XXVII CONGRESS AMPERE

KAZAN 1994

MAGNETIC RESONANCE AND RELATED PHENOMENA

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EXTENDED ABSTRACTS OF THE
XXVIITH CONGRESS AMPERE

Volume I

Editor:
KEV M. SALIKHOV

KAZAN, AUGUST 21–28, 1994

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Published by the Zavoisky Physical-Technical Institute
of the Russian Academy of Sciences, Kazan

EPR OF IMPROPER INCOMMENSURATE FERROELASTICS

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ABSTRACT

A short review of our recent EPR research work results of new improper incommensurate ferroelastics $Mg^{2+}B^{4+}F_6 \bullet 6H_2O$.

INTRODUCTION

In the crystals $ABF_6 \bullet 6H_2O$ the two complex ions $A(H_2O)_6$ and BF_6 have an octahedral structure and can be distributed between two distinct orientations around the C_3 - axis (I). A number of compounds are characterized by an improper ferroelastic phase transition from a rhombohedral modification to a low - temperature monoclinic phase. In $MgSiF_6$ $6H_2O$ (a), $MgGeF_6$ $6H_2O$ (b) and $MgTiF_6$ $6H_2O$ (c) we found and investigated by means of EPR incommensurate states and structural solitons realizing between their rhombohedral and monoclinic phases.

RESULTS AND CONCLUSIONS

The EPR investigations of $MgBF_6 \bullet 6H_2O$ (B = Si, Ge and Ti) crystals containing natural abundance of $3d^n$ - ions show (2) that at cooling of a(b)[c] at T_{i1} = 369(403) $\mp$ 1 K, T_{i2} = 344 (380)[366] $\mp$ 1 K and T_c = 298 (316)[300] $\mp$ 1 K they undergo structural phase transitions of the 2-nd and the 1-st (the latter two) order. The phase transition at T_{i1} is a 2-nd order transition of a paraphase-incommensurate phase type and is accompanied by a smooth inhomogeneous broadening of the ESR lines of Mn^{2+} and Ni^{2+}, which are gradually transformed into a two-peak form. At rotating the crystal around the C_3 - axis, which makes a certain angle O = 0°, 90° with the constant magnetic field direction H, Mn^{2+} hyper - fine structure lines do undergo complicated changes which are repeated every 120°. The amplitude of such changes increases at $T \rightarrow T_c$.

At $T < T_{i1}$ the form of lines can well be described in, the terms of plane-wave modulation of lattice displacements. In (a), at $T \rightarrow T_{i1}$, the amplitude of trigonal modulation decreases according to the power low with a critical exponent β = 0,35 ± 0,02, which makes it possible to consider the crystal behaviour within the Heisenherg's 3d-XY model. Below T_{i2} the quantitave line simulation is possible only in terms of the structural solitons.

In all investigated crystals, between T_{i2} and T_c, a succession of step-wise changes in the slope of Mn^{2+} line shape parameter curves which are less significant than those at T_{i2} is observed. The temperature of these step-wise discontinuities T_{in} (n = 1+6) vary from sample to sample within the limit of ~4°, but whatever and independently on temperature variation direction they occurs at practically the same amounts of line shape parameters. In (b), in the whole interval of incommensurate phase existence

the line shape and the spectrum parameters depend on a temperature changes direction. In (c) the step-wise changes in the slope of Mn^{2+} line shape parameter curves are larger significant than those in another crystals. These breaks are not accompanied by change of a number of the Mn^{2+} nonequivalent positions and its spectrum symmetry. The conclusion was that in this crystals below T_{i2} there is a succession of modulated states with the structural soliton lattice. The transitions between them being realized at certain amounts of the structural modulation parameters, depending on temperature variation direction. It can not be unambiguously reduced to the well-known devil's staircase of discrete changes in the modulation wave vector.

At T_c crystals undergo an improper ferroelastic 1-st order phase transition and their EPR spectra correspond to six space inequivalent centres,two from each orientational domain.

The availability of angular dependence at $\Theta \neq 0°$ and $90°$ for Mn^{2+} line shape at $T < T_{i1}$ allows to draw the conclusion that in the incommensurate 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_3 –axis. The above desorientation of the cubic crystalline field axes is, probably, connected with the modulation of the rotation angle of the complex around the C_3 –axis relative to the position in the paraelastic phase. It is likely that this angle is an order parameter of the paraelastic-incommensurate phase transition and it determines the value of the trigonal modulation.

In all crystals the increase of content of structural defects (admixture ions Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and γ - irradiation defects) leads to: a decrease of T_{i1} , the blurring of phase transition at T_{i2} and an appearance of additional step-wise changes of modulation parameter vs. temperature curves. In crystals with high content of defects the modulation appears (or disappears) at T_{i1} unevenly.

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