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Theoretical Investigation of the Atomic and Electronic Structure of Li_xBC_3 Intercalated Compounds

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Abstract—Li_xBC_3 intercalated compounds with various configurations are studied for their possible application as electrode materials for lithium current sources. For this purpose, the band structure and the density of states were calculated for each structure, and energy stability and possible deformations due to a change in the unit cell volume during intercalation are investigated.

A large number of studies are being carried out at present in the promising trend known as ionics of solids. One of the goals of these studies is the search for and analysis of new crystalline materials exhibiting ionic conduction like liquid electrolyte solutions. The interest in solid electrolytes is due to the possibility of their application in the form of single crystals, dense ceramics, and film coatings in electrochemical devices.

Most interesting in this respect are superionic conductors with Li^+ ionic conduction, which can be used not only as solid electrolytes, but also as electrode materials for lithium current sources, all the more so because lithium ion is the lightest and smallest among metal ions, which ensures its high conductivity and energy density.

Graphite is used as the main material conducting lithium ions. Lithium dissolved in graphite forms layered compounds in the form of ordered intercalated solutions with increased spacing between the layers of graphite's hexagonal cell [1]. In the course of intercalation of lithium into graphite, the limiting resultant compound is LiC_6 with the maximal intercalation capacity (mass fraction of lithium is 0.0886%) [2–6]. In this structure, lithium atoms are located at the centers of hexagons; however, some (two or three) of these centers remain unfilled. Upon further intercalation of lithium, a mechanical mixture is formed, which consists of pure graphite and L_2C_2 compound with a primitive orthogonal lattice [7]. This limits the capacity of graphite materials.

Attempts are also being made at obtaining conducting silicon-based materials with a high intercalation capacity. Silicon can form $Li_{4.4}Si$ intercalation compound with lithium, for which specific capacity is considerably higher than in graphite. However, the intercalation of lithium into silicon is accompanied by a strong change in the specific volume as well as by phase transitions. The change in the specific volume gives rise to mechanical stresses and, as a consequence, to complete failure of the material [8–11].

Since not all of the interlayer space of graphite in LiC_6 is used to the maximal extent for lithium sorption, we can propose an analog of it in which lithium atoms are located in each hexagon. One of such analogs is BC_3, which can theoretically form intercalation compounds with lithium (Li_xBC_3). Thus, our goal is to analyze the atomic and electronic structure of Li_xBC_3 intercalated compounds.

The BC_3 compound was obtained as a result of chemical interaction of benzene and BCl_3 at 800°C [12]. An electron micrograph shows that BC_3 is a homogeneous product consisting of individual planes. Using electron diffraction, the graphite-like symmetry was confirmed and it was also established that the distance between hexagonal layers is 3–4 Å. In spite of this result, the specific arrangement of the layers in the structure relative to one another remains unclear and has been the subject of a number of investigations. For example, various versions of polytypes were considered in [13, 14], and the most stable of them were identified. The electronic and structural properties of some of them have been studied comprehensively [15, 16], but the exact arrangement of layers in the BC_3 crystals has not been determined. The difference in energy between different structures is no more than 0.02 eV per unit cell. The authors of [15, 16] proposed that a structure of mixed type is actually formed; for this reason, we analyze here only three polytypes.

Our analysis was based on quantum-chemical simulation with the help of the VASP (Vienna ab-initio simulation package) [17–19] employing the formal-

ism of density functional theory (DFT) [20, 21] in the basis of plane waves and using Vanderbilt ultrasoft pseudopotentials [22]. Computations were performed in the generalized gradient approximation (GGA), i.e., the PW91 exchange−correlation functional.

The binding energy of lithium atoms in the structures under investigation can be described by the formula

$$E = (E_{Li_xBC_3} - E_{BC_3} - xE_{Li})/x, \qquad (1)$$

where $E_{Li_xBC_3}$ is the total energy of the intercalated compound, E_{BC_3} is the total energy of the most energy-advantageous BC_3 polytype, E_{Li} is the energy of the lithium atom in the crystalline structure, and x is the number of Li atoms in the system.

