



Critical Review of symmetry and structure relationships in graphite intercalation compounds (GICs) and their practical use for lithium ion battery materials

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The stage-I binary M-GIC structure family

Table 1: Hexagonal graphite and binary GIC stage-1 structures from references with complete structural descriptions (*i.e.*: lattice parameters, space group, Wyckoff site or atomic positions). To avoid ambiguity, when referencing different structures in an abbreviated form, it is necessary to extend writing the chemical formula by the Pearson notation [3, 4] and Wyckoff sequence [5]. Only this disambiguates entries like LiC₆(hP7, ka) or LiC₆(hP7, jb) as isotypic or as uniquely different. In case of multiple structure description, only the earliest report is referenced. Incomplete structure data are omitted. Partial or flawed data are corrected if the reference contained sufficient information (see notes below table1).

Introduction:

- Graphite is known for its ability to undergo intercalation reactions since first reports by Fredenhagen et al. [1] about K-GICs
- binding situation and structural details Various binary metal GICs of stage-I are known today Alkali metals (Li, K, Rb, Cs), alkaline earth (Ca, Sr, Ba) and Lanthanides (Eu, Yb, Sm) a good summary is given in the review by Dresselhaus et al. [2] remarkable exceptions Na (no stage-I GIC) and Li (unique A α -structure) Recently increased focus on binary Li-GIC as graphite is most commonly used electrode material in lithium ion batteries reported. For battery development: importance to understand how lithium atoms move in electrodes reversibly to optimize battery performance and life time. This requires detailed knowledge of structures of the
- associated phases in the phase transformation from pure graphite to the fully lithiated stage-I LiC₆ Lithium mobility and diffusion is fundamentally influenced by the chemical

(see notes below table1)

therefore we reviewed the published M-GIC structures in a broader respect and applied chemical bond theory and symmetry rules to construct the GIC structure family Bärnighausen tree in order to allow better

GIC	Stacking sequence	ICSD-#	Space group (No.)	Wyck. pos.	Pearson not.	Lattice parameters [Å]	d(C-C) in-plane [Å]	d(layer-layer) [Å] exp. calc.		d(M-C) [Å]		Ref.
С	A□B□	76767	P 6 ₃ /m m c (194)	cb	hP4	a = 2.464(2) c = 6.711(4)	1.422- 1.423	3.355- 3.356	3.40**	-	-	[6]
KC ₈	ΑαΑβΑγΑδ	70020	F d d d (70)	h²a	oF72	a = 4.920 b = 8.510 c = 21.40	1.418- 1.420	5.350	5.217	3.027- 3.029	2.98	[7]
RbC ₈	ΑαΑβΑγΑδ	200563	F d d d (70)	h²a	oF72	a = 4.926(4) b = 8.532(6) c = 22.471(10)	1.422	5.618	5.579	3.148- 3.149	3.14	[8]
CsC ₈	ΑαΑβΑγ	74641	P 6 ₂ 2 2 (180)	ki²c*	hP27	a = 4.945(10) c = 17.76(3)	1.427- 1.428	5.919- 5.921	6.024	3.285- 3.287	3.34	[9]
CaC ₆	ΑαΑβΑγ	-	R 3 m (166)	ga	hR7	a = 4.333 c = 13.5720	1.444	4.524	4.546	2.684	2.69	[10]
SrC ₆	ΑαΑβ	-	P 6 ₃ /m m c (194)	ic	hP14	a = 4.315(10) c = 9.904(5)	1.438- 1.439	4.952	4.965	2.863	2.87	[11]
BaC ₆	ΑαΑβ	-	P 6 ₃ /m m c (194)	ic	hP14	a = 4.302(6) c = 10.50(4)	1.434	5.250	5.126	2.991	2.96	[11]
EuC ₆	ΑαΑβ	169041	P 6 ₃ /m m c (194)	ic	hP14	a = 4.30 c = 9.74	1.433	4.870	4.593	2.825- 2.826	2.71	[12]
YbC ₆	ΑαΑβ	601565	P 6 ₃ /m m c (194)	ic	hP14	a = 4.320(4) c = 9.147(4)	1.440	4.574	4.475	2.702	2.66	[13]
LiC ₆	Αα	193441	P 6/m m m (191)	ka	hP7	a = 4.3008(1) c = 3.687(2)	1.432- 1.436	3.687	3.439	2.334- 2.335	2.24	[14]
LiC ₆	Αα	-	P 6/m m m (191)	jb	hP7	a = 4.290 c = 3.737	1.430	3.737		2.353		[15]
LiC _e **	ΑαΑα	_	P 6 ₃ /m m c	ib	hP14	a = 4.305(1)	1.435	3.706		2.343-		[16]

a by published site position is 3b. How (veg 4) order to achieve the stacking order description, as well as the ICSD database entry #-74641 apparently contain a flawed description of the Wyckoff sites of the Cs atoms. If Cs is set on 3a or 3b as written in the article and in the ICSD entry, the stacking order of the intercalant would be AaAaAa, which would be a superfluous 3-fold supercell of an Aa-stacking. The described AaAAAy stacking is only achieved if the Cs atoms are placed on site 3d! This does not change any of the interatomic distances depicted in the table. It only affects the symmetry and positioning of the Cs atoms in the structure. The flaw in the published and archived data is also evidenced, by looking for overlooked symmetry on the structure as published with Cs placed in 3b. In that case an equivalent structure with a reduced unit cell can be found. The cell transformation and c-axis reduction (0 -1 0; -1 0 0; 0 0 -1/3) leads to the space group P 6/m m m (191) with a = 4.945 Å and c = 5.9200 Å, Cs 1b (0, 0, 1/2) and C on 2c (1/3, 3/3, 0) and 6l (1/3, 5/4, 0). This strikingly demonstrates the power of group-subgroup relations and shows the necessity to check symmetry considerations and consistency when doing structure refinements, analysis or when analysing published structure data.

