INCOMMENSURATE AND INHOMOGENEOUS PHASES IN IMPROPER FERROELASTIC MgSiF$_6$·6H$_2$O: Mn$^{2+}$ STUDIED BY EPR

P.G. SKRYLNIK and A.M. ZIATDINOV*

Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences.
159, Prosp. 100-letiya, 690022 Vladivostok, Russia

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The results of EPR study of inhomogeneous and incommensurate phases in improper ferroelastic crystals MgSiF$_6$·6H$_2$O·Mn$^{2+}$ are presented. On the basis of analysis of temperature and angular dependences of experimental parameters and numerical calculations the conclusion has been drawn that at $T_{i1}=370\pm0.3$ K considered crystals undergo transition to structurally incommensurate phase and the order parameter of this transition may be angle of Mg[H$_2$O]$_6^{2+}$ octahedra rotation around crystal C$_3$ axis. From $T_{i1}$ to $T_{i2}=343\pm0.3$ K the incommensurate phase evolve according to classical complete scenario: origin of incommensurate structure with plane-wave modulation at $T_{i1}$, appearance of structural phase soliton lattice with temperature decrease, and, finally, abrupt decrease in soliton density at $T_{i2}$ down to values $\approx0.1$. The assumption was expressed that at $T_{i2}$ the crystals investigated undergo phase transition from incommensurate phase to another inhomogeneous phase, in which studied crystals consist of two types of regions characterized by homogeneous and inhomogeneous structural organization. The performed calculation of spectral density functions has shown that the structure of former regions almost does not change with temperature variation whereas that of latter ones considerably modifies when the temperature tends to the improper ferroelastic phase transition temperature $T_C=296.5\pm0.3$ K.

Keywords: incommensurate phase; phase transitions; EPR; improper ferroelastic; MgSiF$_6$·6H$_2$O

1. INTRODUCTION

The crystals MgSiF$_6$·6H$_2$O·Mn$^{2+}$ belong to family ABF$_6$·6H$_2$O (where A and B are divalent metal and tetravalent element, respectively). They possess a wide variety of physical properties and are the traditional objects for EPR spectroscopy\[1-25\]. In these compounds complex ions A[H$_2$O]$_6^{2+}$ and [BF$_6$]$^{2-}$ octahedra

* Corresponding Author.
form rhombohedrally distorted CsCl-type lattice and can be distributed between two orientations around the 3-fold axis\textsuperscript{[26–38]}. Many compounds of this family undergo improper ferroelastic phase transition from the high-temperature rhombohedral phase to the low-temperature monoclinic phase\textsuperscript{[8,9,16,28,30–38]}. Depending on the structure of high-temperature phase ABF\textsubscript{6}.6H\textsubscript{2}O crystals may be divided into two groups. The first one, for instance, contains fluorosilicates of Co, Ni and Zn\textsuperscript{[29,34]}, in which crystals at room temperature disordered structure with space group \textit{R̅3} forms, and two different orientations of [BF\textsubscript{6}]\textsuperscript{2–} ions rotated with respect to each other by some angle around 3-fold crystal axis are present. The fluorosilicates of Mg, Fe and Mn belong to the second group. The presence of superstructure reflections at room temperature for these crystals, in contradiction to the structural model by Hamilton\textsuperscript{[27]} and Syoyama & Osaki\textsuperscript{[28]}, was the reason for Chevrier \textit{et al.}\textsuperscript{[31,32,35–38]} to introduce space group \textit{P3} for the proper treatment. Chevrier \textit{et al.}\textsuperscript{[31,32,35–38]} also supposed two type of domains with different orientations of complex ions, connected with pseudomirror plane (11.0). The analysis of superstructure reflections shows that in the case of Mg and Mn compounds the sizes of domains are near equal and quite large (~300 Å)\textsuperscript{[31,36]}, whereas in Fe fluorosilicate their sizes are temperature dependent\textsuperscript{[32]}. The structural model by Chevrier and Jehanno\textsuperscript{[31]} for MgSiF\textsubscript{6}.6H\textsubscript{2}O above 300 K (space group \textit{P3}) accounts for observed superstructure reflections with periodic antiphase structure, built of ordered low-temperature monoclinic unit cells (space group \textit{P2}\textsubscript{1}/c) with integer period.

