Phase transitions in nickel olivine - studies of thermal and magnetic properties

Among orthorhombic (*Pnma*) olivines, suitable for cathodes of Li-ion batteries, $LiNiPO_4$ is a unique one, because it orders magnetically in two steps, i.e., at 21.8 K, the 2nd order transition to an incommensurate phase, *IC*, and then, at 20.9 K, the 1st order transition to an antiferromagnetic, commensurate phase *C* appear. As a consequence of several competing interactions, the magnetic structure of these phases is very complicated. It has been studied for many years and different its models have been proposed, however, it is not fully understood till now. The presence of a small spontaneous magnetization in the *C* phase is one of the most interesting features, because it means that the presence of a spontaneous electric polarization in the *C* phase is also allowed.

Thus, (i) determining whether any signatures of the phase transition to the ferroelectric phase appear in $LiNiPO_4$ and (ii) explaining whether the complex exchange interactions, layered crystal structure, strong magnetic anisotropy and a quasi - two-dimensional character of the magnetic structure result in any uncommon macroscopic magnetic properties of $LiNiPO_4$, were the main aims of the thesis. Studying details of a low-filed part of the phase diagram in magnetic field parallel to the *c* axis and explaining why the shape of the specific heat anomalies related to the phase transitions in the powder sample is different than in the case of the single crystal and depends on the field value, were the additional aims.

The studies of specific heat were chosen as the main tool for realizing the first task, because this is the quantity very sensitive to phase transitions of all physical nature. For realization of the second goal, angular dependences of torque and magnetic moment were measured for single crystals of $LiNiPO_4$, for magnetic field, **B**, rotating within the *a*-*c* and *b*-*c* planes, for several |**B**| values and fixed temperatures. Additionally, temperature dependences of magnetization at several |**B**| values for **B** parallel to the *a*, *b* and *c* axes were measured.

The specific heat studies revealed a splitting of the specific heat anomaly related to the phase transition between *IC* and the low temperature *C* phase. The splitting suggests that the ferroelectric phase can appear in $LiNiPO_4$. However, measurements of the electric polarization, being beyond the framework of this thesis, would be necessary to confirm this supposition. Based on the specific heat studies, the low-filed part of the phase diagram was clarified and the parameters of parabolic dependences of the phase transitions points on the value of magnetic field directed along the *c* axis were determined. Additionally, the results of the specific heat studies of the single crystal were used to elucidate and describe the evolution of the shape of the specific heat anomaly in the powder sample with increase in |**B**|.

The measured angular dependences of magnetic torque and magnetization were found to have atypical shapes. To explain this phenomenon, the hypothesis that the magnetic moment induced by **B** along the *a*, *b*, and *c* axes depends not only on the **B**-component parallel to the considered main axis but also on the square of the **B**-component perpendicular to this axis was put forward. Then, a very good agreement between the theoretical and the measured dependences was achieved, which confirmed validity of the proposed model. We called this discovered effect the "nonlinear, off-diagonal magnetic susceptibility".

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