Deformational effects in the two-positional lattice gas approach for intercalated systems

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Such widely known cathode of lithium-ion cells as lithium intercalated anatase demonstrates a phase separation into Li-rich and Li-poor phases in the whole range of lithium concentration ($x = 0 - 0.6$) as well as two possible positions for Li ion in the oxygen tetrahedron for both phases. In the Li-rich phase intercalation induces lattice deformation causing the antidistorsive internal field and thus making the Li positions nonequivalent.

Performed here symmetry analysis reveals that the observed $U_{xx} - U_{yy}$ deformation in the ab plane and the ordering of antiferroelectric type along the z axis are both described by the B_{1g} irreducible representation of the initial D_{4h} symmetry group and hence they occur simultaneously (so-called internal piezoeffect). According to the Landau expansion approach a phase transition (or separation) with jump of the concentration can be accompanied by the respective appearance of antipolarization.

Microscopic description of the Li-ion subsystem in anatase is given in the framework of the lattice model combining features of the Blume-Emery-Griffiths and Mitsui models, which takes into account all the abovementioned effects. Analysis of the ground-state phase diagram "external field – chemical potential" establishes values of model parameters providing a phase transition between the empty and half-filled phases with appearance of the ordering of antiferroelectric type for both cases of free and clamped crystal. Respective phase diagrams are built also for non-zero temperatures revealing a complicated structure of phase surfaces and lines of critical points. Thermodynamics of the system is studied for both cases of constant chemical potential and constant lithium concentration (leading to the phase separation onto Li-rich and Li-poor domains). Even at the absence of the total polarization, dielectric and (what seems more important) elastic characteristics of the crystal demonstrate jump-like behaviour in the critical points. Concentrational dependence of the incremental capacity $\mathrm{d}x/\mathrm{d}\mu$ (measured by experiment) is calculated and analysed.