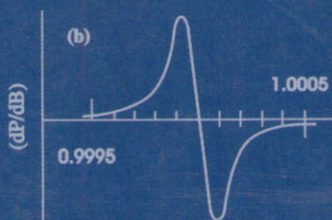
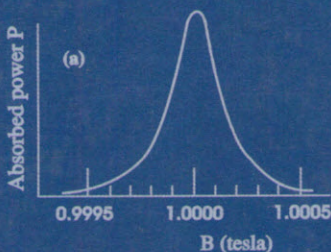
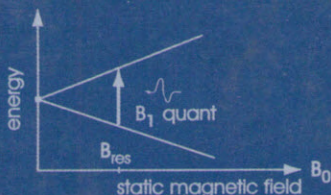


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From Biophysics to Materials Science



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EPR Studies of Phase Transitions and Structural Solitons in Improper Ferroelastic $\text{MgTiF}_6 \cdot 6\text{H}_2\text{O}$ Doped with 3d - ions.

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Abstract. Electron paramagnetic resonance (EPR) of Mn^{2+} and Ni^{2+} in magnesium fluotitanate hexahydrate ($\text{MgTiF}_6 \cdot 6\text{H}_2\text{O}$) crystals has been studied at X - and Q - band frequency in the temperature interval 100 + 400 K. At cooling of crystals with natural abundance of 3d - ions, at $T_c \approx 300$ K they undergo an improper ferroelastic first-order phase transition with the unit cell doubling. Above T_c a succession of step-wise changes in the slope of Mn^{2+} line shape splitting curve is observed. These step-wise discontinuities were interpreted as a result of structural phase transitions of the incommensurate phase - incommensurate phase type. In incommensurate phases the Mn^{2+} line shape was analyzed using the structural soliton model. In mixed ferroelastics $\text{Mg}_{1-x}\text{Zn}_x\text{TiF}_6 \cdot 6\text{H}_2\text{O}$ at $x < 0.75$ (>0.75) the Mn^{2+} EPR spectrum parameters and the phase transition temperatures are close to those in $\text{MgTiF}_6 \cdot 6\text{H}_2\text{O}$ ($\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$) crystals.

1 Introduction

Magnesium fluotitanate hexahydrate (MFTH) belongs to isomorphous compounds of the type $\text{ABF}_6 \cdot 6\text{H}_2\text{O}$ (where A and B are di- and fourvalent metals, respectively) in which two complex ions $\text{A}(\text{H}_2\text{O})_6$ and BF_6 can be distributed between two orientations around the 3 - fold axis [1,2]. The presence of superstructure reflections first observed by X-ray diffraction of Mg, Mn and Fe compounds is inconsistent with the structure models proposed before (space group: $P3m$) [1-5]. Therefore, Chevrier [6-8] had suggested new structure models: the crystals consist of domains (space group: $P3$) with two different octahedra orientations related by pseudomirrors (110), and with equal volume parts. In the case of Mg and Mn fluosilicates ($T > 300$ K [6]; $T > 240$ K [7]), these domains are of great extension, whereas in Fe - fluosilicates ($T > 240$ K [8]), their size is a function of temperature. A number of compounds are characterized by an improper ferroelastic phase transition from a rhombohedral modification to a low-temperature monoclinic phase [3, 5-11]. The latter is stable at low temperatures. According to the literature data at $T \approx 300$ K MFTH

crystals undergo the 1-st order improper ferroelastic phase transition, which was attributed to a direct transition of the type $R3m \rightarrow P2_1/c$ [12]. In this paper we present experimental EPR results of MFTH crystals containing i) natural abundance of 3d - ions (<10 at.%), ii) ≈ 0.1 at. % Mn^{2+} and iii) ≈ 3 at.% Ni^{2+} . Analysis of EPR data suggests that the present point of view of high temperature crystal structure organization is incomplete and indicates the presence of an unknown succession of phase transitions and regions with the lattice displacement modulation (structural solitons) in these crystals at $T > T_c$.

