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# EPR SPECTROSCOPY OF FERROELASTICS

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**The paper presents some results of problems solved in our laboratory in the field of ferroic materials. The EPR method of admixture ions has been applied to study ferroelastic crystals. The method of finding critical exponents in pseudo-proper ferroelastic phase transitions and application of EPR in studying the dense ferroelastic domain structure are described.**

## INTRODUCTION

The structural phase transition, which is accompanied by a change of the point-group symmetry, is called a ferroic phase transition (Aizu, 1970). Ferroelectric, ferroelastic and ferromagnetic materials are typical examples of ferroics. In our work we concentrate on non-magnetic ferroic crystals, in particular on ferroelastics.

The term “ferroelasticity” was introduced (Aizu, 1969) for crystals, where the stress-strain behavior exhibits a hysteresis that is characterized by a spontaneous strain and a coercive stress. Usually ferroelastics exhibit a spontaneous deformation as a result of phase transition between the paraelastic high temperature, high symmetry phase and ferroelastic low temperature, low symmetry phase. A consequence of a transition from the paraelastic phase to the ferroelastic phase is the formation of domains and domain boundaries which constitute the dominant microstructure of the low temperature phase (Aizu, 1969; Salje, 1990;Wadhawan, 2000).

In majority of ferroelastic crystals the physical mechanism of the transition between the paraelastic and ferroelastic phase is only indirectly correlated with the ferroelasticity. The possible correlations between the order parameter (microscopic one) which describes the phase transition and the spontaneous strain (macroscopic one) are described by the coupling theory (Salje, 1990). The coupling between the order parameter and the spontaneous strain produces elastic softening of the crystal. If the physical origin of the order parameter is the elastic softening of the lattice itself, the phase transition is called proper. But the more common cases are related to a bilinear or linear-quadratic order parameter-strain coupling and a pseudo- proper or improper character of phase transition, respectively. The consequences of the coupling type on the physical properties has been discussed by Salje (Salje, 1990).

EPR of admixture ions turned out to be a powerful method in studying structural transitions in crystals, sometimes about two orders more sensitive to crystal structure changes compared with the X-ray method. This was the reason for applying it in studies of ferroelectric and ferroelastic crystals.
Investigations of ferroelastics conducted by our team started in IFM PAN in Poznan and concerned such crystals as $KH_3(SeO_3)_2$ (Zapart, Stankowski, Waplak & Shuvalov, 1978) and $KSc(MoO_4)_2$ (Zapart, Zapart, Stankowski & Zvyagin, 1982). Recently we have mainly focused on ferroelastics which belong to families of double sulphates and trigonal double molybdates and tungstates.

EPR experiments use paramagnetic probes incorporated into crystal lattice to obtain information about local structural changes in their surroundings. All changes in the principal directions of the crystal field as well as its magnitude could be described by changes in the spin Hamiltonian parameters, which allows studying a variation of problems concerning structural phase transitions. Below two examples of such possibilities are given: finding a critical exponent and analyzing a dense domain structure.

## EPR OF FERROELASTIC PHASE TRANSITION IN $CsLiSO_4$ CRYSTAL

The EPR spectra of $Cr^{3+}$ admixture ions in $CsLiSO_4$ revealed the presence of two structurally different chromium complexes marked as $Cr^{3+}$ (I) and $Cr^{3+}$ (II) (Zapart, Zapart & Czaja, 2008). The $Cr^{3+}$ (I) complexes are seen as two structurally equivalent but magnetically nonequivalent paramagnetic centers in the orthorhombic Pcmn phase of $CsLiSO_4$.

The crystal b-axis is a principal axis for the spin-Hamiltonian tensors of the $Cr^{3+}$ (I). This indicates that $Cr^{3+}$ (I) ions replace the $Cs^{+}$ ions when introduced into $CsLiSO_4$ since the point symmetry at the Cs-site is the b-mirror symmetry. The oxygen coordination of the Cs site provides the preferred octahedral coordination for $Cr^{3+}$ ions.

The multiplicity of the observed spectra for $Cr^{3+}$ (II) ($k_m$=4) and the fact that none of the three crystal axes of the host lattice is the principal axis for the ligand field allows us to suggest the position of $Cr^{3+}$ (II) as the interstitial site between two $Cs^{+}$ ions with the inversion symmetry. The 6-fold oxygen coordination is formed from the nearest neighbourhood of cesium ions (Kruglik, Simonov & Aleksandrov, 1978).