After structurally inhomogeneous phase in MgBF\textsubscript{6}.6H\textsubscript{2}O (B=Si, Ge, Ti) crystals, existing between their rhombohedral paraelastic phase and monoclinic ferroelastic one, had been discovered by Ziatdinov \textit{et al.}\textsuperscript{[12–15]} the most attention of researchers\textsuperscript{[12–15,17–25]} was attracted to the nature of this phase (further in this paper called as “intermediate” phase). At present, for the interpretation of experimental data the different models of “intermediate” phase in these crystals have been suggested: some modifications of structural-incommensurate model\textsuperscript{[12,17–19]}, model of static and dynamic disordered structure fragments\textsuperscript{[22,23]}, and domain model\textsuperscript{[25]}. In this paper, on the basis of analysis of MgSiF\textsubscript{6}.6H\textsubscript{2}O:Mn\textsuperscript{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\textsuperscript{[12,19]}, but is free of some disadvantages of models formerly proposed with assuming incommensurate modulation of lattice displacements in mentioned crystals\textsuperscript{[12,17–19]}. Presented model agrees with data on MgSiF\textsubscript{6}.6H\textsubscript{2}O crystals obtained by other physical techniques\textsuperscript{[20,28,30,31,33,39,40]} and allows much better describing the experimental Mn\textsuperscript{2+} EPR spectra in their “intermediate” phase.
2. EXPERIMENTAL

The EPR measurements have been carried out using X-band spectrometer ESR-231 (production of Germany) and Q-band spectrometer RE-1308 (production of Russia) in three mutually perpendicular crystal planes. The orientation of single crystal with respect to the external magnetic field $H_0$ direction was varied with two-axes goniometer system.

Single crystals of MgSiF$_6$·6H$_2$O doped with ~0.1% Mn$^{2+}$ - ions have been grown from the aqueous solution at room temperature according to technique[41]. The fluorosilicates were purchased commercially. The trigonal C$_3$-axis in most of the samples in these experiments was readily identified by inspection and then it was identified as the [111] direction in cubic coordinates.

The temperature range of experiments was 100±380 K. The crystal temperature varying was carried out by changing the temperature of gaseous nitrogen flow passing throw the quartz dewar containing the crystal investigated. To monitor temperature the copper-constantan thermocouples with base point at the ice melting temperature have been used. The accuracy of monitoring and stability of temperature was ~0.3 K and ~0.1 K/hour, respectively.

3. RESULTS

At temperature above $T_{\text{i1}}=370±0.3$ K and $H_0 \parallel C_3$ the EPR spectrum of MgSiF$_6$·6H$_2$O:Mn$^{2+}$crystals consists of $5 \times 6$ hyperfine structure (HFS) lines. The analysis of angular dependence of spectrum in different planes demonstrates that it is of axial character with $z$-axis being parallel to C$_3$- axis and corresponds to one type of Mn$^{2+}$ centres. The Mn$^{2+}$ (3d$^5$, S=5/2, I=5/2) EPR spectrum is described by conventional axial spin Hamiltonian with the parameters as follows ($T=372$ K):

$$g_\perp \cong g_{||} = 2.0009 \pm 0.0003, \quad D = (-258 \pm 1) \times 10^{-4} \text{ cm}^{-1},$$

$$a = (8 \pm 0.5) \times 10^{-4} \text{ cm}^{-1}, \quad A_\perp \cong A_{||} = (-90 \pm 0.5) \times 10^{-4} \text{ cm}^{-1},$$

This Mn$^{2+}$ spectrum is typical of rhombohedral (R3) phase of the crystals of considered family[2,7,9,16].

With temperature decrease below $T_{\text{i1}}$ all HFS spectral lines at first smoothly broaden (the low field HFS line has been chosen for detailed lineshape analysis), and then, excluding central set lines, corresponding to the $l\pm1/2$, $m\rightarrow$ transitions, gradually transform into the two-peak ones (Figure 1). However, in spite of substantial changes in Mn$^{2+}$ HFS lineshapes below $T_{\text{i1}}$, EPR spectrum...
FIGURE 1 The temperature evolution of the Mn$^{2+}$ EPR low field HFS line for MgSiF$_6$·6H$_2$O:Mn$^{2+}$ crystals at X-band and $H_0C_3$. Dots and solid lines correspond to experimental and theoretical spectra, respectively.

symmetry and its principal axis direction remain the same. With temperature increase the reversed evolution of the Mn$^{2+}$ EPR spectrum is observed. The temperature of transition from one spectrum type to another does not depend on
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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 $T_{i2} = 343.0 \pm 0.3$ K a step-wise changes with temperature hysteresis $\sim 1$ K both in EPR spectra parameters and HFS lineshapes are observed (Figures 1 and 2). It is worth to note that changes in HFS lineshapes at $T_{i2}$ are of qualitative character: spectral lines transform into the two distinct components with different linewidths; one component broadens with temperature decrease whereas another almost does not change. However, despite substantial HFS lineshape changes below $T_{i2}$, EPR spectrum symmetry and its principal axis direction remain invariable.