2 Experimental Procedure

The EPR measurements were carried out using X - and Q - band spectrometers in three mutually perpendicular crystal planes. The studies were performed in the temperature range 100 + 400 K. Cooper-constantan thermocouples were used to monitor temperatures with one junction attached to the outside of the wave -guide close to the sample. The accuracy in the measuring temperature was ≈ 0.3 K. Single crystals of MFTH were prepared from aqueous solutions at 300 K.

3 Result

The EPR investigations of MFTH crystals containing natural abundance of Mn^{2+} and other ions show (Figure 1) that at cooling at $T_c = 300 \pm 1$ K they undergo the 1st order improper ferroelastic phase transition. (The T_c is defined as the temperature at which intensities of Mn^{2+} EPR low field hyperfine structure (HFS) lines from different crystal phases are equal.) The value of the temperature hysteresis of transition is ~ 10 K. Below T_c , the EPR spectra of ~ 0.1 at. % Mn^{2+} and ~ 3 at. % Ni^{2+} correspond to six spatially inequivalent rhombohedral centres, two of which came from orientational domain. The principal axis of a single centre for both kinds of ions and the crystal trigonal axis are rotated by $(8 \pm 2)^\circ$. The angular dependence of a single magnetic centre spectrum for Mn^{2+} (Ni^{2+}) is in good agreement with the spin Hamiltonian of a rhombohedral symmetry with the following parameters at 300 (250) K: $g = 2.0009 \pm 0.0003$, $D = -203 \pm 1$, $|E| = 28 \pm 0.5$, $a = 9 \pm 1$, $A_{\perp} = A_{\parallel} = -89 \pm 1$ ($g = 2.25 \pm 0.01$, $D = 2.20 \pm 0.02$, $|E| = 0.22 \pm 0.03$), where D , E , A and a are presented in units of 10^{-4} cm^{-1} . The above type of 3dⁿ ions EPR spectra is characteristic for the monoclinic phase $P2_1/c$ in studied crystals. At $T > T_c$ and at a constant external magnetic field (H) parallel to c - axis the Mn^{2+} EPR spectrum consists of 6x5 HFS lines. Outlines of Mn^{2+} HFS lines depend on electron

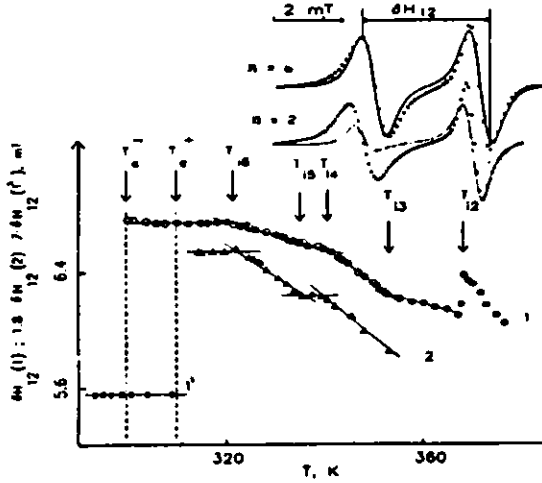


Fig 1. Temperature dependence of the value of ~ 0.1 at.% Mn^{2+} EPR low field HFS line splitting δH_{12} in MFTH crystals at angles $\theta=0^\circ$ (1,1') and 55° (2). The black and white points correspond to parameters at heating and cooling of the crystals, respectively. Comparison between the experimental (pointed line) and simulated (solid line) (~ 0.1 at %) Mn^{2+} EPR low field HFS line shapes were obtained using the following values of modulation parameters: $h_1=3.0$ (3.7) mT, $h_2=-3.25$ (-3.0) mT, $\delta W=1.3$ (1.3) mT, $\Delta = 0.36$ (0.6) mT, $b=0.2$ (0.1) mT, $\Phi_0=0^\circ$ (1°), $n=6$ (2). The Q-band $H \parallel c$.

