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EPR Investigation of Phase Transitions and Incommensurate Phases in Improper Ferroelastic $MgGeF_6 \cdot 6H_2O$: Mn^{2+}

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The results of EPR investigation of improper ferroelastic crystals $MgGeF_6 \cdot 6H_2O:Mn^{2+}$ allow to conclude that at T_{i1}=403 K these crystals undergo transition to structurally incommensurate phase. The order parameter of this transition is probably the angle of $Mg[H_2O]_6^{2+}$ octahedra rotation around crystal C_3 axis, which determines the presence of only even terms in expanding the EPR spectra fine structure parameter on the powers of order parameter. Below 360K the appearance of structural phase soliton lattice and effect of variation of the spin-lattice relaxation rate over the spectrum have been taken into account.

1. Introduction

The crystals $MgGeF_6 \cdot 6H_2O$ belong to $ABF_6 \cdot 6H_2O$ family (where A and B are divalent metal and fourvalent element, respectively). In these compounds complex ions $A[H_2O]_6^{2+}$ and $[BF_6]^{2-}$ octahedra form rhombohedrally distorted CsCl-type lattice and can be distributed between two orientations around the 3-fold axis[1, 2]. Many crystals of this family undergo improper ferroelastic phase transition from the high-temperature rhombohedral phase to the low-temperature monoclinic phase (space group $P2_1/c$)[3,5-10]. The presence of superstructure reflections at room temperature first observed with X-ray diffraction on Mg, Fe and Mn compounds, in contradiction to the structural model proposed before (space group: $R\bar{3}m$)[1-5] was the reason for Chevrier *et al.*[6-8] to introduce space group $P\bar{3}$ for the proper treatment. Chevrier *et al.*[6-8] also supposed two type of domains with different orientations of complex ions, related by pseudomirror plane (11.0). The room temperature X-ray powder diffraction data[11] for $MgGeF_6 \cdot 6H_2O$ reported space group $R\bar{3}$.

The structurally inhomogeneous phase in $MgGeF_6 \cdot 6H_2O$ crystals, existing between their rhombohedral paraelastic phase and monoclinic ferroelastic one ('intermediate' phase), discovered by Ziatdinov *et al.*[9, 10], and its nature are of special interest. In this paper, on the basis of analysis of $MgGeF_6 \cdot 6H_2O:Mn^{2+}$ single crystals EPR experiments, we suggest the model of their structural organization in inhomogeneous phase, which relies on our previous ideas on incommensurate structure of this phase[9, 10], but is free of some disadvantages of model formerly proposed with assuming incommensurate modulation of lattice

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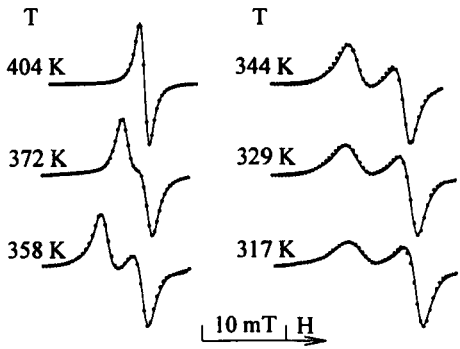

Fig.1. The temperature evolution of the EPR Mn^{2+} spectra lineshape (scattered points correspond to experimental spectra, solid line - theoretical simulated spectra), $\mathbf{H}_0 \| \mathbf{C}_3$.

displacements in mentioned crystals. Presented model provides successful describing the experimental Mn^{2+} EPR spectra in their 'intermediate' phase.

2. Results

The EPR measurements have been carried out using X-band spectrometer ESR-231 (Germany) in three mutually perpendicular crystal planes. Single crystals of $MgGeF_6 \cdot 6H_2O$ doped with ~0.1% Mn^{2+} have been used in experiments.

At temperature above T_{i1}=403±0.3 K and $\mathbf{H}_0 \| \mathbf{C}_3$ ($\mathbf{H}_0$ is external magnetic field, $\mathbf{C}_3$ is a 3-fold axis of crystal) the EPR spectrum of $MgGeF_6 \cdot 6H_2O$:Mn^{2+} crystals, consisting of 5×6 hyperfine structure (HFS) lines, is of axial character with z-axis being parallel to $\mathbf{C}_3$-axis and corresponds to one type of Mn^{2+} centres. With temperature decrease below T_{i1} all HFS spectral lines at first smoothly inhomogeneously broaden (the low field HFS line has been chosen for detailed lineshape analysis), and then, excluding central set lines, gradually transform into the two-peak ones (Fig. 1); temperature increase results in reversed evolution. Moreover, the EPR lineshape is typical for incommensurate one-dimensional modulated systems. The temperature of transition from one spectrum type to another does not depend on direction of temperature varying, microwave field frequency, orientation of $\mathbf{H}_0$ with respect to crystal axes, and HFS line chosen to detect the temperature changes in the sample. These facts unambiguously testify that T_{i1} is the second-order phase transition temperature, instead of the temperature of dynamic averaging in EPR time scale of structurally inequivalent positions of complex ions. At T_{i2} = 380±0.3 K a small step-wise changes with temperature hysteresis ~1 K in EPR spectra parameters were observed. It is worth to note that, in spite of substantial changes in Mn^{2+} HFS lineshapes, EPR spectrum symmetry and its principal axis direction remain the same within entire intermediate phase range. At T_C = 311±0.3 K the $MgGeF_6 \cdot 6H_2O$ crystals undergo the first order phase transition to monoclinic

