

m19.p19

X-ray and neutron diffraction studies on cation distribution in the $\text{LiMn}_2\text{O}_4/\text{LiFe}_5\text{O}_8$ spinel solid solutions

E. Wolska^a, J. Darul^a, W. Nowicki^a, P. Piszora^a, M. Tovar^b, O. Prokhnenko^b, C. Baehtz^c, M. Knapp^c

^aLaboratory of Magnetochemistry, Adam Mickiewicz University, Grunwaldzka 6, PL-60780 Poznań, ^bHahn-Meitner Institute, Glienickerstr.100, D-14109 Berlin, ^cInstitute of Materials Science, University of Technology, Petersenstr.23, D-64287 Darmstadt.

Keywords: neutron and X-ray diffractometry, magnetic structures, phase transition crystal characterization

Crystal and magnetic structures of the single phase solid solutions $\text{Li}_x\text{Mn}_{3-x-y}\text{Fe}_y\text{O}_4$, formed between the normal spinel LiMn_2O_4 and the ordered inverse spinel $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$, have been investigated by synchrotron X-ray and neutron powder diffraction. Our previous results evidenced changes in the distribution of Li^+ ions over the both spinel cationic sublattices, caused by Fe^{3+} substitution in the system. The preference of lithium to occupy the octahedral sites increases with the increasing iron content, resulting in the inverse spinel $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ phase [1]. X-ray powder diffraction results show clearly that a structural phase transformation, from cubic ($Fd3m$) to orthorhombic ($Fddd$), occurs at about 285K in the stoichiometric LiMn_2O_4 [2]. Substitution with Fe^{3+} ions reduces this effect and stabilizes the $Fd3m$ structure [3]. Due to the low scattering power of Li, and similar form factors of Fe and Mn, neither the Li^+ nor the Fe^{3+} and $\text{Mn}^{3+}/\text{Mn}^{4+}$ cation positions could be established by X-ray diffraction. Neutron powder diffraction experiments enable the location of Li^+ in the A and B spinel positions, and the atomic distribution of the Fe and Mn ions. What more, investigation on the magnetic structure appears to be essential, because the samples of solid solution series $\text{Li}_x\text{Mn}_{3-x-y}\text{Fe}_y\text{O}_4$ reveal different magnetic properties, from the low-temperature spin-glass behaviour of pure LiMn_2O_4 , through the antiferromagnetic ordering found for $0 < n_{\text{Fe}} < 0.3$, where $n_{\text{Fe}} = \text{Fe}/(\text{Mn} + \text{Fe})$, to the distinct ferrimagnetic exchange occurring between the A and B sublattices in AB_2O_4 , with the increase of Fe^{3+} ions content. We report new results obtained for spinel solid solutions, with $n_{\text{Fe}} > 0.3$. Thermal evolution of the magnetic reflection (111) enabled to separate the nuclear and magnetic scattering effect.

[1] S.M. Woodley, C.R.A. Catlow, P. Piszora, K. Stempin, E. Wolska, *J. Solid State Chem.* 153 (2000) 310.

[2] P. Piszora, W. Paszkowicz, C. Baehtz, E. Wolska, *J. Alloys and Compounds* 322 (2004) 119.

[3] E. Wolska, M. Tovar, B. Andrzejewski, W. Nowicki, J. Darul, P. Piszora, M. Knapp, *Solid State Sciences*, 8 (2006) 31.

m20.p01

Modified Voronoi approach to the analysis of crystal structures: binary intermetallics

Igor A. Baburin

Department of Inorganic Chemistry, Samara State University, Russia.
E-mail: baburinssu@mail.ru

Keywords: Dirichlet domain, crystal structure topology, binary alloys

A modified Voronoi approach to the analysis of crystal structures is proposed. It allows one to study crystal structures at different levels. At first level of representation all the atoms that contribute faces to the Voronoi polyhedron around any atom are considered to be coordinated. The solid angle subtended by the face of the Voronoi polyhedron at its central atom is assumed to be proportional to the strength of inter-atomic interaction [1]. All the contacts so defined are clustered in groups according to the following condition: two contacts fall into different groups if their solid angles deviate by more than a certain value. Then the minimum solid angle value is found for each group and the contacts with the solid angles less than the minimum value for the first, second, etc. group are successively omitted. Thus, a set of the representations for a given crystal structure is formed. The number of representations is equal to the number of groups obtained after clustering. To represent a crystal structure at different levels physically means to consider all possible contacts (even the weakest) and successively extract the stronger and stronger ones.

This method was applied to analyse 547 intermetallic binary compounds AX selected from the CrystMet Database. As a result, about 60% of all the studied crystal structures were assigned to the well-known topological types (b.c.c., primitive cubic lattice, f.c.c., etc.) at first level of representation and for most of these cases clustering leads to the nets interrelationships already described in the literature (e. g. f.c.c.-b.c.c.) [2]. About 40% of all the studied crystal structures cannot be related to any known topological types at first level of representation and are classified into more than 70 new topological types. To investigate these new types in more detail, the topologies of atomic subnets were analyzed. For this purpose, Voronoi polyhedra were constructed for the subnets of the atoms of the same chemical sort having also the same site symmetry. Then the 'clustering' procedure was applied as described above. Most of the atomic subnets can be considered as deformed homogeneous sphere packings (not necessarily close packed ones) and for these cases clustering leads to different transformations of sphere packing graphs. This result reinforces the role of homogeneous sphere packings in the crystal chemistry of binary compounds [3] because many of the new found topological types can be described as combinations of at least two sphere packings.

Transformations of sphere packings were explained using group-subgroup relations and the graph theory [4]. In particular, a new orthorhombic sphere packing that has not been reported before was found as a result of clustering. This packing is an intermediate between the FeB packing [2] and hexagonal one $6/4/h2$ [3].

[1] O'Keeffe, M. (1979). *Acta Cryst.* A35, 772-775.

[2] O'Keeffe, M., Hyde, B. G. (1996). *Crystal Structures I: Patterns and Symmetry*. Washington: Mineralogical Society of America.

[3] Sowa, H., Koch, E., Fischer, W. (2003). *Acta Cryst.* A59, 317-326.

[4] Eon, J. G. (2006). *Z. Kristallogr.* 221, 93-98.