![FIGURE 2 The temperature dependence of the Mn$^{2+}$ EPR low field HFS lineshape parameters for MgSiF$_6$·6H$_2$O·Mn$^{2+}$ crystals at Q – band and $\mathbf{H}_0\parallel C_3$. 1- $\Delta H_1$, 2- $\Delta H_{12}$. The black and white dots refer to parameters at heating and cooling of the crystals, respectively. Definitions of the studied lineshape parameters are presented too.](image_url)

The temperature decrease below $T_{i2}$ leads to the sequence of step-wise changes in the slope of temperature dependences of broad component lineshape parameters.
FIGURE 3 Angular dependences of the value of Mn$^{2+}$ EPR low field HFS line splitting $\Delta H_{12}$ for MgSiF$_6$-6H$_2$O:Mn$^{2+}$ crystals at rotating of the sample around the $C_3$-axis (along the $\phi$-angle), which makes the angle $\theta=50^\circ$ with $H_0$. The X-band
ters (Figure 2), though these changes are small by comparison with those at $T_{i2}$. The temperature values of slope discontinuities $T_{in}$ $(n=2\pm6)$ depend on direction of temperature change and vary from sample to sample within 4 K, but they occur at practically the same values of lineshape parameters.

At $T_C=296.5\pm0.3$ K the MgSiF$_6$-6H$_2$O crystals undergo the first order phase transition to monoclinic phase with the temperature hysteresis ~3 K. Below $T_C$ the EPR spectrum corresponds to six spatially inequivalent rhombic centres. At $H_0|C_3$ the positions and linewidths of the Mn$^{2+}$ HFS lines immediately after phase transition are approximately the same as for corresponding narrow component of Mn$^{2+}$ HFS lines in inhomogeneous phase immediately before phase transition (Figure 1).

The investigation of the MgSiF$_6$-6H$_2$O crystal with polarization microscope, analysis of angular dependences and variation of relative intensities (from sample to sample and from experiment to experiment for the sample) demonstrate that the crystal under study below $T_C$ consists of orientational domains of three kinds connected with each other by $120^\circ$ rotation around $C_3$ and each domain...
contains two inequivalent $\text{Mn}^{2+}$ sites. Therefore, the MgSiF$_6$·6H$_2$O crystal is improper ferroelastic at $T=T_C$.

Below $T_C$ z-axis of each $\text{Mn}^{2+}$ centre is deviated by angle $(8\pm2)^\circ$ with respect to $C_3$ axis above $T_C$. The EPR spectra of all spatially inequivalent $\text{Mn}^{2+}$ centres are in good agreement with conventional rhombic spin Hamiltonian with the following parameters ($T=290$ K):

\[
\begin{align*}
g_\perp &\approx g_{||} = 2.0010 \pm 0.0005, \\
 D &= (-275 \pm 2) \times 10^{-4} \text{ cm}^{-1}, \quad |E| = (30 \pm 5) \times 10^{-4} \text{ cm}^{-1}, \\
 a &= (8 \pm 2) \times 10^{-4} \text{ cm}^{-1}, \quad A_\perp \approx A_{||} = (-92 \pm 1) \times 10^{-4} \text{ cm}^{-1}.
\end{align*}
\]

The number of $\text{Mn}^{2+}$ sites and symmetry of individual magnetic ion EPR spectrum in single crystal MgSiF$_6$·6H$_2$O:$\text{Mn}^{2+}$ below $T_C$ agree with the data of structural investigation of this crystal, having reported space group $P2_1/c^{[28,30,31,33]}$ and three kinds of orientational domains.
Within the temperature range from $T_C$ to $T_{i1}$, at rotation of single crystal around $C_3$ (varying azimuthal angle $\phi$) which makes a certain angle $\theta \neq 0^\circ$, $90^\circ$ with $H_0$ direction, the $120^\circ$-angular dependence of Mn$^{2+}$ EPR lineshape has been observed (Figure 3). The amplitude of these variations in lineshape parameters increases with temperature decrease (Figure 3).

At $T<T_{i2}$, the low-field broad component of HFS line narrows, when the polar angle $\theta$ tends to "magic" angle value (Figure 4). Simultaneously, the high-field component of HFS line broadens (Figure 4).