At the initial stage, the optimal geometry of hexagonal unit cells of graphite (of the ABAB type) and BC_3 (Fig. 1a) was calculated; these cells were subsequently used for studying the stability of intercalated compounds formed as a result of intercalation of lithium. In this case, calculations were made for three polytypes of the BC_3 compound. In one structure, the planes of hexagonal BC_3 were arranged over one another. In the other two structures, one of the layers was shifted relative to the second layer along the AC direction by 1.58 Å (Fig. 1b) and 2.83 Å (Fig. 1c), respectively.

The reciprocal space in the first Brillouin zone was automatically covered by a mesh in accordance with the Monkhorst−Pack scheme [23]; the number of k points in each direction was $6 \times 6 \times 2$. The cutoff energy for plane waves in our computations was 257 eV.

After computing the optimal geometry, we analyzed the electronic structure of BC_3. According to our results, this compound is a conductor, which coincides with the experimental data [12].

Then, we analyzed intercalation of lithium into BC_3. For this purpose, we modeled the structures of the Li_xBC_3 compound with different lithium concentrations beginning from complete filling, in which lithium atoms are present in all hexagons (about 22.95% Li). For each concentration, we analyzed several configurations differing in the distance between lithium atoms in different layers and in the same layer. In all cases, the configuration with the maximal dis-
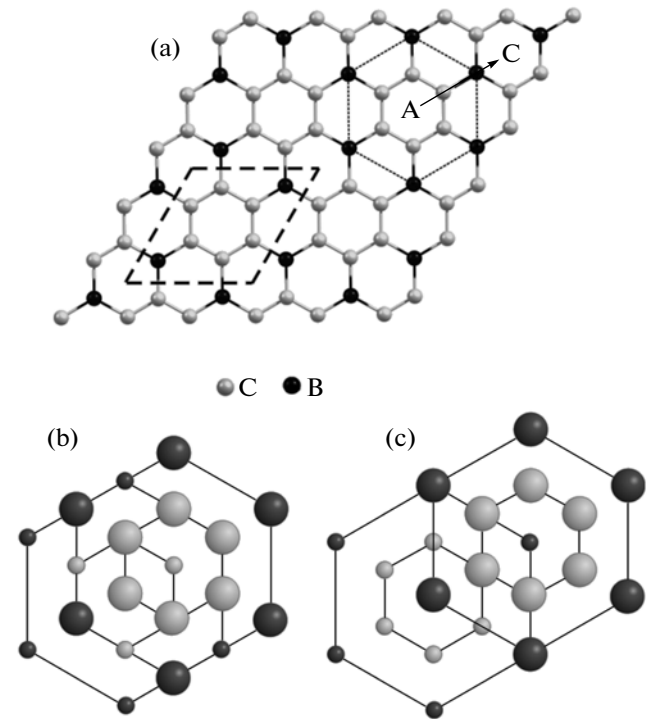

Fig. 1. (a) Unit cell of BC_3 (marked by dashed lines); structure with a shift of layers in the AC direction by (b) 1.58 Å and (c) by 2.83 Å (larger atoms correspond to the first layer and smaller atoms, to the second layer).

tance between lithium atoms was found to be most advantageous. For each structure, we considered three modes of layer stacking. In the first case, the layers were above one another. In the second case, one of the layers was shifted relative to the second layer along the AC axis by 1.58 Å (see Fig. 1b). In the third case, one of the layers was displaced in the same direction AC, but now by 2.83 Å (Fig. 1c). The results of calculating the binding energy for lithium are given in Table 1.

In optimizing the geometry of the structure with complete filling, it was found that in contrast to BC_3 itself, the configuration without a shift of the layers is most advantageous (see Table 1). Consequently, in the course of intercalation, a transition from a structure

Table 1. Values of binding energy depending in the concentration and layer stacking type

