Microscopic Approach to the Magnetoelectric Coupling in RCrO$_3$ (R = Y, La, Lu and Eu) Compounds

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Abstract: A microscopic theory of magnetoelectric (ME) effects in multiferroic RCrO$_3$ compounds, where R is a non-magnetic ion (R = Y, La, Lu and Eu) is presented. Taking into account the influence of polar lattice displacements on symmetric and antisymmetric exchange interactions, two types of coupling between the magnetic and the ferroelectric subsystems are defined. The first magnetoelectric interaction is biquadratic with respect to the spin and pseudo-spin operators. The second, called antisymmetric, is induced by the appearance of spontaneous polarization in RCrO$_3$. The built-in microscopic model describes the occurrence of a temperature-dependent spin-reorientation (SR) transition and defines it as continuous (continuous rotation of the magnetic spins in the zx-plane within a given temperature interval). The emergence of additional polarization as a consequence of a magnetic phase transition has been proven theoretically. This is due to the induction of an antisymmetric magnetic interaction of type Dzyaloshinski-Moriya (DM) interaction, which is a consequence of the occurrence of spontaneous polarization in these compounds. The influence of magnetoelectric interactions on the magnetic and ferroelectric subsystems has been investigated. The behaviour of magnetization at the application of an external electric field is qualitatively explained with the renormalization of the exchange symmetric and antisymmetric magnetic interactions by the spontaneous polarization $P_S$. The dependence of spontaneous polarization on the direction of external magnetic field was explained by the occurrence of feedback between $P_S$ and magnetization. It has been established that the width of the temperature interval $\Delta T_{SR}$, in which the SR transition takes place, decreases with the increase of the value of the external magnetic field. The method of Green’s function is used for the numerical calculations.

Keywords: multiferroics, magnetoelectric interactions, Green’s functions, spin-reorientation transition, induced Dzyaloshinsky-Moriya interaction.

I. INTRODUCTION

Multiferroics (MF) are compounds, in which a polarization and magnetization are simultaneously observed in one phase under a certain temperature. There is an interaction between both systems called magnetoelectric. Because of this, the magnetization can be controlled by an external electric field and polarization through applying of an external magnetic field. This determines these compounds as unique for creating of new multifunctional devices - memories with more than two states, combining the computer processor and memory in one device, application in medicine for selective drug delivery to tumour formations with subsequent hyperthermic therapy [1-7], etc.

Multiferroic properties show rare-earth chromites with structural formula RCrO$_3$, where R is a rare earth ion. They are multiferroics showing weak ferromagnetism for temperatures below $T_N = 113$-$291$ K and spontaneous polarization at temperatures under $T_c = 472$-$516$ K. RCrO$_3$ crystallize in an orthorhombic perovskite structure Pbnm (Fig. 1) with three types of G-type antiferromagnetic configurations $\Gamma_a$, $\Gamma_2$ and $\Gamma_3$ in accordance with designations of Bertaut [8]. In these substances with decrease of the temperature a spin-reorientation transition from the $\Gamma_a(\Gamma_2)$ to the $\Gamma_3(\Gamma')$ magnetic structure is observed. Yamaguchi [9] established that magnetic antisymmetric exchange interaction (so-called Dzyaloshinskii-Moriya interaction) between R and Cr ions is responsible for this transition and is observed only when R is magnetic. Rajeswaran et al. [10] experimentally obtained the appearance of extraordinary polarization $\Delta P$ in RCrO$_3$ below the point of magnetic phase transition only when R is a magnetic ion. They suggest that the interaction between R$^{3+}$ and Cr$^{3+}$ ions is responsible for the occurrence of polar phase and extraordinary polarization $\Delta P$. When R is non-magnetic, this effect is not observed. In our previous article [11] we propose a microscopic model for describing of the multiferroic properties in RCrO$_3$ when R is magnetic. Taking into account the influence of lattice vibrations on the magnetic exchange interactions, we prove that additional polarization is the consequence of a magnetostriiction mechanism leading to distortion of the centrosymmetric and antisymmetric Dzyaloshinsky-Moriya interactions, which
is responsible for the frustration of the magnetic subsystem. We assume that the change of the position of R-ion in the xy-plane, due to the magnetic phase transition lowers the symmetry of the crystal from Pbnm to P2₁. This change in position changes the magnitude of symmetric and antisymmetric exchange interactions.

Meher et al. [12] experimentally observe the occurrence of extraordinary polarization ΔP under Tₑ in LuCrO₃, showing that ΔP is observed only in the presence of magnetic rare earth ions is inaccurate (incorrect). They show that the magnetoelastic effect is much weaker in LuCrO₃ compared to ErCrO₃. This shows that besides the microscopic mechanism have developed by us to explain the occurrence of ΔP, there is another one that does not depend on whether R is magnetic or not. This new mechanism obviously is very weak and in the case of magnetic R is masked by the mechanism proposed in Ref. [11]. In Ref. [12] a qualitative explanation for the occurrence of extraordinary polarization is provided: the presence of double domain walls in which residual tension accumulates around the magnetic phase temperature due to the ferroelastic nature of the walls. At lowering of the temperature this may lead to distortion of the centrosymmetry and to displacement of the Cr ions additionally from their equilibrium positions. However, this requires further experiments related to tensile deformation. Another hypothesis of them is based on the occurrence of mixed valence of Cr ions. Under Tₐ, Cr³⁺ - Cr⁴⁺ the exchange interaction may locate the charges of the electronic pairs in Cr²⁺ or Cr⁴⁺, which will lead to spontaneous disproportion (i.e. to charge order) and a occurrence of additional polarization. In our opinion, this charge order leads to the formation of a structure where Cr³⁺ and Cr⁴⁺ alternate in successive (1,1,1) planes. Then the planes are arranged in the configuration ↑↑↓↓ of the spins, which naturally gives polarization in the same direction. This will be possible if a structural phase transition from the crystallographic symmetry Pbnm to the monoclinic type P2₁/n is performed. Such a structure, however, in RCrO₃ is not observed. This means that the mechanism of occurrence of ΔP in LuCrO₃ remains unexplained.

