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ABSTRACTS

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EPR Study of Inhomogeneous Phases in Improper Ferroelastics $Mg_xZn_{(1-x)}TiF_6 \cdot 6H_2O:Mn^{2+}$

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The results of EPR study of inhomogeneous phases in improper ferroelastics $Mg_xZn_{(1-x)}TiF_6 \cdot 6H_2O$ are presented. The $MgTiF_6 \cdot 6H_2O:Mn^{2+}$ (MFTH, $x = 1$) crystals undergo transition of the first order from monoclinic ferroelastic phase to structurally inhomogeneous phase above $T_C^+ = 311 \pm 0.3$ K ($T_C = 300 \pm 0.3$ K), as concluded on the basis of analysis of temperature and angular dependences of experimental parameters and numerical calculations. In this phase studied crystals consist of two types of regions characterized by homogeneous and inhomogeneous structural organization. In the latter both the angle of $Mg[H_2O]_6^{2+}$ octahedra rotation around crystal C_3 axis and their axial distortion along C_3 are modulated parameters. The assumption was expressed that at $T_{i2} = 370$ K these crystals may undergo phase transition from inhomogeneous phase to incommensurate phase. The mixed crystals $Mg_xZn_{(1-x)}TiF_6 \cdot 6H_2O:Mn^{2+}$ ($x = 0.64$, 0.34, 0.2; denoted as MZT1, MZT2 and MZT3) have been investigated as well, with special attention paid to inhomogeneous phase, observed at temperatures above ferroelastic phase transition. There is evident qualitative difference between spectra of mixed crystals with $x > 0.5$ (line shape with two peaks, being similar to MFTH spectra) and $x < 0.5$ (one peak line shape), as well as in their temperature dependences. Overall line shape character is preserved within entire temperature range of inhomogeneous phase for all mixed crystals studied, though parameters of line shape are temperature dependent. Within the frameworks of the model utilized for MFTH the successful description of experimental Mn^{2+} EPR spectra of MZT1 crystals has been reached, therefore nature of inhomogeneous phase being similar to MFTH is supposed. On the contrary, experimental spectra of MZT2 and MZT3 crystals are not described by that model, which confirms their qualitative difference from MFTH and MZT1 (i.e., $x > 0.5$) crystals. Therefore, we proposed a qualitative model for description of considered mixed crystals with $x < 0.5$. The essence of the model is that axial fine structure parameter D of particular paramagnetic center (connected with trigonal distortion of $[Mn(H_2O)_6]^{2+}$ octahedra), which influence the position of line in the spectrum, is determined mainly by two similar octahedral complexes (above and below along the C_3-axis) through the hydrogen bonds. Taking into account the probability for site to be occupied by particular ion in mixed crystals, the resulting line shape can be calculated. These theoretical calculations demonstrate the agreement with experimental data.