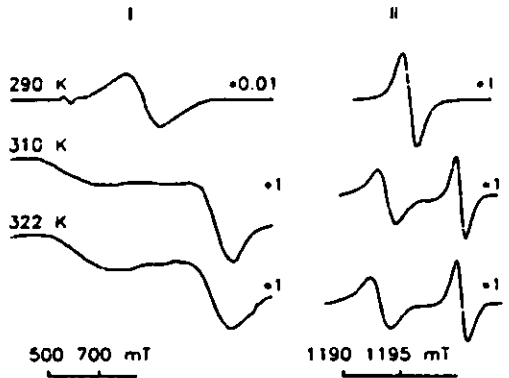


Fig 2. Temperature evolution of the (~ 5 at%) Ni^{2+} EPR line shape in MFTH crystals (I). At 290 K (in ferroelastic phase), the low field line with small intensity corresponds to the transitions between the $M_L=\pm 1$ doublet. For comparison, the evolution of the Mn^{2+} (natural abundance) EPR low field HFS line shape of the same crystal is shown (II). The Q-band $H \parallel c$.

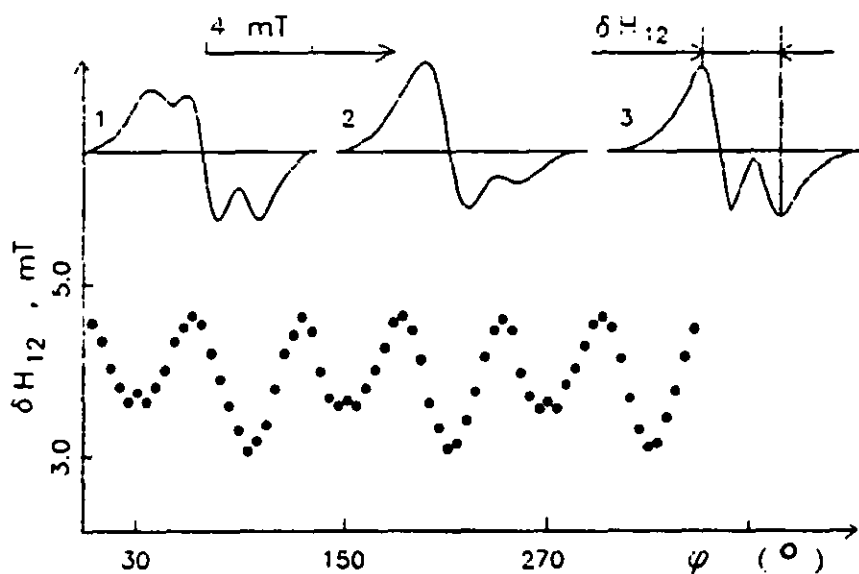


Fig 3. Angular dependence of the value of (~0.1 at%) Mn^{2+} EPR low field HFS line splitting δH_{12} in MFTH crystals at rotating of the sample around the c-axis (along the φ angle), which makes the angle $\theta = 55^\circ$ with H_0 . 1- $\varphi_n = n \times 60^\circ$; 2- $\varphi_n = 30^\circ + n \times 120^\circ$, $\varphi_n = 90^\circ + n \times 120^\circ$ ($n=0,1,2,\dots$). The X-band $H \parallel c$. $T=320 \text{ K}$.

quantum number M_l , however all except for the slightly asymmetric HFS lines of the central group have a two peak form (see Figure 1 and 2).