4. DISCUSSION

The shape of Mn$^{2+}$ HFS lines in MgSiF$_6$·6H$_2$O:Mn$^{2+}$ (presence of two edge singularities with spectral continuum between them) and their evolution at temperature decrease from $T_{i1}$ to $T_{i2}$ (increase in difference between magnetic field values, corresponding to edge singularities with continuum conservation) are characteristic of magnetic resonance spectra of incommensurate structures with one-dimensional modulation of lattice displacements [42,43]. Taking into account, that symmetry and principal axis direction of Mn$^{2+}$ EPR spectrum for MgSiF$_6$·6H$_2$O:Mn$^{2+}$ from $T_{i1}$ to $T_C$ do not change, and $\theta$-angle dependence of lineshape and spread of inhomogeneous HFS lines observed below $T_{i1}$ may be reached only at presence of axial fine structure parameter variation, one may conclude, that in the crystals investigated at $T<T_{i1}$ the incommensurate modulated lattice displacement is the trigonal distortion of [Mg(H$_2$O)$_6$]$^{2+}$ octahedra.

In general case incommensurate one-dimensional spatial modulation of the lattice displacements is determined by the following equation [44]:

$$u(x) = A(x) \cos[\varphi(x)],$$

(1)

where $A(x)=A_0+\delta A(x)$ is amplitude and $\varphi(x)=\Phi(x)+\Phi_0$ ($\Phi_0$ is the initial phase shift) is phase of the lattice displacements. In the plane-wave regime of modulation $\delta A=0$ and $\varphi(x)$ is a linear function of spatial variable $x$ (along the modulation direction). As a rule, with temperature decrease a transition from the plane-wave regime to the multisoliton one occurs [42,43]. Moreover, phase solitons appear first, as consequence of the fact, that phase (transversal) susceptibility with respect to distortion of modulation wave is much greater than amplitude (longitudinal) one [44]. For the phase solitons $A=A_0$ and phase function $\varphi(x)$ becomes non-linear function expressed with the solution of one-dimensional sine-Gordon equation:
\[
\frac{\partial^2 \Phi(x)}{\partial x^2} = -\alpha^2 \sin[p \Phi(x)], \quad (2)
\]

where \( p \) is the superstructure multiplicity, \( \alpha \) is the constant determined by the soliton density \( n_S \). According to Blinc et al., \( n_S = 2\pi/(p d \varphi'_{\text{max}}) \), with \( d \) being equal to the distance between solitons, \( \varphi'_{\text{max}} \) - maximum value of the phase function derivative. With further decrease of temperature the amplitude variations \( \delta A(x) \) may become significant, resulting in the amplitude solitons appearing. At \( \delta A \ll A_0 \) function \( A(x) \) is determined by the approximate expression:

\[
\frac{\partial A(x)}{\partial x} \approx -C \frac{\partial^2 \Phi(x)}{\partial x^2}, \quad C > 0. \quad (3)
\]

It is worth to note that, in many experimental cases, amplitude solitons are not observed and multisoliton lattice may be well described in the frameworks of \( A(x) = A_0 \) approximation, i.e. within phase solitons approximation. The soliton density decreases with temperature decrease down to temperature of transition to commensurate state (“lock-in” transition). However, within some temperature range below \( T_C \) soliton density may remain a non-zero value.

In incommensurate phase the resonance magnetic field \( H_r \) for the certain paramagnetic centre is a function of the small lattice displacements parameter \( u(x) \). It may be expanded into the power series:

\[
H_r = H_{r0} + h_1(x) \cos[\varphi(x)] + h_2(x) \cos^2[\varphi(x)] + \ldots, \quad (4)
\]

where \( h_i \) are the constant values for the plane-wave and phase soliton regimes. Resulting spectrum shape may be calculated by integration on possible \( H_r \) values with using some single line shape (Lorentzian in most cases) for certain \( H_r \).

In the crystals under investigation every paramagnetic ion is situated on the symmetry axis and inversion centre simultaneously. Therefore, according to symmetry consideration, at \( H_0 | C_3 \), only even terms in Equation (4) should be held. This conclusion may be drawn from the microscopical consideration as well. Because of the special importance of correct choice of the expansion Equation (4) for the subsequent experimental data analysis, this consideration is presented below in details.

The appearance of \( \phi \)-angle dependence of EPR lineshape in \( \text{MgSiF}_6 \cdot 6\text{H}_2\text{O}:\text{Mn}^{2+} \) crystals below \( T_{i1} \) (Figure 3) is an evidence for appearance of disorientation of cubic crystal field axes on different \( \text{Mn}^{2+} \) ions, i.e. rotation of complex ions \( \text{Mg}[\text{H}_2\text{O}]_6^{2+} \) around trigonal axis in incommensurate phase. The amplitude of this disorientation increases at temperature decrease. Besides, in ferroelastic phase within each orientational domains two spatially inequivalent complexes \( \text{Mg}[\text{H}_2\text{O}]_6^{2+} \), rotated with respect to each other around \( C_3 \) axis by the certain angle, are present. The facts cited allow to conclude that angle
FIGURE 5 Dependence of Mn$^{2+}$ EPR lineshape parameter $\Delta H_{12}$ on $\phi$-angle for MgSiF$_6$H$_2$O:Mn$^{2+}$ crystals. Dots (1) correspond to experiment (the X-band; $H_{\|}$C$_3$; T=360 K). Solid lines correspond to calculated dependences (2 - model of quadratic modulation of D parameter $\delta D=\delta_2 \phi^2$, $\phi(x)=\delta \phi_1 \cos(x)$, $\delta \phi_1=7^\circ$, $\delta_2=0.121 \times 10^{-4}$ cm$^{-1}$/degree$^2$; 3 - model of two discrete octahedra orientation: $\delta \phi=5^\circ$; 4 - model of linear modulation of D parameter $\delta D=\delta_1 \phi$, $\phi(x)=\delta \phi_1 \cos(x)$, $\delta \phi_1=1.2^\circ$, $\delta_1=2.470 \times 10^{-4}$ cm$^{-1}$/degree$)$

