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Investigation of Inhomogeneous Phases in Mixed Crystals $Mg_xZn_{(1-x)}TiF_6 \cdot 6H_2O : Mn^{2+}$ by EPR

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The mixed crystals of improper ferroelastics $Mg_xZn_{(1-x)}TiF_6 \cdot 6H_2O:Mn^{2+}$ have been studied by EPR. The $MgTiF_6 \cdot 6H_2O$ (MFTH, x=1) crystals undergo transition of the first order from monoclinic ferroelastic phase to structurally inhomogeneous phase above T_C^+=311±0.3 K (T_C^-=300±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 (lineshape with two peaks, being similar to MFTH spectra) and x<0.5 (one peak lineshape) (Fig. 1), as well as in their temperature dependences.

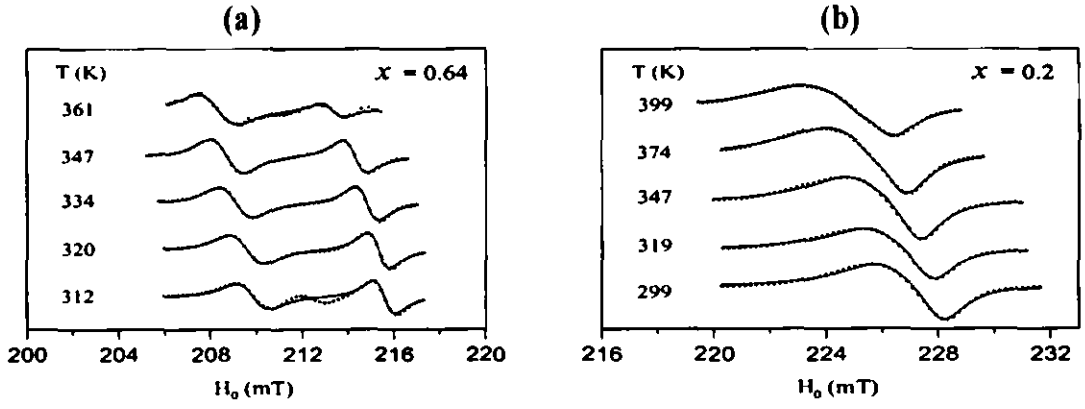

Fig. 1. EPR spectra of mixed crystals $Mg_xZn_{(1-x)}TiF_6 \cdot 6H_2O:Mn^{2+}$ (x=0.64 (a) and x=0.2 (b)). Dots and solid lines correspond to experimental and theoretical calculated spectra, respectively.

Overall lineshape character is preserved within entire temperature range of inhomogeneous phase for all mixed crystals studied, though parameters of lineshape 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 (Fig.1a), 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 centre (connected with trigonal distortion of $[Mn(H_2O)_6]^{2+}$ octahedra), which influences the position of line in the spectrum, is determined by configuration of nearest neighbouring sites (octahedral aqua complexes connected via hydrogen bonds) occupied by particular ions (Mg^{2+} or Zn^{2+}). Taking into account the probability of different configurations in mixed crystals, the resulting lineshape can be calculated. The rhombic distortions of the octahedral complexes, resulting from the strain caused by significant amount of Zn^{2+} ions, should be taken into account in the calculation model as well. These theoretical calculations are in good agreement with experimental results (Fig.1b).