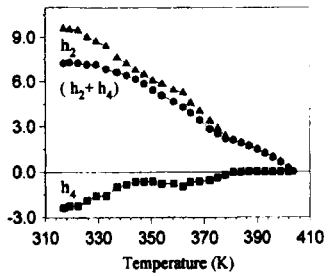

Fig. 2. The temperature dependences of incommensurate modulation parameters of the second and fourth order (mT) calculated from the EPR spectra.

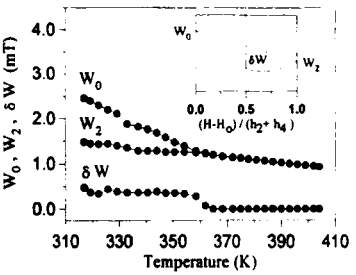

Fig. 3. The temperature dependences of the parameters W_0, W_2 and δW (inset presents the definitions of these parameters).

phase with the temperature hysteresis ~5 K. Below T_C the EPR spectrum corresponds to six spatially inequivalent rhombic centres. The number of Mn^{2+} sites and symmetry of individual magnetic ion EPR spectrum in single crystal $MgGeF_6{\cdot}6H_2O{:}Mn^{2+}$ below T_C agree with the space group $P2_1/c$ and three kinds of orientational domains related with each other by 120° rotation around C_3, each domain contains two inequivalent Mn^{2+} sites.

3. Discussion

For the crystals under investigation the Mn^{2+} EPR lineshape in inhomogeneous phase is formed mainly by the modulation ΔD of the fine structure parameter D. However, the presence of angular dependence of EPR lineshape shows that the angle φ of complex ions orientation around crystal C_3 axis must be a primary order parameter[9, 10]. Further, we suppose that parameter D is connected with φ. For the reasons of symmetry, we should conclude that $\Delta D = \Delta D(\varphi^2)$ (quadratic case for $\Delta D \sim \varphi^2$). Experimental Mn^{2+} EPR lineshape has been treated in the terms of model analogous to that of Blinc[12] for the interpretation of magnetic resonance spectra of crystal incommensurate phases. The resonance field of a given paramagnetic centre was expanded in powers of order parameter (holding even terms up to fourth power), soliton density depending on temperature has been taken into account. Multiplicity parameter of the superstructure p was chosen to be equal to 3 according to the Raman spectroscopy data above T_C for related crystals[13]. Basing on these assumptions we have calculated the temperature dependences of modulation parameter h_2 and h_4 (Fig. 2). The calculations have shown that smooth evolution of incommensurate phase follows to the predictions of a classical theory[12] below T_{i1}: the modulation follows from a plane-wave regime to multisoliton regime at ≈ 370K with decreasing the soliton density down to $n_S \approx 0.7$. As against to $MgSiF_6{\cdot}6H_2O$ case for which n_S step-wise decreases at T_{i2} down to ≈ 0.1 and

incommensurate spectral distribution nearly disappears[14], at further cooling this value remains almost the same down to T_C. Below T_{i2} the spectra lineshape changes somewhat differ from magnetic resonance spectra evolution in conventional incommensurate systems with one-dimensional modulation. A successful description of the lineshapes (Fig.1) has been obtained below ≈360K taking into account the variation of spin-lattice relaxation rate T_1^{-1} over the incommensurate spectral distribution. This phenomenon was predicted theoretically and observed experimentally by direct T_1^{-1} measurements in some compounds[12, 15]. The reason for such variation may be different contributions of amplitudon and phason fluctuations to the T_1^{-1} at different parts of the inhomogeneous magnetic resonance lines[12,15]. Within entire range of inhomogeneous phase the value of indicated variation remains reasonable (Fig.3).

4. Conclusion

The results presented show that the EPR spectra of Mn^{2+} in $MgGeF_6 \cdot 6H_2O$ intermediate phase may be qualitatively described as incommensurate system spectra. On the other hand, the temperature evolution of experimental spectra has some peculiarities. They may be accounted for under the next additional assumptions: structural solitons existing and presence of spin - lattice relaxation rate T_1^{-1} variation over the incommensurate spectral distribution simultaneously.

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