FERROIC MATERIALS STUDIED BY EPR

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EPR is very sensitive method in their contribution to static properties of phase transition. However like as may other resonance technique EPR have to be supported by other bulk-like methods. In this short description of EPR application to study of ferroic materials in IFM PAN main emphasis has been done to close connection between local (EPR) and bulk (P_s) parameters. For that it is shown how to get (for example) hysteresis loop and order parameter from EPR data alone. How to detect incommensurability and/or two component order parameters etc.

INTRODUCTION

We can call crystal as „ferroic" if it has two or more orientational (energy) states and can be transformed to one of them by the external forces like magnetic, electric, mechanical etc. Especially the phase transition phenomena which are realized by jumpwhise and/or tiny changes in atoms positions could be tracked by EPR. The emphasis is now on collective phenomena in systems where disorder and/or nonlinearity are the major ingredients: mixed crystals, incommensurate structure, proton-glasses, charge density wave, superparaelectric, nanosized etc. In these cases, magnetic resonance techniques have provided unique microscopic information especially powerful if used commonly with traditional bulk methods. Brief historical evolution of EPR devoted to study of ferroics in laboratories of Institute of Molecular Physics Polish Academy of Sciences is done in this presentation.

FIRST STEP TO EPR IN POZNAŃ

I was employed in 1963 at Jan Stankowski laboratory. It was the time where the first LASER and MASER were build in Poznań. The first conferences REK (Radio and Quantum Electronics) were organized by Adam Mickiewicz University and Polish Academy of Sciences. So more emphasis were devoted to quantum electronics devices rather than EPR application. Stankowski laboratory worked on home made EPR spectrometer, where mainly free radical were investigated. First of more advanced EPR studies on monocrystals were done with triglicyne sulphate (TGS). TGS-crystal family and

KDP were and are still "model" one for study of ferroelectricity. Two types of paramagnetic centers were introduced to TGS crystal structure: free radical after γ-irradiation, Cu^{2+} or Cr^{3+} ions. Temperature dependence of EPR spectra parameters reveals that mainly paramagnetic centers with effective spin S≥1 are especially useful for study of subtle effect below and/or around of ferroelectric/paraelectric critical temperature T_c. Such paramagnetic probes (S≥1) are marked by EPR with fine structure characterized by **D**-tensor. This tensor describes the dipole-dipole interaction and/or spin-orbit coupling with internal electric filed (crystal field). Because the ferroelectricity is evoked by electric interaction, the **D**-tensor ($D\sim\lambda^2/\Delta$) have to be also influenced by spontaneous polarization P_s. Crystal field influence spin levels by spin-orbit coupling. This polarisation effect on EPR is hardly visible on g-factors, because g-factors weakly depends on λ/Δ like:

$$g = g_e\left(1 \pm \frac{A\lambda}{\Delta} + ...\right) \qquad (1)$$

where: λ-spin orbital coupling, Δ - energy difference to first excited level above, *A* - constant number. Nevertheless radical like NH_3^+, and others especially with superhyperfine ligand structure are also informative on crystal lattice dynamics.

TGS PROPER FERROIC DOPED WITH Cr^{3+} IONS

Small amount of Cr^{3+} ion (the order of one per 10^4 elementary unit cell of TGS) is introduced during of

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pure $(NH_2CH_2COOH)_3H_2SO_4$ (TGS) crystal growth. EPR anisotropy investigations allow to evaluate spin-Hamiltonian parameters and Cr^{3+} ion coordination in TGS. In results it has been found that Cr^{3+} is coordinated with glycine II and glicyne III and two SO_4 groups to form deformed octahedron (Stankowski, Waplak & Yurin, 1974). Phase transition in TGS is the second order type at $T_c = 322$ K with the symmetry change 2/m → 2. Vanishing of mirror plane leads to the spontaneous P_s polarization along the b-axis and 180° type domain structure. Cr^{3+} ion feels spontaneous polarization value and direction because is coordinated with oxygen of SO_4 group which is bonded by long hydrogen bond with glicyne I (Gl I). Tilting of Gl I molecule results in crystal polarization. Figure 1 shows the outlook on the crystal orientation applied to study of the influence of polarization reversal on the chosen fine structure line ($\pm 3/2 \leftrightarrow \pm 1/2$) of Cr^{3+} EPR spectra. Z_1, Z_2 – axes show the main axes of the crystal field gradient acting on Cr^{3+} ion. Above T_c only A and B complexes are recorded. Complexes A', B' are seen only below T_c due to the domain structure appearance. The A ↔ A' or B ↔ B' line splitting versus temperature allows to measure the order parameter S. This splitting follows the temperature dependence of fine structure D-parameters.