**This P 6₃/m m c structure description of LiC₆ is a twofold-supercell of the P 6/m m m hP7[jb]-type with minimally deviating lattice parameters and doubled c-axis. It was published as an alternate model describing the same experimental data, however it can be considered as superfluous since it is not a minimal representation of the structure. This can be easily tested by looking for overlooked symmetry. It is also reflected by the stacking sequence. Both structure descriptions give an identical diffraction pattern if the exact same lattice parameters are used (that is either a = 4.290, c = 3.737 or a = 4.305, c = 3.706 in the P 6/m m m setting, respectively a = 4.290, c = 7.474 or a = 4.305, c = 7.412 in the P 6₃/m m c description). A really different structure would be the A α A β -type with MC₆ also described in the P 6₃/m m c setting but only with different Wyckoff positions (see figure 2).

*the radius of an "aromatic" bound carbon atom was taken as the average of the sum of radii of a covalently single-bonded (0.77 Å) and a double-bonded (0.67 Å) carbon atom, thus (0.77 + 0-67)/2 = 0.72 Å. **the distance between two graphene layers assuming they are only bound by van-der-Waals-forces and thus the contact distance would be 2x the according van-der-Waals-radius of 1.7 Å, thus 2x1.7 = 3.4 Å

The stage-I binary *M*-GIC structure family Bärnighausen tree

- Reliable structure information is crucial for
- this, and such is mostly obtained by diffraction experiments
- Surprisingly only scarce reports with complete structure data of GICs are published in databases and only few complete unambiguous structural reports are found in literature and no structure data of higher-stage GICs, except for Li are
- Table 1 shows accumulated and reviewed data published on binary stage-I GICs.
- The compilation of the data made us aware of many pitfalls in publishing diffraction data and diffraction experiments and structural ambiguity or misinformation can remain
- comparison of the structures
- · In total five different structure types exist for binary stage-I *M*-GICs
- These structure types are shown in figure 1.
- Two key bond features common in all GICs: I) graphene layers with aromatic C-C bonds anisotropic metallic conductivity (in-plane) II) metallic atoms bind to graphene layers and interconnect the delocalized electron perpendicular to the plane
- GICs are (more) isotropic metallic conductive than pristine graphite
- We discuss the problem of such ambiguity in certain structure models, especially in the case of the lightest element, lithium, which is most relevant for battery research.



Figure 1: The five binary *M*-GIC structure types shown in projection along the *a*-axis. The stacking arrangement, is visible and is also shown by the structure type labels below. Uppercase latin letters depict symmetry equivalent carbon-layers, lowercase greek letters show equivalent metal ion layers.

Resume

- For best structural comparison symmetry related structures, like the GICs structure family, can be described by the use of a Bärnighausen tree [17-18] (see figure 2).
- The tree shows, starting from the aristotype of the structure family, a hypothetical MC_2 -type stage-I, that phase transformations between different branches of the tree will often lead to twinning, as observed for KC₈ [20], or anti-phase domain growth phenomena. Transitions between the MC₈ and MC₆-branch are not simple and can only proceed in a 1st order transition, while the rearrangement from MC_6 -A α and MC_6 -A α A β branch can proceed via a 2nd order transition
- However, in regard to the importance of LiC_6 structures in the battery research we note that there is an unexpected inability to easily distinguish some of the structures, like $A\alpha A\beta$ from the $A\alpha$ -stacking, by powder diffraction. Figure 3 shows the comparison of calculated XRD-patterns of LiC₆(hP7, jb) = $A\alpha$ and LiC₆(hP14, ic) = $A\alpha A\beta$. For LiC₆ both are nearly indistinguishable with <u>powder diffraction</u> methods (neither with x-ray nor by neutrons!)
- The combination of symmetry relationships with the aid of family trees together with structure predictions (bond constrains) from principle chemical bond theory and modelling, e.g. with DFTB methods [19], allows systematically checking for "chemically sensible" structure models together with very careful evaluation of existing and future diffraction data







Figure 3: Simulated powder x-ray and neutron diffraction patterns for LiC_6 in two different stacking arrangements A α and A α A β . The peak with maximum intensity difference is marked with an arrow.

Outlook

- The family tree gives new insights on possible pitfalls for structure determination by diffraction and can be especially applied to improve the current view of the lithiation mechanism and the graphite to LiC_6 phase transition as it may prove very helpful in interpreting experimental data.
- use symmetry relationships for known LiGIC structure and combine with bond distance constrains from basic chemical bond theory to gain more insight about the validity of the commonly accepted transformation mechanism to avoid wrong structure models
- This is specially true for there is a fundamental difference if a transition occurs from A α to A α A \square or A α A β to A α A \square arrangement (e. g. LiC₆ => LiC₁₂), and in the following pathway to pristine graphite (AB-stacking)

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