$\delta \phi$ of octahedra Mg[H$_2$O]$_6^{2+}$ rotation around trigonal axis with respect to their position in paraelastic phase can be a primary order parameter of paraelastic -
incommensurate phase transition in MgSiF$_6$·6H$_2$O. (Obviously, the trigonal distortion of octahedra Mg[H$_2$O]$_6^{2+}$ with respect to their distortion in paraelastic phase can not be a primary order parameter of this transition, because such assumption leads to at least two Mg[H$_2$O]$_6^{2+}$ configurations with different values of trigonal distortion (and D values) in ferroelastic phase, which does not agree with the X-ray$^{[28,31]}$, and EPR$^{[10-12,17-19]}$ data.)

Further, one may suppose that rotation of octahedra around trigonal axis, as consequence of change in lengths and orientations of hydrogen bonds, is accompanied by the change in trigonal distortion of complexes and, therefore, by variation of the fine structure parameter, i.e. D=D$_0$(T)+AD(δφ), where D$_0$(T) is a value of fine structure parameter for complex not distorted by modulation wave, AD(δφ) is a contribution to fine structure parameter by modulated distortion. For the reasons of symmetry (the presence of symmetry axis and inversion centre), one should draw a conclusion that AD(δφ) is an even function. Hence, with neglecting modulation of other spin Hamiltonian parameters, Equation (4) at H$_0$/C$_3$ should contain only even terms (in this orientation H$_r$ does not directly depend on crystalline cubic axes orientation). The conclusion made is consistent with the data of the angular φ – dependence of the Mn$^{2+}$ HFS lineshape analysis also. Below T$_{11}$ this dependence may be qualitatively described only within the frameworks of the model of quadratic modulation of D parameter connected with trigonal lattice distortions (Figure 5 demonstrates that the model of linear modulation of D parameter, as well as the model of two discrete octahedra orientation result in clear qualitative differences from experimental dependence).

Therefore, both from general symmetry consideration and from microscopic one, for the crystal investigated at H$_0$/C$_3$ Equation (4) is reduced as follows:

$$H_r = H_{r0} + h_2(x) \cos^2[\varphi(x)] + h_4(x) \cos^4[\varphi(x)] + \ldots$$

Using Equation (5) we were able to describe the Mn$^{2+}$ HFS lineshapes well within the temperature range from T$_{11}$ to T$_{12}$ (Figure 1). Resulting positions of spectral singularities are shown in Figure 6. Moreover, close to T$_{11}$ the HFS lineshape is similar to the symmetric one, and, as consequence, h$_4$ value is small and spectra may be described with good accuracy with taking into account quadratic modulation term only (Figure 7). The h$_2$ values at T→T$_{11}$ is successfully approximated with power function:

$$h_2(T) = a(T_{11} - T)^{2\beta},$$

where $a=0.41$ mT, $\beta=0.36\pm0.03$ (Figure 7, inset). The $\beta$ value calculated is in a good agreement with the results of theoretical consideration within the frameworks of 3d-XY model ($\beta=0.345\pm0.002^{[45]}$). Taking into account that h$_2\sim$(δφ)$^2$, this fact is an indirect evidence for the correctness of choice of paraelastic –
incommensurate phase transition order parameter and adopted model of incommensurate modulation of lattice displacements.