$$D_t = D_0 \pm S\Delta D \tag{2}$$

where: D_0 – the saturated value at low temperature, $\Delta D \cong$ A ↔ A' or B ↔ B' the line splitting at low temperature (saturated value).
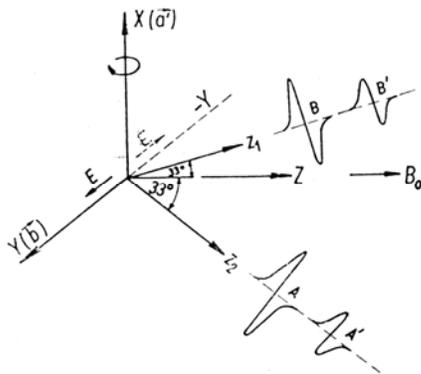

Fig. 1. Crystal orientation applied when studying the influence of the P_s polarisation on the line intensities of complexes A', B' and B, B' in TGS:Cr^{3+} monocrystals.

An external electric field influence on EPR spectra of ferroelectric is stronger than on normal dielectrics. For TGS:Cr^{3+} an external DC field order of coercitive field value (~300 V/mm) leads to reversal of spontaneous polarisation - P_s. Due to the coupling of ferroelectric dipole moment (carried by Glycyne I) with Cr^{3+} local

moment EPR lines A → B or B ← A exchange intensities depending on P_s directions. Combining an intensity ratio K plot versus an external electric field

$$K(E) = \frac{I_A - I_B}{I_A + I_B}$$ the hysteresis loop may be obtained.

Next, the bulk value of P_s polarization for pure and doped TGS with known Cr^{3+} concentration, allows to find the number of TGS unit cell "blocked by Cr^{3+} ions (Waplak & Stankowski 1978). It has been evaluated that the radius R inside of which ferrolectric dipole moments (Gl-I) are "blocked" (are not reversible) is order of 80 Å. The emergence of uncompensated charge on the surface R clamp dipole moments within and this value of volume charge is the source of internal field E_b (Fig. 2a, b).
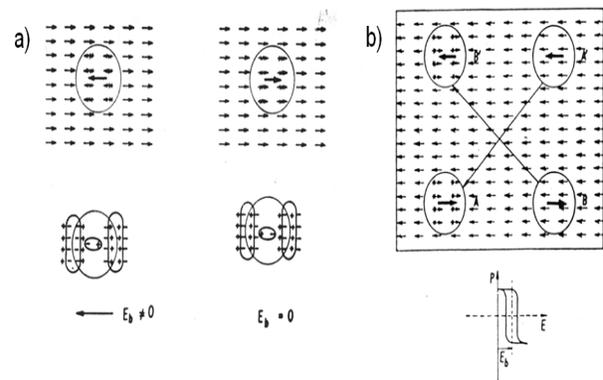

Fig. 2. The emergence of uncompensated charge on surface R, the clamped dipole moments within the sphere being directed oppositely to the polarization within domain a). Disposition of the dipole moments of complexes A, A' and B, B' in the single-domain crystal subsequent to polarization reversal with field (without rejuvenation) b).

This field shifts the center of histeresis loop and is called as "internal bias" field. Than EPR directly defines sources of bias field. The next advantage of applying of EPR on probes with spin S≥1 shows our discovery of new method EMMEPR (Electrically and Magnetically Modulated EPR) described by us in detail (Stankowski, Waplak & Yurin, 1974). This method resides essentially on applying an additional electric DC field (80 Hz) directly to the sample electrodes and signal detection as "a second derivative" operation in SE/X-s Radiopan spectrometers. This procedure allows to record the EPR lines in reversal phases for centers placed in opposite domains as will be shown below.

