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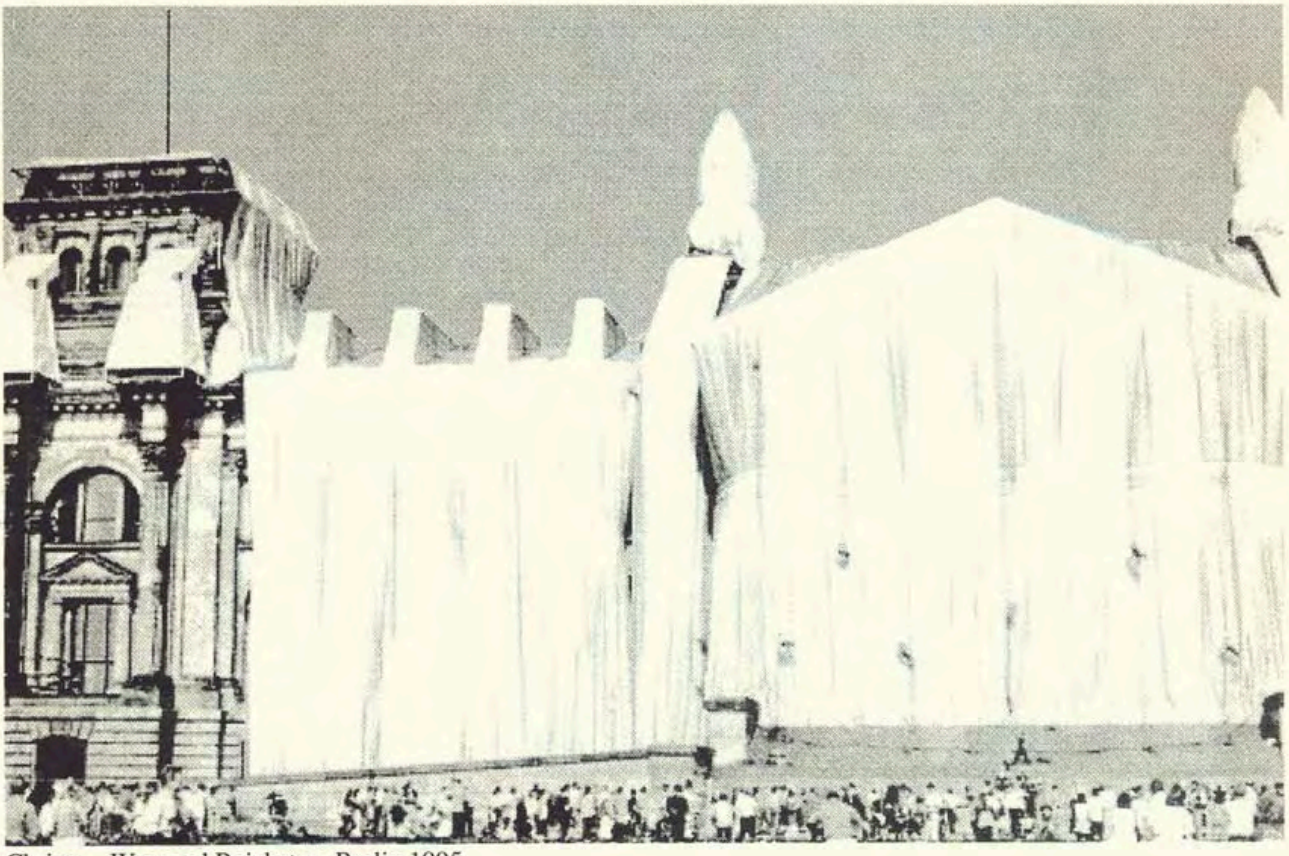

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EPR of Incommensurate Phases in Ferroelastic $MgSiF_6 \cdot 6H_2O : Mn^{2+}$: Lineshape Simulation with Variation of the Spin-Lattice Relaxation Rate

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The availability of angular dependence of the EPR spectra line splitting indicates that the angle of complex ions $Mg[H_20]_6$ disorientation around the C_3 - axis may be chosen as a primary order parameter for the phase transition from paraelastic phase to incommensurate phase. This choice of order parameter determines the presence of only even terms in expanding of the EPR spectra fine structure parameter on the powers of order parameter. A successful description of experimental lineshapes may be reached under the following additional assumptions: 1) solitons existing within the wide temperature range; 2) variation of the spin - lattice relaxation rate T_1^{-1} over the spectral distribution; 3) presence of nearly independent subsystems of solitons and domains within the temperature range from 300 K to 310 K.

Introduction

Magnesium fluorosilicate hexahydrate (MFSH) belongs to isomorphous compounds of the type $ABF_6 \bullet 6H_2O$ (where A and B are di- and fourvalent metals, respectively) in which two complex ions $A[H_2O]_6$ and BF_6 can be distributed between two orientations around the 3-fold axis [1,2]. A number of these compounds are characterized by an improper ferroelastic phase transition from a rhombohedral modification to a monoclinic phase, which is stable at low temperature [2]. According to the crystallographic studies [3] for MFSH the space groups are $R\bar{3}m$ and $P2_1/c$, respectively. The presence of intermediate states between mentioned phases in crystals $MgBF_6 \bullet 6H_2O$ (where B - Si, Ge, Ti) have been established and investigated by various methods including electron paramagnetic resonance (EPR) [4-8]. However, the nature of this phase is not understood finally. In this paper we present the new approaches to describing the mentioned EPR experimental data on $MgSiF_6 \bullet 6H_2O$ crystals and the ideas concerning motifs of intermediate phase crystal structure.

