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Combinatorial Modeling of the 1,P- Structures of Ordered and Disodered Intercalation Phases into Alkali Metals – Graphite System

Keywords: *ordered intercalation phases, disordered intercalation phases, graphite, carbon containing compounds, first stage p-layered structures*

Annotation *- The possible first stage p-layered ordered structures of the alkali-graphite intercalated phases MC_n (1 < n < 12) and structures of the alkali-graphite disordered intercalated phases M_xC (0,03 < x < 0,5) were made by combinatorial modeling method. The descriptions of all structures were reduced on tongue of the occupied lattice complexes with indication of its characteristics.*

The ordered structural state forming is maybe at a certain concentration of metal M into some s,p-structure of intercalated phases (1,2). This state is characterized by a regular filling intercalate certain crystallographic positions between layers and a periodic alternation of these M-layers (s > 1, p > 1) in the direction perpendicular to them. To solve the problem 2D-modeling used the set of possible r_i-vectors connecting the geometric centers of hexagonal prisms C_6 in the base P6/mmm structure. A specific set of three vectors (**r_i, r_j, (r_i-r_j)**), where 8 ≥ i,j ≥ 1, defines the trigon of the M-sublattice and symmetry of the possible 1,p- structure MC_n phase. The identity periods into M-sublattice of all orderly phases are maybe characterized by the modules of these vectors.

Will consider only 1,p-structure intercalated phases MC_n, where M - alkaline metal. The possible first stage p-layered ordered structures of the alkali metal -graphite intercalated phases MC_n (1 < n < 12) were made by theoretic combinatorial modeling method (3-5). The descriptions of some structures on tongue of the occupied lattice complexes with indication of its characteristics were reduced in tab. 1-2. The possibility of the ordered phases formation with compositions MC_{14} and MC_{18} (where M - Rb, Cs) in graphite electrodes were established by comparative crystal chemical analysis. The possible first stage p-layered disordered structures of the alkali-graphite intercalation phases M_xC (0,03<x<0,5) were made by combinatorial modeling method, too (3-5). Identification of the received 1,p-structures was conducted in accordance with the methodology (6,7). The descriptions of these structures with their main characteristics were made in accordance with (6) and presented in tab. 1-2.

Table 1.

Descriptions of possible 1,p-structures of the ordered intercalated phases MC_n, where n = 6-12.

Composition of intercalated phase	Number of the layers, p	Packing code of the layers	Symmetry and number of formulae unites in elementary cell	Relative metric parameters of the elementary cell
MC_2	1	αα	P6/mmm (1)	$a = a_0$, $c = c_0$
MC_6	1	(αα)	P6/mmm (1)	$a = 3^{1/2} a_0$, $c = c_0$
MC_6	2	(αβα)	$P6_3/mmc$ (4)	$a = 3^{1/2}a_0$, $c = 2c_0$
MC_6	3	(αβγα)	$R\bar{3}m$ (3)	$a = 3^{1/2} a_0$, $c = 3c_0$
MC_8	1	(αα)	P6/mmm (1)	$a = 2a_0$, $c = c_0$
MC_8	1	(αα)	Pmmm (1)	$a = 3^{1/2}a_0$, $b = 2a_0$, $c = c_0$
MC_8	2	(αγα)	Fmmm (4)	$a = 2a_0$, $b=3^{1/2}a_0$, $c = 2c_0$
MC_8	3	(αβγα)	$P6_{2(4)}22$ (3)	$a = 2a_0$, $c = 3c_0$
MC_8	4	(αβγδα)	Fddd (8)	$a = 2a_0$, $b = 2*3^{1/2}a_0$, $c = 4c_0$
MC_{10}	1	(αα)	Cmmm (2)	$a = 3^{1/2}a_0$, $b = 5a_0$, $c = c_0$
MC_{10}	4	(αβγδα)	$Pmn2_1$ (8)	$a = 3^{1/2}a_0$, $b = 5a_0$, $c = 4c_0$
MC_{12}	1	(αα)	Pmmm (1)	$a = 3^{1/2}a_0$, $b = 3a_0$, $c = c_0$
MC_{12}	1	(αα)	P2/m (1)	$a = 2a_0$, $b = c_0$, $c = 7^{1/2}a_0$, $\beta = 101^0$
MC_{12}	4	(αβγδα)	$P2_1$ (4)	$a =2a_0$, $b = 4c_0$, $c =7^{1/2}a_0$, $\beta = 101^0$
MC_{12}	4	(αβγδα)	$Pmn2_1$ (4)	$a = 3^{1/2}a_0$, $b = 3a_0$, $c = 4c_0$

Table 2.

Descriptions of 1,p-structures possible disordered intercalation phases $M_{1+x}C_n$, where n = 6-32.

Composition of intercalated phase with 1,p-structure	Packing code of the layers (at s = 1)	Symmetry and number of formulae unites in elementary cell	Occupied crystallographic positions in the structure
$M_{1+x}C_6$ (0<x<2)	αβ'γ'	P6/mmm (z=1/3)	[(1+x)/3]M:1(a), 2C:2(d)
$M_{1+x}C_8$ (0<x<0,33)	αβ'γ'δ'	P6/mmm (z=1/4)	[(1+x)/4]M:1(a), 2C:2(d)
$M_{1+x}C_{10}$ (0<x<0,25)	αβ'γ'δ'η'	P6/mmm (z=1/5)	[(1+x)/5]M:1(a), 2C:2(d)
$M_{1+x}C_{12}$ (0<x<0,2)	αβ'γ'δ'η'θ'	P6/mmm (z=1/6)	[(1+x)/6]M:1(a), 2C:2(d)
$M_{1+x}C_{14}$ (0<x<0,17)	αβ'γ'δ'η'θ'μ'	P6/mmm (z=1/7)	[(1+x)/7]M:1(a), 2C:2(d)
$M_{1+x}C_{18}$ (0<x<0,125)	αβ'γ'δ'η'θ'	P6/mmm (z=1/9)	[(1+x)/9]M:1(a), 2C:2(d)
$M_{1+x}C_{20}$ (0<x<0,1)	αβ'γ'δ'η'θ'	P6/mmm (z=1/10)	[(1+x)/10]M:1(a), 2C:2(d)
$M_{1+x}C_{24}$ (0<x<0,08)	αβ'γ'δ'η'θ'	P6/mmm (z=1/12)	[(1+x)/12]M:1(a), 2C:2(d)

$M_{1+x}C_{26}$ (0<x<0,07)	αβ'γ'δ'η'θ'	P6/mmm (z=1/13)	[(1+x)/13]M:1(a), 2C:2(d)
$M_{1+x}C_{32}$ (0<x<0,048)	αβ'γ'δ'η'θ'	P6/mmm (z=1/16)	[(1+x)/16]M:1(a), 2C:2(d)

It is necessary to note, in a totally ordered solid solutions $M_{1+x}C_n$ phase their structure can be realized in the form of homogeneous phase structure, either in the form of a "heterogeneous" structure consisting of oriented a certain way identical domains. The theoretic modeling results are maybe the basis for the interpretation of the experimental electrochemical and diffraction dates, which were made in alkali metal – graphite systems.

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