

EPR STUDIES OF PHASE TRANSITIONS AND INCOMMENSURATE STATES IN FERROELASTIC $\text{MgGeFe}\cdot 6\text{H}_2\text{O}$ DOPED WITH 3d-IONS

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Abstract The succession of phase transitions and incommensurate states has been found and investigated in $\text{MgGeFe}\cdot 6\text{H}_2\text{O}$ crystals doped with $\text{Mn}^{2+}(3d^5, S=5/2, I=5/2)$ and $\text{Ni}^{2+}(3d^8, S=1)$ by means of electron paramagnetic resonance (EPR) at X - and Q - band frequencies in the temperature interval from 77 to 430 K.

INTRODUCTION

Magnesium fluogermanate hexahydrate (MFGH) belongs to isomorphous compounds of the type $\text{ABFe}\cdot 6\text{H}_2\text{O}$ (where A and B are di- and fourvalent metals, respectively) in which two complex ions $\text{A}(\text{H}_2\text{O})_6$ and BFe can be distributed between two orientations around the 3-fold axis.¹⁻² The presence of superstructure reflections first observed by X-ray diffraction on Mg, Mn and Fe compounds³ is inconsistent with the structure models proposed before (space group: $R\bar{3}m$).¹⁻⁵ Therefore, Chevrier⁶⁻⁸ had suggested new structure models: the crystals consist of domains (space group: $P\bar{3}$) with two different octahedra orientations related by pseudomirrors (11.0), and with equal volume parts. In the case of Mg and Mn fluosilicates ($T > 300 \text{ K}$;⁹ $T > 240 \text{ K}$ ⁷), these domains are of great extension, whereas in Fe-fluosilicates ($T > 240 \text{ K}$), 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. At present only room temperature X-ray powder diffraction data is known for the MFGH, according to which they belong to the space group $R\bar{3}$.¹²

In this paper we present experimental EPR result of MFGH crystals containing i) natural abundance of 3d - ions ($\leq 10^{-3}$ at. %), ii) ≤ 1 at.% Mn^{2+} and iii) ≤ 5 at. % Ni^{2+} with emphasis on features related to the discovered structure modulated phases of crystals realized at $T > 316 \text{ K}$.

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 from 77 to 430 K. Copper-constantan thermocouples were used to monitor temperatures with one junction attached to the outside of the waveguide close to the sample. The accuracy in measuring the temperature was about ± 0.2 K.

Single crystals of MFGH doped with 3d - ions were prepared from aqueous solutions at 300 K. The trigonal c-axes in most of the samples were readily indentified by inspection.

RESULTS

The EPR investigations of MFGH crystals containing natural abundance of 3d - ions show (Figure 1) that they undergoes structural phase transitions of 2-nd and 1-st order at cooling (or heating) at $T_{11} = 403 \pm 1$ K, $T_{12}(T_{1\bar{2}}) = 381(380) \pm 1$ K and $T_{2}^{\pm}(T_{\bar{2}}^{\pm}) = 316(311) \pm 1$ K, respectively. Thus MFGH crystals have 4 structural modifications which are further designated as I, II, III and IV with decreasing temperature.

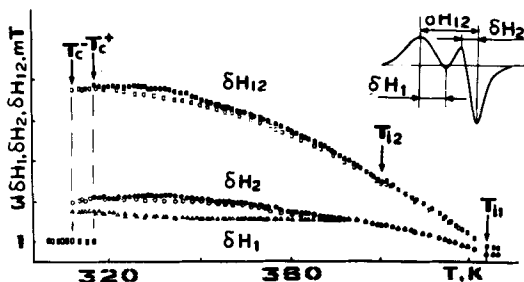


FIGURE 1 The parameters of the Mn^{2+} EPR low field HFS line in MFGH crystals at $H \parallel c$ (the X-band) vs. temperature. The black (white) points refer to parameters at heating (cooling) of the crystals.