Experimental

The single crystals of improper ferroelastic $MgSiF_6 \bullet 6H_2O$ have been investigated by means of X - band EPR on admixture ions Mn^{2+}. At $T_{il} \cong 370K$ and $T_C \cong 299K$ the crystals undergo phase transitions from paraelastic phase to incommensurate phase and from incommensurate phase to ferroelastic phase, respectively [4]. The temperature decrease below T_{il} is accompanied by smooth inhomogeneous broadening of the Mn^{2+} hyperfine structure lines followed by splitting of these lines (Fig.1). Moreover, the EPR lineshape is typical for incommensurate one-dimensional modulated systems. The evidences for the incommensurate structure of MFSH were obtained by optical studies [6] too. The inhomogeneous phase similar to that in magnesium fluorosilicate have been observed in mixed single crystals $Mg_xZn_{1-x}SiF_6 \bullet 6H_2O$. It is worth mentioning that this phase forms at $x \approx 20\%$, indicating on a special role of Mg^{2+} ions in the incommensurability emersion.

Results and Discussion

In crystals under investigation the 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 [5]. This

statement seems to be physically reasonable and qualitatively accounts for the principal experimental data. 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 $\Delta D \sim \varphi^2$).

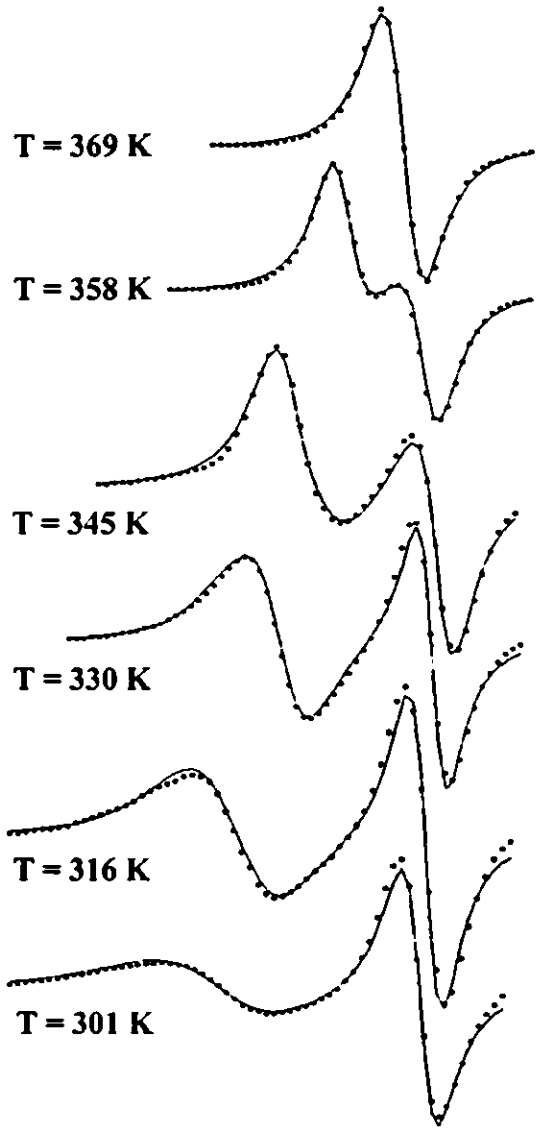

Fig.1. The temperature evolution of the EPR Mn^{2+} spectra lineshape (scattered points correspond to experimental spectra, solid line - theoretical simulated spectra).

Experimental Mn^{2+} EPR lineshape has been interpreted in the terms of model analogous to that of Blinc [9] 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 [10].

Basing on these assumptions we calculated the temperature dependence (Fig. 2) of modulation parameter h_2 ($h_2 \sim (T_{i1} - T)^{2\beta}$) which allows to determine the critical index $\beta = 0{,}36 \pm 0{,}02$ of a transition to incommensurate phase. This value of β is a typical magnitude for the system with one-dimensional incommensurate modulation and close to $\beta = 0{,}345 \pm 0{,}002$ for the 3d-XY model [11]. This fact may be considered as indirect evidence for the correctness of our order parameter choice.