RbH$_3$(SeO$_3$)$_2$:Cr^{3+} IMPROPER FERROELECTRIC-FERROELASITIC

In improper ferroelectric the spontaneous polarization is the second order effect to deformation. In case of RbH$_3$(SeO$_3$)$_2$ there is also narrow range incommensurate phase. In classical (ordinary) EPR spectra of Cr^{3+} ion the single line ($\pm$ 3/2 $\leftrightarrow$ $\pm$1/2) above 155K start to be split when temperature is gradually lowered (Fig. 3) (Waplak, Jerzak & Stankowski, 1981).
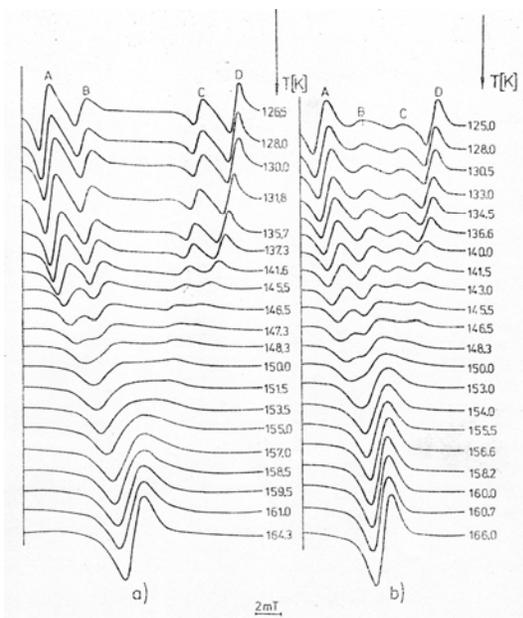

Fig. 3. Temperature evolution of EPR spectra of RbH$_3$(SeO$_3$)$_2$:Cr^{3+} recorded for "Y" a) and "Z" b) orientation.

The characteristic nonsymmetrical line intensity (C, D) vanishing is characteristic for incommensurability. The EMMEPR method, mentioned above, allows to clarified four split lines ABCD as shown in Fig. 4.
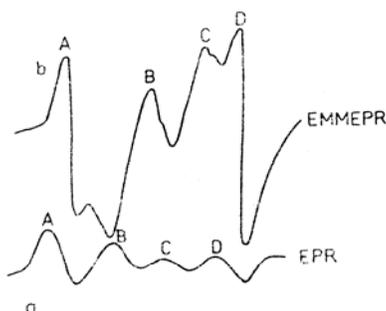

Fig. 4. EPR and EMM EPR spectra in RbH$_3$(SeO$_3$)$_2$:Cr^{3+}.

The lines A, B and C, D belongs to oppositely polarized domains. Figure 5 shows their resonance field evolution versus temperature.
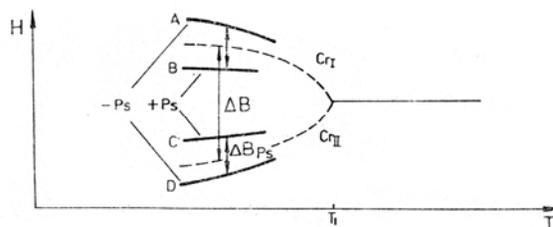

Fig. 5. Resonance line position evolution versus temperature in RbH$_3$(SeO$_3$)$_2$:Cr^{3+}.

Static hysteresis loop for RbH$_3$(SeO$_3$)$_2$:Cr^{3+} obtained directly from combined intensity ratio:
$$K(E) = \frac{I_A - I_B}{I_A + I_B}$$ versus DC field is shown in Fig. 6.