The Ni^{2+} spectrum at Q-band and $H \parallel c$ consist of a broad two peak line of fine structure (FS) (see Figure 2). Up to $\approx 400 \text{ K}$, the Mn^{2+} and Ni^{2+} spectrum axial axes are preserved along c-axis. At $T_{12} > T_c$, all spectrum and line shape parameters of Mn^{2+} undergo small and close to step-wise changes with the temperature hysteresis of $\sim 1 \text{ K}$. Between T_{12} and T_c , a succession of step-wise changes in the slope of Mn^{2+} line shape parameter curves which are less than those at T_{12} is observed (see Figure 1). The temperatures of these step-wise discontinuities T vary from sample to sample within the limit of $\sim 4 \text{ K}$, but whatever and independently on temperature variation direction they occurs at practically the same amounts of line shape parameters. Having larger FS line width and, as a consequence, a larger value of experimental error, Ni^{2+} parameters do not fix these step-wise changes. At rotating the crystals around c-axis which makes a certain angle $\theta = 0, 90^\circ$ with H , Mn^{2+} HFS lines do undergo complicated changes which are repeated every 120° (see Figure 3). The amplitude of the HFS line two-peak splitting value variation vs. φ angle increases at $T \rightarrow T_c$. In mixed crystals $\text{Mg}_{1-x}\text{Zn}_x\text{TiF}_6 \cdot 6\text{H}_2\text{O}$ containing natural abundance of Mn^{2+} ions, up to $x < 0.75$, the Mn^{2+} EPR spectrum is qualitatively similar to its spectrum

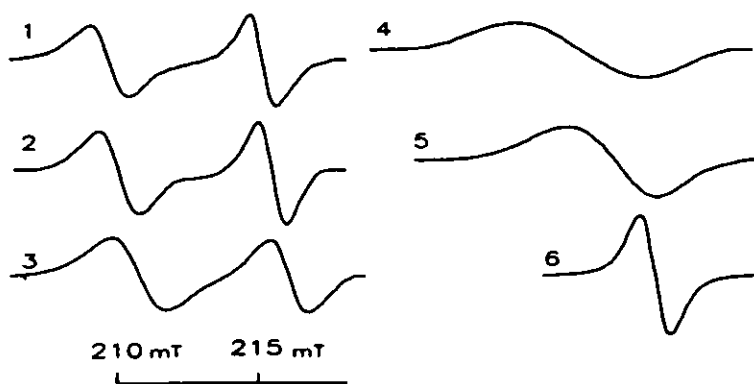


Fig 4. Shape and position of the (~ 0.1 at%) Mn^{2+} EPR low field HFS line in $Mg_{1-x}Zn_xTiF_6 \cdot 6H_2O$ crystals vs Zinc concentration (x). Spectra 1,2,3,4,5 and 6 correspond to $x=0.0,0.33,0.75,0.8,0.9$ and 1.0 , respectively. The X-band $H||c$.

in MFTH crystals (see Figure 4). In crystals with $x > 0.75$ Mn^{2+} EPR spectrum is qualitatively analogous to its spectrum in crystals $ZnTiF_6 \cdot 6H_2O$ (see Figure 4). It is interesting to note that in all crystals investigated only one of the above-mentioned type of Mn^{2+} EPR spectra was observed. In crystals with $x < 0.75$ and $x > 0.75$ the critical temperature regions, in which the improper ferroelastic phase transition is observed, were close to those in MFTH and in $ZnTiF_6 \cdot 6H_2O$ crystals, respectively (see Table 1).

Table 1. The ferroelastic phase transition parameters in crystals $Mg_{1-x}Zn_xTiF_6 \cdot 6H_2O$

x	T_c^+	T_c^-	$\delta T (^\circ)$
0.00	310 ± 1	300 ± 1	~ 3
0.13	312 ± 1	299 ± 1	~ 3
0.33	315 ± 1	299 ± 1	~ 6
0.45	310 ± 2	296 ± 2	~ 10
0.64	304 ± 2	292 ± 2	~ 16
0.75	300 ± 2	290 ± 2	~ 20
0.81	199 ± 2	194 ± 2	~ 24
0.92	190 ± 2	187 ± 2	~ 10
1.00	183 ± 2	180 ± 1	~ 5

δT is the temperature interval near T_c in which the Mn^{2+} EPR low field HFS line intensity decreases by 90 %.