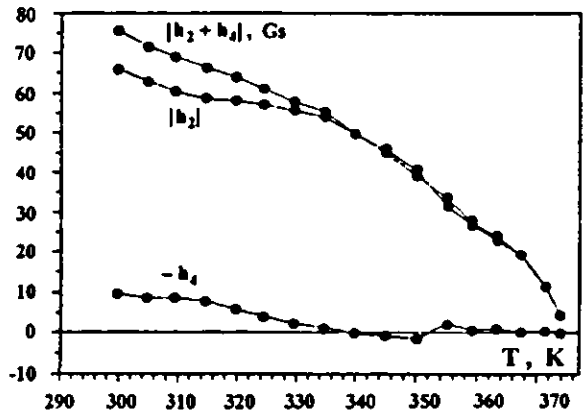

Fig. 2. The temperature dependence of incommensurate modulation parameters of the second (h2) and fourth (h4) order calculated from the experimental spectra.

The calculations show that smooth evolution of incommensurate phase follows to the predictions of a classical theory [9] between T_{i1} and T_{i2} ($T_{i2} \cong 343$K) : the modulation follows from a plane-wave regime to multisoliton regime with decreasing soliton density n_S at $T \rightarrow T_{i2}$ (Fig. 3). Below T_{i2} the spectra lineshape changes differ essentially from magnetic resonance spectra

evolution in conventional incommensurate systems with one-dimensional modulation (Fig. 1). The calculations performed in particular show that n_S undergoes a step-wise decrease at T_{i2} to a small value about $\approx 0{,}1$ (Fig. 3).

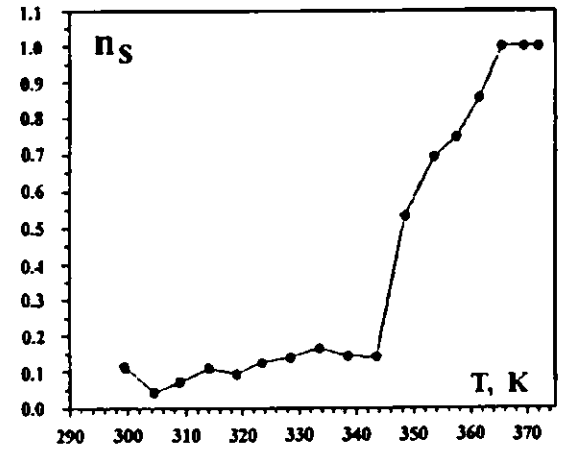

Fig. 3. The temperature dependence of soliton density n_S for the model taking into account variation of T_1^{-1} over the spectrum.

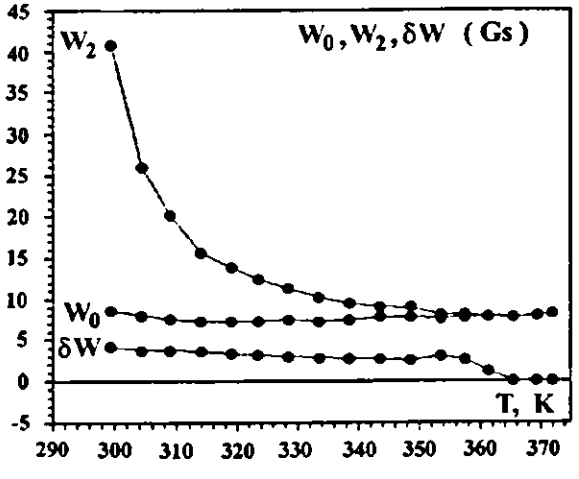

Fig. 4. The temperature dependence of the parameters W_0, W_2, and δW. Parameters W_0 and W_2 indicate the value of Lorentzian linewidth at the points of incommensurate spectral distribution singularities, δW is a deviation from linear function in a proposed parabolic dependence W(H).

A successful description of the lineshape (Fig. 1) may be in principle obtained between T_{i2} and T_C + 10K 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 [9, 12]. 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 [9, 12]. However, below $T \approx T_C$ + 10K the value of variation indicated becomes too large (Fig. 4).

Therefore, we have proposed and examined another reason for EPR spectra evolution below T_{i2}. We supposed the reversible crystal division into subsystems of domains and soliton-like areas at this temperature. The model allows to describe rather satisfactorily the experimental spectra with two distinct components from T_{i2} to T_C. It is notable that soliton-like component lineshape is typical for multidimensional 2q (or 3q) incommensurate modulation (absence of edge singularities) rather than one-dimensional case at $T > T_{i2}$. The step-wise changes in parameters describing EPR spectrum lineshape at T_{i2} may be attributed to the presence of nearly independent aforementioned subsystems below T_{i2}. The soliton density n_S is almost invariable within some temperature range. However, the interaction between these subsystems probably restores at $T \rightarrow T_C$ resulting in soliton density n_S decrease (close by T_C) followed by a transition to commensurate ferroelastic phase.

Conclusion

The results presented show that the EPR spectra of Mn^{2+} in $MgSiF_6 \cdot 6H_2O$ intermediate phase may be qualitatively described as incommensurate system spectra. On the other hand, the temperature evolution of experimental spectra has some peculiarities. They, in principle, 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. However, taking into account too large values of these variation parameters near T_C, we suppose, as alternative model, the presence of two nearly independent subsystems of soliton-like areas and domains. All presented results give evidence for non-trivial structure of $MgSiF_6 \bullet 6H_2O$ crystals in its intermediate phase and, we hope, will stimulate further investigations of this compound.

Acknowledgements

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