 K. The insets show the atomic structure of the periodic CoC supercell for the indicated time steps.

(2000 K) was performed using the Nosé−Hoover thermostat [15, 16]. The total time of simulation was 4 ps with a time step of 0.1 fs.

RESULTS AND DISCUSSION

At the first stage, we optimized unit cells and calculated phonon spectra of different atomic geometries of two-dimensional CoC in order to reveal dynamically stable nanostructures. First, we studied the hexagonal and tetragonal lattices corresponding to the previously considered two-dimensional structures of boron nitride and copper oxide [7]. It was found that the most obvious planar graphene-like structure with hexagonal symmetry (*h*-CoC) is not energetically favorable: carbon atoms in the unit cell tend to leave

the plane and to form a corrugated layer like silicene (Fig. 1a). The phonon dispersion relation in such a two-dimensional crystal has a pronounced negative branch of the bending mode, which indicates the tendency of the film to curl from the plane. The tetragonal lattice (*t*-CoC) is also unstable, which is confirmed by negative frequencies of both the bending mode near the center of the Brillouin zone and the longitudinal modes near the edge of the Brillouin zone in the X−S−Y and Γ−S directions (Fig. 1b).

At the same time, it was found that the triangular lattice of cobalt and carbon atoms having orthorhombic symmetry (*o*-CoC) is dynamically stable (see Fig. 1c). This structure is monolayer and all atoms in it lie in one plane. The stability of such a structure was also very recently shown for iron monocarbide [5].
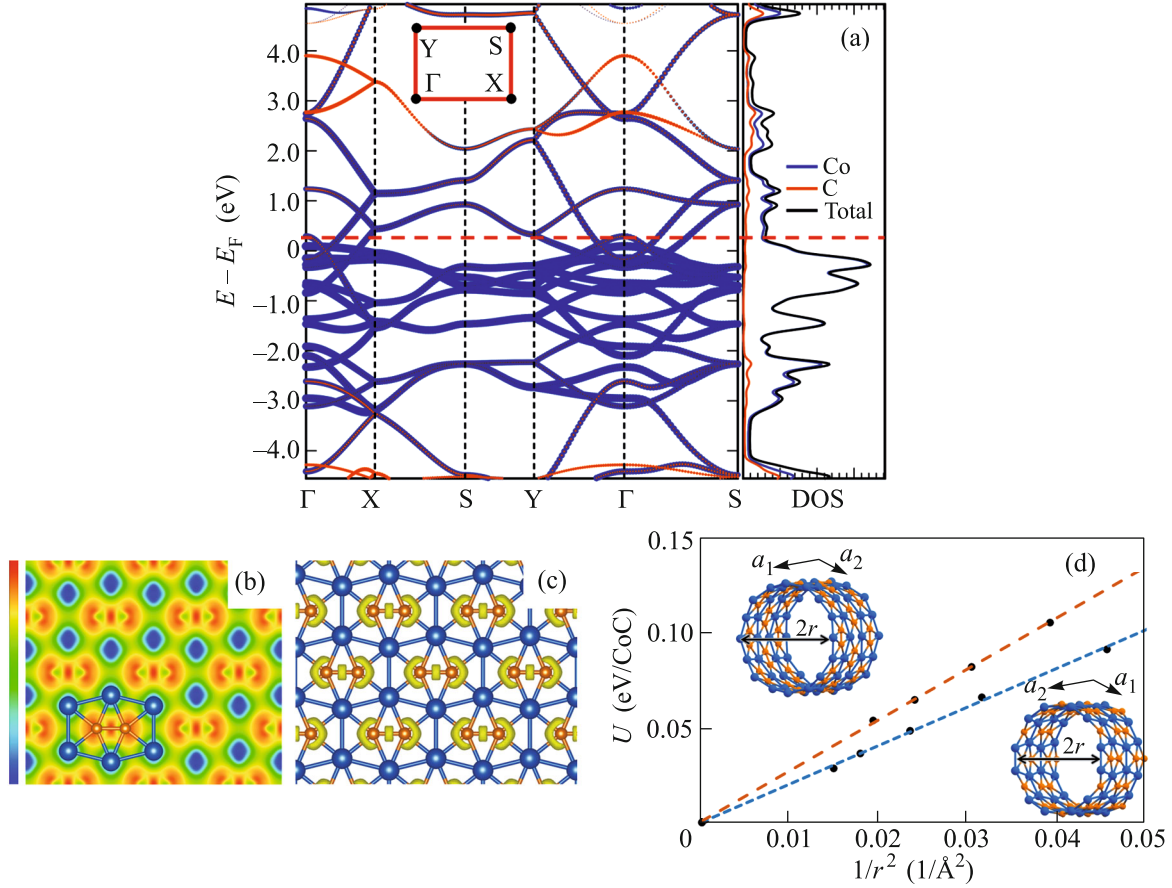
Fig. 2. (Color online) (a) Band structure and density of electronic states of *o*-CoC with contributions from carbon and cobalt. The energy is measured from the Fermi level marked by the horizontal dashed straight line. (b) Electron density difference in the *o*-CoC compound and superpositions of atomic electron densities. The vertical color scale corresponds to the incoming and outgoing charges. The maximum incoming (0.052 $e/\text{Å}^3$) and outgoing (0.076 $e/\text{Å}^3$) charges are shown in red and blue, respectively. The absence of change in the charge is shown in green. (c) Distribution of the electron localization function in *o*-CoC with a value of 0.75. (d) Elastic energy of *o*-CoC versus the radius of curvature of the layer. The lower and upper insets show the structure of the layers bent in the directions of the crystal lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, respectively.