Shift	Binding energy, eV		
	Li_2BC_3 (about 22.95% Li)	LiB_4C_{12} (about 3.59% Li)	LiB_8C_{24} (about 1.83% Li)
Along AC by 1.58 Å	−	−1.51	−1.86
Along AC by 2.83 Å	−	−1.61	−1.75
No shift	−0.77	−1.86	−1.38
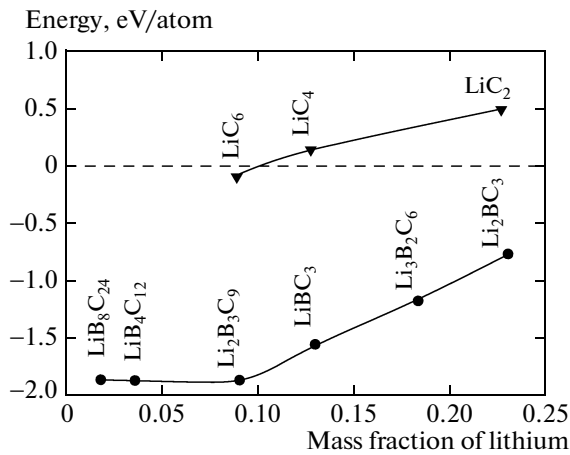
Fig. 2. Binding energy vs. the mass fraction of lithium in intercalated compounds of graphite and BC_3.

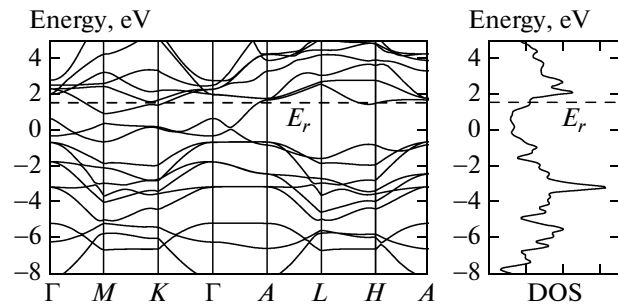**Fig. 3.** Band structure and densities of states of the Li_2BC_3 compound (about 22.95% Li).

with shifted layers to a structure without a shift must take place.

In the LiB_4C_{12} structure (about 3.59%), the stacking of the layers remains the same as in the structure with complete filling. For a lithium concentration on the order of 1.83%, the structure with a stacking similar to that in BC_3 (i.e., with a shift in the AC direction by 2.83 Å) was found to be advantageous. This means that in the concentration range 3.59–1.83%, a transition from the structure with shifted layers to the structure without a level shift takes place.

At the next stage, we estimated the energy stability of BC_3-based intercalated compounds with different lithium concentrations and compared these compounds with graphite analogs. Figure 2 shows the dependence of the binding energy of lithium on its mass fraction. It can be seen from the diagram that graphite-based structures with a lithium concentration exceeding that in LiC_6 are not advantageous from the energy point of view, which is in accordance with the available experimental data. In the case of BC_3, the energy stability of intercalated compounds decreases

Table 2. Strain in the unit cell (relative to the BC_3 volume) for the Li_xBC_3 structures with different lithium concentrations

C_{Li}, %	Strain in the unit cell, %
0	0
1.83	2.60
3.59	2.46
9.03	0.62
12.96	2.57
18.26	0.27
22.95	5.79

upon an increase in the lithium concentration. However, even for high concentrations, Li_xBC_3 compounds remain more advantageous in energy as compared to metallic lithium and graphite-like BC_3 existing separately.

In the search for the state corresponding to the energy minimum, optimization of the unit cell volume was performed, which enabled us to estimate the possibility of structure deformation in the course of intercalation (Table 2).

In accordance with the values of the unit cell volume given in Table 2, no appreciable deformation of the structure occurs during intercalation.

After optimization, we analyzed the electronic properties of the Li_xBC_3 compound and constructed the densities of states and the band diagrams for each system. In calculating the band structure, there were ten intermediate points in the directions under investigation. Figure 3 shows the band structure and the density of states for the compound with the maximal filling with lithium atoms (Li_2BC_3). It can be seen that this compound exhibits conductor properties, which follows from overlapping of the energy bands at the Fermi level. Analogous results were obtained for compounds with other lithium concentrations.

All Li_xBC_3 compounds investigated in this study are stable in energy; the strains emerging in the course of intercalation are insignificant (0.27–5.79%). Our computations revealed that during the formation of intercalates in the lithium concentration range 3.59–1.83%, a transition from the structure with shifted layers to that without a shift must take place. Irrespective of the arrangement of the layers, these compounds possess conducting properties, which makes it possible to use graphite-like BC_3 as an ionic conductor as well as the electrode material in lithium-ion cells.

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