At $T \rightarrow T_{i2}$ a good describing of experimental spectra is possible only with introducing the phase solitons with superstructure multiplicity parameter $p = 3$ (at cooling below $T \approx 360$ K plane-wave regime of modulation transforms into the multisoliton one). In general, if direction of one-dimensional modulation coincides with the direction of multiple increase of unit cell in ferroelastic (ferroelectric) phase with respect to that of paraelastic (paraelectric) phase, value of $p$ is assumed to be equal to this multiplicity\cite{42}. According to the structural data\cite{28,30,31,33} in MgSiF$_6$·6H$_2$O unit cell size is doubled in direction of monoclinic $b_m$ axis (which is perpendicular to the trigonal axis in paraphase) in ferroelastic phase compared to paraelastic phase value. However, the calculation carried out for multisoliton regime with $p=2$ results in lineshapes being qualitatively different from experimental spectra. At that, introducing phase solitons with $p=3$ provides well description of experimental spectra near $T_{i2}$ (Figure 1).
From our point of view, this contradiction is explained with assuming that at transition to incommensurate phase at first incommensurate multislon lattice appears with $p=3$ and modulation along $C_3$ axis, not with $p=2$ and modulation along $b_m$ axis. This supposition is indirectly proved by the results of Raman spectroscopy investigation of related ferrous and manganese fluorosilicates crystals\cite{46}, having reported that above $T_C$ experimental data agree better with $P\overline{3}$ crystal symmetry group with $Z=3$ and direction of unit cell multiplication coinciding with $C_3$ axis, not $R\overline{3}$ group with $Z=1$. The reason for unit cell doubling in direction of monoclinic $b_m$ axis in ferroelastic phase is, to our opinion, the existence of two antiphase modulation waves along $C_3$ axis in intermediate phase. Therefore, the rotation angles of octahedra in adjacent columns (which are parallel to $C_3$) are characterized by equal absolute values (which result in equal octahedra distortions along $C_3$ and variations in $D$ parameter) and by opposite signs.

According to the data of theoretical studies of classical incommensurate systems at $T\rightarrow T_C$ significant amplitude variations of the order parameter may result
in the amplitude solitons appearing\textsuperscript{[44]}. But below $T_{i2}$ in crystals investigated the temperature evolution of Mn$^{2+}$ EPR lineshape qualitatively differs from that of magnetic resonance spectra of those systems. In particular, in classical model of incommensurate phases both calculations performed with taking into consideration the amplitude solitons and without them result in significant step-wise decrease in soliton density down to $n_S \approx 0.1$ at $T_{i2}$ (Figure 8). Besides, the calculations of spectral lineshapes taking into account amplitude solitons effect have not led to successful description of experimental spectra (Figure 9, curve 1).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{soliton_density.png}
\caption{The temperature dependence of soliton density $n_S$ for the model taking into account variation of $T^{-1}$ over the Mn$^{2+}$ EPR low field HFS line for MgSiF$_6$·6H$_2$O:Mn$^{2+}$ crystals. The X-band.}
\end{figure}

For the theoretical describing of Mn$^{2+}$ HFS lineshape from $T_{i2}$ to $T_C$ the following approaches have been tested by us.

Theoretical\textsuperscript{[43]} and experimental\textsuperscript{[47,48]} studies of spin-lattice relaxation rate $T_1^{-1}$ in incommensurate systems demonstrate that $T_1^{-1}$ may considerably vary over the incommensurate spectral distribution. Amplitude of this variation increases with temperature decrease. Authors of aforementioned papers account for $T_1^{-1}$ variation over incommensurate continuum by the difference in contributions of phasons and amplitudons to the effective spin-lattice relaxation rate.
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FIGURE 9 The comparison of theoretical spectra, calculated within frameworks of different models (solid lines), with experimental spectrum (dots) for MgSiF₆·6H₂O:Mn²⁺ at 317 K (the X-band, \( H_0 \) C₃). (1 – model of incommensurate modulation with amplitude solitons: \( h_2 = 6.58 \text{ mT} \), \( h_4 = -0.29 \text{ mT} \), \( W_4 = 0.87 \text{ mT} \), \( n_s = 0.096 \), parameter of amplitude modulation (amplitude variation maximum) \( \delta A = 50\% \); 2 – domain model by W. Zapart and M.B. Zapart²⁵: \( h_2 = 5.46 \text{ mT} \), percentage contribution of domain wall volume with respect to the crystal volume is 29.5\%, \( W_d = 0.76 \text{ mT} \); 3 – model of 3D incommensurate modulation: \( h_2 = h_2 = h_2 = 1.08 \text{ mT} \), \( W = 0.85 \text{ mT} \); 4 – model of incommensurate modulation with variation of spin-lattice relaxation rate over spectrum: \( h_2 = 5.82 \text{ mT} \), \( h_4 = 0.58 \text{ mT} \), \( n_s = 0.094 \), \( W_0 = 1.38 \text{ mT} \), \( W_2 = 0.74 \text{ mT} \), \( \delta W = 0.34 \text{ mT} \); 5 – model of coexisting systems of domains and disordered soliton-like regions assuming Gaussian distribution of resonance magnetic field within latter regions: \( \sigma_T = 0.997 \text{ mT} \), \( W = 0.811 \text{ mT} \).
Basing on these results we undertook an attempt to describe experimental line-shapes with assuming the dependence of $T_1^{-1}$ on resonance magnetic field in magnesium fluorosilicate too. The calculations have been carried out assuming the parabolic dependence of EPR linewidth $W$ on resonance magnetic field (Figure 10, inset). Within the frameworks of this model we have reached both some improvement of experimental spectra describing close to $T_C$ (Figure 1) and above $T_{i2}$. However, near $T_C$ ($T_C<T<T_C+10$ K) inexplicably large variation of linewidth over spectrum is necessary for the satisfactory approximation of experimental data (Figure 10). We should note, that within the frameworks of considered model introducing the quartic term into the Equation (5) does not result in considerable improvement of experimental spectra fitting, whereas without consideration of phase solitons even qualitative description may not be reached.