The resonance lines of these complexes react to the temperature changes by a change in their positions and below the temperature of ferroelastic phase transition they split into two components (Figure 1). The observed line splitting is a result of dividing the crystal into two kinds of ferroelastic domains.

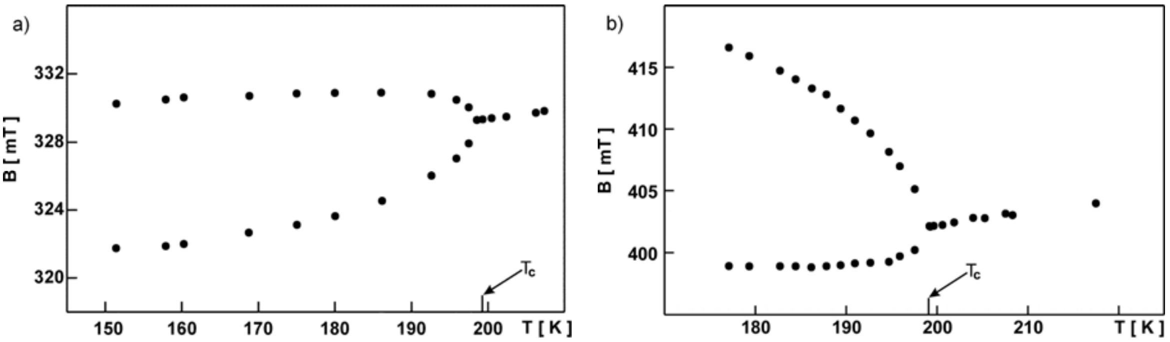

Fig. 1. Temperature changes of resonance line position in $CsLiSO_4$ for: (a) $Cr^{3+}$(I) centers, (b) $Cr^{3+}$(II) centers.

The temperature dependence of resonance field difference ΔB of split lines could be given in the form:

$$\Delta B = a\left(T_c - T\right)^{\alpha} \tag{1}$$

where $T_c$ =198.5 K. The value of the exponent α is 0.25 for the $Cr^{3+}$ (I) centers and 0.5 for the $Cr^{3+}$(II) centers.

A critical behaviour of the order parameter in pseudo-proper and improper ferroelastic phase transitions studied by EPR method through temperature changes of splitting of the resonance lines was reported in (Muller, Berlinger, 1972; Zapart, Zapart, 1985; Zapart, Zapart, 1988). In the above approach, it is assumed that the temperature changes of the resonance field in both kinds of ferroelastic domains can be expanded into the power series of the order parameters in the following way:

$$B_1 = a_1 Q_1 + a_2 Q_1 + \ldots + b_1 Q_2 + b_2 Q_2 + \ldots \tag{2}$$

for paramagnetic centers in one kind of ferroelastic domains and:

$$B_2 = -a_1 Q_1 - a_2 Q_1 + \ldots + b_1 Q_2 + b_2 Q_2 + \ldots \tag{3}$$

for the second kind of domains, where $Q_1$ and $Q_2$ are the primary and secondary order parameters and $a_1$, $a_2$, $b_1$, $b_2$ are coefficients. From the above:

$$\Delta B = 2a_1 Q_1 + 2a_2 Q_1 + \ldots \tag{4}$$

The presence of the coefficients $a_1$, $a_2$... depends on the site symmetry of the Cr ion. For $Cr^{3+}$ (I) centers the parameter $a_1$ is different from zero whereas for the $Cr^{3+}$ (II) centers, due to the inversion symmetry of this site, parameter $a_1$ is equal to zero. There is no symmetry limitation on $b_i$ coefficients. For continuous pseudo-proper phase transitions the following relations between the primary and secondary order parameters are satisfied:

$$Q_1 \sim \left(\mathrm{T_c} - T\right)^{\beta}; Q_2 \sim Q_1 \tag{5}$$

Using equation (5) and limiting the series from equation (4) to the lower order terms one can get $\Delta B\ (T) \sim (T_c - T)^{\beta}$ and $\Delta B\ (T) \sim (T_c - T)^{2\beta}$ for $Cr^{3+}$(I) and $Cr^{3+}$(II) ions, respectively. Using the obtained values of α, given in equation (1) one can find that the critical exponent β of the order parameter is equal to 0.25. This value is very close to that obtained from the X-ray studies (Asahi, Hasebe, 1988). The value of β obtained by the EPR method is in accordance with earlier suggestions (Asahi, Hasebe, 1988; Ivanov, Pietraszko, 1988) that the transition point of $CsLiSO_4$ is very close to the tricritical one.