In phase I ($T > T_{11}$) at a constant external magnetic field (H) parallel to c -axis the Mn^{2+} EPR spectrum consists of 6x5 hyper-fine structure (HFS) lines with Lorentzian line shapes corresponding to one type of Mn^{2+} axial centres with the axial symmetry axis parallel to the c -axis in the sites of Mg^{2+} substitution. It is described by an axial spin Hamiltonian with (415 K): $g = 2,0009 \pm 0.0003$, $D = -265 \pm 1$, $a = 8 \pm 1$, $A_{\perp} = A_{\parallel} \pm -89 \pm 1$, where D , A and a are represented in the unit of 10^{-4} cm^{-1} .

The transition at T_{11} is accompanied by a smooth inhomogeneous broadening of EPR lines. Below T_{11} , Mn^{2+} HFS and Ni^{2+} fine structure (FS) lines are gradually transformed into a two-peak spectrum except for the slightly asymmetric HFS lines of the central Mn^{2+} group (Figures 1 and 2). Up to T_c , the spectrum axial axes are preserved along c-axis. The T_{11} value is independent of the direction of the temperature changes and the value of HFS or FS line splittings. Consequently, T_{11} may be considered as the actual temperature of the 2-nd order phase transition. At T_{12} , all spectrum and line shape parameters of Mn^{2+} undergo small and close to step-wise changes with the temperature hysteresis of ≈ 1 K. Lower T_{12} the line shape and spectrum parameters depends on direction of temperature variation. At $T_c < T < T_{12}$, a succession of step-wise changes in the slope of Mn^{2+} line shape parameter curves which are less significant than those at T_{12} is observed (Figure 3). The temperatures of these step-wise discontinuities T_{1n} vary from sample to sample with in the limit of ~ 4 K, but whatever and independently on temperature variation direction they occurs at practically the same amounts of line shape parameters (Figure 3). At rotating the crystals around the c-axis (along the φ angle), which makes a certain angle $\theta = 0^\circ, 90^\circ$ with H, Mn^{2+} HFS lines do undergo complicated changes which are repeated every 120° (Figure 4). The amplitude of the HFS line two-peak splitting value variation vs. φ angle increases at $T \rightarrow T_c$.

The improper ferroelastic phase transition occurs at cooling of the undoped samples at 316 ± 0.3 K. The value of the temperature hysteresis of transition is ~ 3 K. In phase IV, the EPR spectra of Mn^{2+} and Ni^{2+} correspond to six spatially inequivalent rhombohedral centres, two of which came from orientational domain. 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 K (250 K): $g = 2.0009 \pm 0.0003$, $D = -253 \pm 1$, $|E| = 36 \pm 5$, $a = 8 \pm 1$, $A_{\perp} = A_{\parallel} = -92 \pm 1$ ($g = 2.25 \pm 0.01$, $D = 2,26 \pm 0.02$, $|E| = 0,25 \pm 0,05$, where D , E , A and a are presented in the units of 10^{-4} cm^{-1}). The above type of the 3d-ion EPR spectra at $T > T_{11} (< T_c)$ is characteristic for the phase $R\bar{3} (P2_1/c)$ in studied crystals.⁹⁻¹¹

DISCUSSION

In discovered "intermediate" phases II and III of MFGH crystals, Mn^{2+} and Ni^{2+} EPR lines have the form, whose temperature and angular dependences characteristic for dielectric crystal incommensurate (IC) phases. Temperature dependence

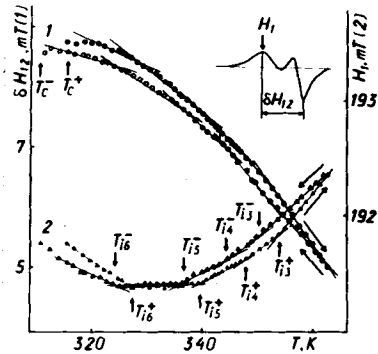
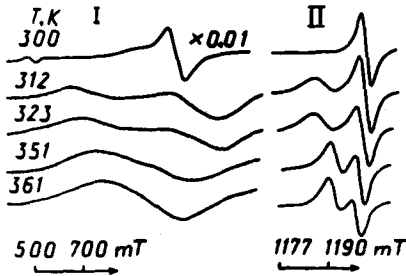


FIGURE 2 The Ni^{2+} EPR line shape in MFGH crystals at $H_{11}c$ (the Q-band) vs. temperature (I). For comparison, the evolution of the Mn^{2+} (natural abundance) EPR low field HFS line shape of the same crystal is shown (II).