Further, within the frameworks of aforementioned model, we attempted to reach better fitting of experimental spectra near $T_C$ ($T_C<T<T_C+10$ K) with reasonable values of linewidth variation over spectrum by introducing the amplitude parameters $W_0$, $W_2$, and $\delta W$ calculated for the Mn$^{2+}$ EPR low field HFS line for MgSiF$_6$·6H$_2$O·Mn$^{2+}$ crystals at the X-band and $H_0$C$_3$. Parameters $W_0$ and $W_2$ indicate the value of Lorentzian linewidth at the points of incommensurate spectral singularities, $\delta W$ is a deviation of proposed parabolic dependence $W(H)$ from linear function (inset).
solitons into calculations. However, improvement in lineshape fitting have not been reached at any values of modulation of order parameter amplitude. Experimental data on the θ-angular dependence of EPR lineshape at T<T_{i2} (simultaneous narrowing and broadening of single inhomogeneous and single narrow components of HFS line, respectively, at θ-angle increase (Figure 4)) and, as it will be demonstrated below, appearance of inner structure of broad component at T→T_C also do not confirm the supposition about the variation of linewidth over spectrum. Therefore, phenomenon of variation of linewidth may be engaged in spectrum simulation only near T_{i2}.

Evolution of incommensurate phase of crystal MgSiF_6·6H_2O from T_{i1} to T_{i2} according to classical complete scenario (origin of incommensurate structure with plane-wave modulation at T_{i1}, appearance of structural soliton lattice with temperature decrease, and, finally, abrupt decrease in soliton density at T_{i2}) and impossibility to describe Mn^{2+}HFS spectral lineshape evolution in this crystal below T_{i2} in the frameworks of known ideas about incommensurate structures lead us to conclusion that T_{i2} is temperature of transition to inhomogeneous phase with structure organization being different from incommensurate phase.

As possible model of crystal structure below T_{i2} a reversible division of crystal at this temperature into subsystem of microscopic domains and subsystem of disordered (single-soliton-like) regions may be introduced. Under such assumption about crystal organization below T_{i2}, broad component of HFS line should be referred to soliton-like regions and narrow component to domains, respectively. This conclusion is based upon the following experimental data. The linewidth of narrow component almost does not change with temperature variation, increases with θ angle increase, is approximately equal to the corresponding HFS linewidth in ferroelastic phase. The linewidth of broad component considerably depends on temperature, decreases with θ angle increase, is much greater than the corresponding HFS linewidth in ferroelastic phase and is absent in ferroelastic phase. We should note, that above-stated model agrees also with the data of structural investigations reporting that the crystals immediately above T_C consists of "stripe" domains with low-temperature monoclinic unit cell. Moreover, recently, Torii et al. reported possible presence of submicroscopic domains in manganese fluorosilicate crystals related to MgSiF_6·6H_2O crystals. The calculated lineshape using the Gaussian distribution of parameter D as appropriate for disordered regions is presented in Figure 9 (curve 5), which shows well description of experimental spectra. At the same time, the HFS lineshape of Mn^{2+} in MgSiF_6·6H_2O:Mn^{2+} calculated in the frameworks of the W. Zapart and M.B. Zapart model of periodic antiphase domain structure with the temperature dependent width of antiphase domains (in other words, in assumption that domains and domain walls constitute a single system) are far
from one observed really within temperature interval considered (Figure 9, curve 2). Besides, this model contradicts to the X-ray diffraction data for MgSiF$_6$·6H$_2$O crystals\(^{[31]}\), according to which the sizes of antiphase domains in these crystals do not depend on temperature.