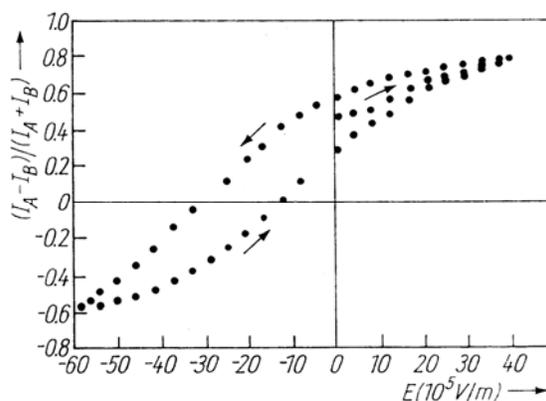Fig. 6. Static ferroelectric hysteresis loop obtained by EPR for RbH$_3$(SeO$_3$)$_2$:Cr^{3+} crystal at T = 141 K.

The role of EPR spectroscopy in chemistry and biology is widely known. In this short review of our EPR method improvement we pay main attention to the connection of bulk (dielectric) and local (EPR) data. Currently EPR technique is used by us to study of molecular mechanisms of proton transport.

EPR STUDY OF PROTON TRANSPORT AND PRETRANSITIONAL PHENOMENA IN FAST-PROTON CONDUCTORS

The M$_3$H(XO$_4$)$_2$ crystal family, where: M = NH$_4$, Rb, K, Cs; X = S, Se reveals many interesting properties related to phase transitions, especially a high proton conductivity which reaches values of the order of 10^{-1} Ω^{-1}cm^{-1} in the superprotonic phase. The interest in studies

of fast-proton conductors arises from their application potential, especially as solid electrolytes in fuel cells. Doped $M_3H(XO_4)_2$ crystals with different paramagnetic ions VO^{2+}, Cu^{2+}, Mn^{2+} and $(CrO_4)^{3-}$ (cationic and anionic paramagnetic impurities differently coupled with crystal lattice) is very useful for complex studies of pretransitional phenomena of fast proton conducting phase (proton jumps and anions oscillations and reorientations) (Ostrowski, Bednarski & Waplak, 2003; Ostrowski, Waplak & Bednarski, 2005; Ostrowski, 2005). In addition the presence of superhyperfine structure (SHFS) of EPR spectra origin from protons, make possible a direct studies their dynamic versus temperature. Figure 7 shows the temperature evolution of SHFS spectra of VO^{2+} ion in $K_3H(SO_4)_2$ crystal. VO^{2+} ion occupies K^+ ion vacancy and the extra charge is compensated by a proton vacancy. In this position the interaction of vanadium ion with two another protons of $SO_4^{2-} - H\cdots SO_4^{2-}$ dimers (second coordination sphere) is possible (Ostrowski, Waplak & Bednarski, 2005). A "smearing out" of SHFS with increasing temperature is clearly visible. This behaviour results from the increase in frequency of interbond proton/vacancy motion as the temperature increases. Such effect for Cu^{2+} centre also was observed (Ostrowski, Bednarski & Waplak, 2003). This phenomenon appears when proton jump frequency τ_c^{-1} becomes faster than the SHFS splitting A^H (in frequency units):

$$\tau_c \geq A^H / 2\pi h \qquad (3)$$

For A^H = 2,3 G the following value was obtained: $\tau_c^{-1} \geq 3.8 \cdot 10^7$. The smearing out" of the SHFS is observed above about 400 K.
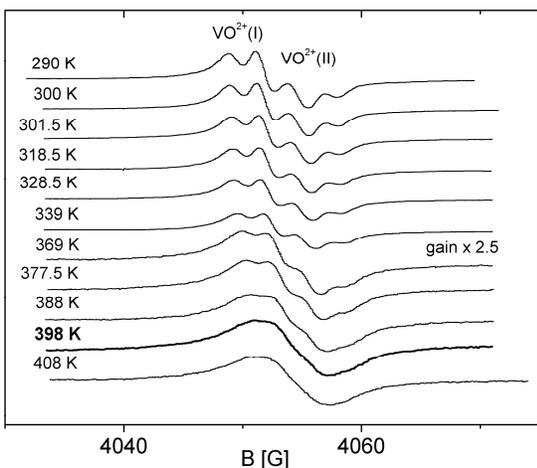

Fig. 4. Evolution of the superhyperfine (SHF) component of (M_s = 1/2; m = 7/2) ↔ (M_s = 1/2; m = 7/2) transition versus temperature for VO^{2+}(I) and VO^{2+}(II) complexes.

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