To additionally confirm the stability of the predicted structure, we performed an ab initio molecular dynamics simulation at finite temperature. As is seen in Fig. 1d, the structure of the monolayer remains undistorted even at a temperature of 2000 K and the maximum amplitude of vibrations of atoms of the monolayer is less than 10% of the parameters of the cell under consideration. The insets of Fig. 1d show a change in the atomic structure of the cobalt carbide at the chosen simulation steps.

In the atomic structure of the proposed material, a carbon atom dimer is surrounded by six metal atoms, each carbon atom has five nearest neighbors, and each cobalt atom is surrounded by three metal atoms and four carbon atoms (Fig. 1c). The parameters of the unit cell of the structure are $a_1 = 5.872$ Å and $a_2 = 4.492$ Å. The main contribution to the band structure at the Fermi level comes from the *d* states of cobalt atoms and the main contribution from carbon atoms is below the Fermi energy by 2.5 eV (see Fig. 2a). The partial contribution from *p* orbitals of carbon atoms near the Γ points indicates the formation of a bond between carbon and cobalt because of the overlapping of *p*−*d* atomic orbitals. The Bader analysis [17] showed the transfer of a charge of $0.60e$ from each metal atom to a carbon atom, which indicates covalent ionic bonds between them. In addition, the map of the redistribution of the atomic electron density in the compound (Fig. 2b) shows an increase in the electron density near carbon atoms and in the middle of the C−C bond against the background of the general charge transfer. The analysis of the electron localization function shows the presence of localized orbitals between carbon atoms and between a carbon atom and two of its four neighboring cobalt atoms, whereas the electron density in the Co sublattice is formed mainly by delocalized states (Fig. 2c).

Table 1. Elastic characteristics of o-CoC

C_{11} (N/m)	229
C_{12} (N/m)	71
C_{22} (N/m)	241
C_{66} (N/m)	68
ν_{12}	0.31
ν_{21}	0.29
D_1 (eV)	1.23
D_2 (eV)	1.63

All these indicate that each carbon atom forms a covalent bond with a neighboring C atom and covalent ionic bonds with two Co neighbors, whereas a bond with the other two Co atoms has a more ionic character, which explains the unique nature of five-coordinated carbon atoms in this compound. The conducting nature of the o-CoC compound (Fig. 2a) and the distribution of the electron density difference (Fig. 2b) indicate a metallic bond between cobalt atoms, which finally confirms the existence of a combination of covalent, ionic, and metallic bonds in the structure, which was previously demonstrated in crystalline cobalt carbide Co_2C [18] and iron carbide Fe_2C [19].

To estimate the elastic properties of o-CoC, we calculated the elastic constant tensor (Table 1). The elastic constants are presented in units of newtons per meter disregarding uncertainty in the determination of the thickness of the two-dimensional layer. The elastic constants of uniaxial deformation (C_{11}, C_{22}) are slightly smaller than the corresponding value for h-BN (293 N/m [20]), are 30% smaller than that for graphene (358 N/m [21]), and are almost two times greater than that for MoS_2 (140 N/m [22]). The Poisson's ratios for o-CoC $\nu_{12} = -\dfrac{s_{21}}{s_{11}} = 0.31$ and $\nu_{21} = -\dfrac{s_{12}}{s_{22}} = 0.29$ are larger than the respective values for graphene (0.17 [21], 0.15 [23]) and h-BN (0.23 [20], 0.21 [23]), and are comparable with the Poisson's ratio for MoS_2 (0.29 [22]).

The flexural rigidities D_1 and D_2 were determined by calculating the energy of the layer uniformly bent in the corresponding directions (see Fig. 2d) from the dependence of the elastic energy of the layer U on its curvature [23]: $U = \dfrac{D}{2r^2}$, where r is the radius of curvature of the layer modeled in the form of a nanotube with the radius r. The resulting values are presented in Table 1. A similar flexural rigidity for graphene is 1.46 eV [23].

CONCLUSIONS

We have proposed a novel quasi-two-dimensional phase of the CoC compound, which supplements the family of previously studied MX monolayers (where M is a transition metal and X = O, C). The considered atomically thin films based on cobalt carbide can potentially be used as catalysts in reactions of hydrocarbon synthesis. The efficiency of this catalysis was previously shown on cobalt carbide nanoprisms [24]. The metallic conductivity allows the possible application of o-CoC as an ultrathin conducting layer. Such a structure can be assumingly synthesized in a nanoreactor between other two-dimensional films. The possibility of this process, the applicability of these films as catalysts, and their chemical stability and conducting, magnetic, and optical properties should be studied in the near future.

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