4 Discussion

The two-peak form of Mn^{2+} HFS lines and Ni^{2+} FS lines indicates on magnetically inequivalent centres of these ions in high temperature phase of MFTH crystals. This fact is incompatible with attributing MFTH crystals to the space group $R3m$ with $Z=1$. On the other hand, at $T > T_c$ the Mn^{2+} and Ni^{2+} EPR line shapes, their temperature, φ and θ angular dependences are qualitatively identical to the characteristics of these ions in incommensurate (IC) phases of dielectric crystals, in particular, in IC phases of $MgSiF_6 \cdot 6H_2O$ [13, 15] and $MgGeF_6 \cdot 6H_2O$ [14, 15] crystals. The aforesaid allows to suggest that in high temperature phase the MFTH crystals have also an IC structure. As for the IC phase-paraelastic (P) phase transition which is observed in the latter two crystals at $T_{11} > T_{12}$, it may be suggested that temperature of such transition in MFTH crystals is higher than temperature of its dehydration. Therefore, Mn^{2+} EPR line shape in the high temperature phase of MFTH crystals have been interpreted in terms of the model analogous to that of Blinc [16] for the interpretation of magnetic resonance spectra in crystal IC phases. The scheme of calculations is as follows. The calculations of the Mn^{2+} HFS line shape in high temperature phase are carried out in the assumption of the one-dimensional lattice modulation which is given by

$$U(x) = A(x)\cos[\Phi(x) + \Phi_0] = A(x) \cos\alpha(x),$$

where $\alpha(x)$ is the phase of the local modulation in the direction of the one-dimensional modulation x , Φ_0 is the phase shift, $A(x) = A_0 + \delta A(x)$ is the amplitude of the lattice displacement, assumed at calculations as $\delta A(x) \ll A_0$. The resonance field of a given paramagnetic centre can be expanded in powers of $\cos\alpha(x)$

$$H = H_0 + h_1 \cos\alpha(x) + h_2 \cos^2 \alpha(x) + \dots$$

where H_0 indicates the resonance field corresponding to the structure without modulation, parameters h_1 and h_2 are certain functions of x .

The overall line shape $F(H)$ can then be given by analogous to Blinc[16] by the distribution density of the lines

$$f(H) = \text{const}/(|-\sin\alpha[\Delta^2 + \cos(n\alpha)]^{1/2} + b \cos\alpha \cos(n\alpha) \sin(n\alpha)|) dH/dU \quad (1)$$

and the Lorentzian line shape of the individual lines $L(H)$ with full width at half maximum height δW , as follows,

$$F(H) = \int L(H-H_R) f(H_R) dH_R.$$

In equation (1) b is the numerical parameter and Δ connected with the soliton density n_s as $n_s = (1 + \Delta^2)^{1/2} / 2K$, where K is the complete elliptic integral of the 1-st kind. The line shape computer simulation results are given in Figure 1. As shown, the experimental and calculation results are in good agreement. Thus, it is reasonable to admit that the trigonal distortion of an aquacomplex which determines the value of FS line parameter of Mn^{2+} and Ni^{2+} EPR spectra are modulated at $T > T_c$.

The fact that in IC phase of MFTH crystals, $n_s < 1$ implies that the crystal consist of two types of areas: one with a lattice displacement modulation (solitons), the other without it (domains).

The existence of angular dependence on φ for Mn^{2+} line shape in high temperature phase allows to draw the conclusion that in the IC phase the cubic crystalline field axes for different Mn^{2+} ions do not coincide due to the rotation of complex ions around the crystal c-axis. We assumed [13, 15] that the similar disorientation of the cubic crystalline field axes in IC phase of $MgSiF_6 \cdot 6H_2O$ and $MgGeF_6 \cdot 6H_2O$ crystals must be connected with the modulation of the rotation angle of the complex around the c-axis relative to the position in the P-phase and that this angle is an order parameter of P \rightarrow IC phase transition and it, therefore, determines the value of the trigonal distortion modulation. Similar suggestions may be made according to an origin of the disorientation of the cubic crystal line field axes in high-temperature phase of MFTH crystals. The calorimetric investigations of MFTH crystals in temperature interval 120 + 400 K recorded two new phase transition [17]. Temperatures of these transitions are near T_{14} and T_{16} . So, one can conclude that other T_m are also the phase transition temperatures. In this case, these transitions formed previously unknown in MFTH crystals succession of IC phase \leftrightarrow IC phase type phase transitions.

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