FIGURE 3 The value of the Mn^{2+} EPR low field HFS line low field peak position H_1 and splitting δH_{12} in MFGH crystals at $H_{11}c$ (the X-band) vs. temperature.

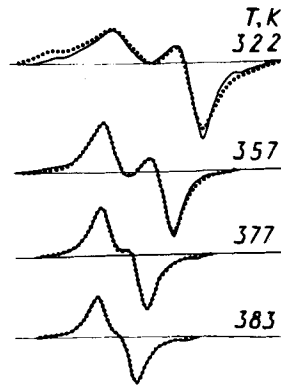
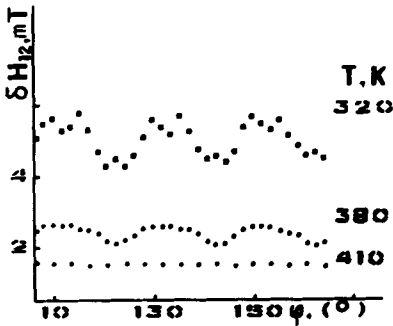


FIGURE 4 The value of the Mn^{2+} EPR low field HFS line splitting H_{12} in MFGH crystals vs. φ angle (the X-band, $\theta = 50^\circ$).

FIGURE 5 Comparison between the experimental (solid line) and the simulated (pointed line) Mn^{2+} EPR low field HFS line shapes in MFGH crystals (the X-band, $H_{11}c$). The simulated line shapes were obtained using the corresponding values of the parameters from Table I.

of the Mn^{2+} line shape in the phases II and III have been interpreted in terms of the Blinc's model.¹³

The calculations of the Mn^{2+} HFS line shape in phases II and III are carried out in the assumption of the one-dimensional lattice modulation which is given by

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

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

$$H = H_0 + h_1(x)\cos a(x) + h_2(x)\cos a(x) + \dots$$

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

The overall line shape $F(H)$ can then be given by analogous to Blinc¹³ by the distribution density of the lines

$$f(H) = \frac{\text{const.}}{|-\sin a[\Delta^2 + \cos^2 3a]^{1/2} + b \cos a \cdot \cos 3a \cdot \sin 3a| dH/dU} \quad (1)$$

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

$$F(H) = \int L(H - H_x) \cdot f(H_x) dH_x.$$

In Equation (1) b is the numerical parameter and Δ connected with the soliton density n_s as $n_s = \pi/2K(1 + \Delta^2)^{-1/2}$, where K is the complete elliptic integral of the 1-st kind. The line shape computer simulation results are given in Figure 5 and in Table I.

TABLE I Values of the Mn^{2+} EPR low field HFS line shape modulation parameters in MFGH crystals.

T(K)	h_1 (mT)	h_2 (mT)	dW (mT)	b	Φ_0 , rad.	n_s
322	0,12	-8,10	1,38	0,415	-0,655	0,66
357	2,83	-0,24	1,62	0,015	-0,113	0,65
377	1,60	-0,2	1,45	0,005	0	0,62
383	1,35	-0,15	1,35	0	0	1

As is shown in Figure 5, 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 in phase II and III.

The availability of dependence of Mn^{2+} line shape in phases II and III on the angle φ allows us 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. The above disorientation of the cubic crystalline field axes is, probably, connected with the modulation of the rotation angle of the complex around the c - axis relative to the position in the paraelastic (P) phase. It is likely that this angle is an order parameter of the P-IC phase transition and it determines the value of the trigonal distortion modulation.

Below T_{12} , n_s is lower than one and decreases at lower temperatures, i.e., the crystal consist of two types of areas: one with a lattice displacement modulation (solitons) and the other without it (domains). The number of solitons and the size of domains are functions of temperature.

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