## DOMAIN WALL MODEL

The ability to observe signals from the paramagnetic centres lying in the domain walls was reported by Zapart *et al.* (Zapart, Zapart & Jeong, 1995). In such a case the EPR lines from the centers lying in the domain walls overlap with the EPR lines from centers lying inside the domains. As a result the total spectrum forms a broad continuum limited by two edge singularities. Such a spectrum resembles the one observed in the incommensurate phases (Zapart, Sneock & Saint-Gregoire, 1997). The basic theory describing the spectrum in the case of antiphase domain structures was given by Zapart and Zapart (Zapart, Zapart, 1999; Zapart, Zapart, 2000).

The considered continuous domain wall model is based on the assumption that the boundaries have a linear structure that is represented by the kink-like solution:

$$Q(x) = Q_0 \tanh(kx) \qquad (6)$$

where 1/k is the measure of domain wall thickness, the x-axis is normal to the APB plane and $Q_0$ is the value of the order parameter inside the two domains . If the resonance field can be expanded into the power series of the order parameter then this field is given by formula:

$$B = B_0 + A_1 Q + A_2 Q^2 + \ldots \qquad (7)$$

where $B_0$ is a magnetic resonance field in absence of the order parameter Q.
From equations (6) and (7) it follows:

$$B = B_0 + B_1 \tanh(kx) + B_2 \tanh^2(kx) + \ldots \qquad (8)$$

The coefficients $B_1$, $B_2$ depend on the symmetry of the paramagnetic center site and the direction of the external magnetic field with respect to the symmetry elements of the crystal lattice. The resonance field distribution function f (B) that determines the EPR line shape is given by:

$$f(B) = 2\pi / (dB/dx) \qquad (9)$$

The overall EPR line shape F (B) is given by convoluting the resonance field distribution function f (B) with the line shape function L ($B-B_c$) of a single line:

$$F(B) = \int L(B - B_c) f(B_c) dB_c \qquad (10)$$

The zeros of the derivative dB/dx in equation (9) determine the singularities in the line shape. It is worth to consider two special cases:
a) when the linear term in equation (8) is dominant ($B_1 \neq 0$, $B_2 = 0$)
Then the resonance field distribution function f (B) becomes:

$$f(B) = \left(\frac{2\pi}{k}\right)\frac{\cosh^2(kx)}{B_1} = \frac{2\pi/k}{\left[B_1 - \frac{(B-B_0)^2}{B_1}\right]} \qquad (11)$$

We find that it has the characteristic edge singularities at two values of the magnetic field,

$$B\pm = B_0 \pm B_1 \qquad (12)$$

b) when the quadratic term is dominant, ($B_1 = 0$ and $B_2 \neq 0$) equation (9) becomes:

$$f(B) = \frac{2\pi \cosh^2(kx)}{B_2 k \tanh^2(kx)} = \frac{2\pi/k}{2B_2\sqrt{\frac{(B-B_0)}{B_2}\left(1 - \frac{(B-B_0)}{B_2}\right)}} \qquad (13)$$

It is worth noting that now f(B) is asymmetric in shape. There are two singularities at:

$$B = B_0 \text{ and } B = B_0 + B_2 \qquad (14)$$

The position of one singularity represents a continuation of the para-phase line at $B=B_0$.
The f(B) dependence for these two cases is shown in Figure 2.

Fig. 2. Distribution function against $B-B_0$ for linear (a) and quadratic (b) cases.

The above approach allows to simulate the EPR line shape with regard to the parameters $B_1$, $B_2$ and domain wall thickness (Zapart, *et al.* 1997; Zapart, 2003; Zapart, 2004).

## REMARKS

To obtain valuable results the EPR method should be applied in a sophisticated way. Results of EPR studies of ferroelastics with dense domain structure and finding the critical exponents in ferroelastic phase transitions are examples of original results obtained in our laboratory. Several other topics concerning ferroic materials were done in our laboratory in collaboration with Dr. Cierniewska-Muskala G., Dr. Solecki J., MSc. Reng P., Dr. Czaja P. and MSc. Mila T.

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