With object of obtaining the data on structure and temperature evolution of soliton-like regions in MgSiF$_6$·6H$_2$O below $T_{i2}$ we have calculated spectral density functions $p(H)$ (according to technique\(^{[51]}\)) and corresponding distribution functions $p(D)$ for the experimental spectra at different temperatures $T<T_{i2}$ (Figure 11). The calculations provide evidence that low-field broad component of HFS line shows origin of inner structure at $T^* \approx 307$ K. This temperature is close to $T_{i6}$ (Figure 2) and to the temperature ($T \approx 305$ K) of phase transition observed by NMR in studied crystals\(^{[40]}\). These facts show, that at decrease of temperature below $T_{i2}$ in soliton-like regions the structural ordering takes place and $T_{in}$ (n=3+6) may be the temperatures of structural phase transitions in these regions.

![Figure 11: Distribution functions $p(D)$ for the axial fine structure parameter $D$ of the Mn$^{2+}$ EPR spectra for MgSiF$_6$·6H$_2$O:Mn$^{2+}$ crystals at various temperatures at the X-band and $H_0C_3$. The structure of $p(D)$ distribution corresponding to the broad low-field component of Mn$^{2+}$HFS line at 300 K is presented in inset.](image)
As Figure 11 demonstrates, below $T^*$ the low field component of $p(D)$ is similar to spectral distribution functions for the spectra of multidimensional modulation systems$^{[43]}$. But according to our calculations, using the model treating the spectrum as consisting of two distinct component, and assuming that narrow component corresponds to domain regions and broad one to the soliton-like regions with three-dimensional modulation (3D and 2D modulation result in similar lineshapes, but former provides better description of experiment) of order parameter experimental spectra may be fitted better (Figure 9, curve 3), than within the frameworks of model with amplitude solitons (Figure 9, curve 1) and model of single domains and domain walls system (Figure 9, curve 2), but significant worse than in the frameworks of model of coexisting systems of domains and disordered soliton-like regions (Figure 9, curve 5).

Thus, the only model of crystal MgSiF$_6$·6H$_2$O:Mn$^{2+}$ structure from $T_{i2}$ to $T_C$ of considered ones in this paper, which result in well approximation of experimental Mn$^{2+}$ EPR spectra, is the model of coexisting systems of domains and disordered soliton-like regions.

Note, that X-ray diffraction study of MgSiF$_6$·6H$_2$O crystals at room temperature$^{[31]}$ have not revealed disordered regions of crystals. We suppose that such failure of X-ray diffraction method in crystals investigated results from using the single crystal technique, whereas technique for amorphous samples probably would be more successful. The EPR method has advantages with respect to structural methods such as X-ray diffraction since it is exceptionally sensitive to local structure of samples investigated. This feature enabled us to detect and study disordered regions in MgSiF$_6$·6H$_2$O crystals and their transformation with temperature variation.

5. CONCLUSION

In the present paper, with basing on EPR data for MgSiF$_6$·6H$_2$O:Mn$^{2+}$ single crystals, structural organization motifs for their inhomogeneous phases between monoclinic and rhombohedral ones ($T_C=296.5\pm0.3$ K<$T<T_{i1}$=$370\pm0.3$ K), are proposed. It is shown that at $T_{i1}$ considered crystals undergo transition to structurally incommensurate phase with modulation of the order parameter, which may be angle of Mg[H$_2$O]$_6^{2+}$ octahedra rotation around crystal $C_3$ axis. At cooling below $T$=360 K plane-wave regime of modulation transforms into the multi-soliton one with structural solitons density decreases as far as temperature decreases. At $T_{i2}$=$343\pm0.3$ K soliton density step-wise decreases down to small values $\approx$0.1. The assumption was expressed that mentioned temperature is tem-
perature of transition from incommensurate phase to another inhomogeneous phase, in which the studied crystals consist of two type of regions characterized by homogeneous and inhomogeneous structural organization. The structure of former regions almost does not change with temperature variation whereas that of latter ones considerably modifies. As against the formerly proposed models of structural organization of MgSiF₆·6H₂O crystals in intermediate phase, the model presented in this paper agrees with all known data of other techniques utilized to study these crystals and does not contradict symmetry reasons. Concerning the nature of unusual structure and temperature transformation of the crystals studied between Tc and Ti₂ we can suppose that in this phase they may be ferroelastic analogues of the ferroelectric relaxor-type crystals but special investigation of their properties is necessary to confirm this supposition.

At present the complete understanding of nature of step-wise changes in slope of temperature dependences of Mn²⁺ EPR lineshape parameters between T₁₂ and Tc also is not reached. The investigation of these problems and possibility of application of considered in this paper models of structural organization of MgSiF₆·6H₂O “intermediate” phase to examination of related “intermediate” phases observed in MgGeF₆·6H₂O₁⁴,₂¹ and MgTiF₆·6H₂O¹³, are in progress.

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References
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