Raman spectra are a powerful experimental tool for determining the influence of lattice vibrations on the magnetic and polarization properties of MF. In RCrO₃, when R is a magnetic ion, besides the anomaly around the temperature of the magnetic phase transition Tₐ, the anomaly for temperatures corresponding to the spin-reorientation transition Tₐk is observed as well. Chatturvedi et al. [13] qualitatively explain the anomalies around the Tₐk with the modulation of the Cr-R magnetic interaction of the lattice vibrations, i.e. with the presence of a strong spin-phonon interaction. Also such anomalies have been observed experimentally and from other authors [14-16]. Sharma et al. [17] experimentally observed two anomalies in the temperature behaviour of the phonon modes in YCrO₃: near the Neel’s temperature Tₐ = 142 K and one around T* = 60 K, as the authors explains this with a change in spin dynamics. The displacement of the Raman frequencies between Tₐ and T* assumes a competition between weak ferromagnetism and antiferromagnetic interaction. Such anomalous behaviour of phonon modes is also observed in EuCrO₃ [18]. In the Raman spectra of RCrO₃, when R is non-magnetic (Y, La, Lu and Eu), two typical behaviours are observed: 1) below Tₐ the energy of the phonon mode first increases as around T* there is a “kink” with additional hardening of the mode and subsequent saturation at very low temperatures; 2) below Tₐ the energy of the phonon mode first decreases, as around T* there is a "kink" with an additional frequency increase and subsequent saturation at very low temperatures. It is clear that under T the hardening of the mode is not a consequence of anharmonic effects, because at such low temperatures the same do not have a remarkable influence. Note that such anomalies also appear in SmCrO₃ [19], GdCrO₃[20] and ErCrO₃ [21] in the vicinity of the spin-reorientation transition. This leads to the hypothesis that for RCrO₃, when R is non-magnetic in the vicinity of T*, a temperature-dependent spin-reorientation transition may occur, which changes the spin dynamics. The spin-phonon interaction then causes anomalies in the phonon frequency. Experimentally observed by Duran et al. [22] wide peak of about 60 K in the magnetic component of the specific heat capacity in YCrO₃ is confirmation of this hypothesis, which authors explain with a temperature-dependent SR transition. Similar behaviour is observed in highly frustrated manganites [23]. In RMnO₃, this behaviour is explained by large geometric frustration, whereas for RCrO₃ it is a consequence of the large value of DM interactions between Cr-Cr and Cr-R spins, resulting in a significant change in spin dynamics. It is known that in (Pb,Bi)CrO₃ a temperature-induced SR transition of second

Fig. 1. Schematic presentation of the unit cell in RCrO₃, where R-ion is blue, Cr is red and O is green.
order [24,25] is observed. Arevalo-Lopez et al. [24] experimentally observed in PbCrO$_3$ the same peak in the magnetic component of the specific heat capacity, as it is in YCrO$_3$, and they proved that it is a consequence of a temperature-dependent SR transition. This transition is explained by a change in magnetic anisotropy in these compounds due to the compositional modulation of the Pb-atoms and the spin-phonon interaction. What is the mechanism of SR transition in RCrO$_3$ when R is non-magnetic, it is not clear. We think that if we construct a microscopic mechanism of this SR transition we can also explain the occurrence of extraordinary polarization $\Delta P$ in RCrO$_3$, when R is not magnetic. This is the main purpose of this article.

II. MODEL

Under $T_N$ the magnetic structure of YCrO$_3$ and LuCrO$_3$ is $\Gamma_4$ [9]. From the analysis made in the introduction it is clear that spin reorientation transition is observed in these compounds. The change in the magnetic structure is transition from $\Gamma_4$ to $\Gamma_2$ or $\Gamma_1$ configurations, $\Gamma_1$ is totally anti-ferromagnetic configuration and macroscopic magnetization is not observed. Experimental data for YCrO$_3$ [10,22] and LuCrO$_3$ [10,12] show that in these compounds that macroscopic magnetization is observed throughout the whole temperature interval from $T_N$ to 0 K, as when the temperature decreases the magnetization increases reaching saturation. This means that if there is a SR transition, the magnetic configuration with a decrease in temperature can only change from $\Gamma_4$ to $\Gamma_2$.

On the other hand, Jacobs et al. [26] in YCrO$_3$ observe SR transition induced by an external magnetic field. When the magnetic field, applied in the direction of the easy axis magnetization ($z$ -axis), grows a smooth rotation of the antiferromagnetic vector in the $xz$ -plane is observed. If we have a temperature-dependent SR transition in this compound, with the decreasing of the temperature, the spins have to rotate in the same way as in the case of an external magnetic field. However, $Y$ is a non-magnetic ion, the antisymmetric exchange interaction $Y$-Cr is zero and the model of Yamaguchi [9] is not applicable. Which interaction is responsible for the presence of temperature-dependent SR transition? It is logical to assume that the exchange interactions between Cr ions and their dependency of the spontaneous polarization $P_s$ will stimulate both the temperature SR transition and occurrence of the additional spontaneous polarization $\Delta P$ under $T_N$

We think this phenomenon can be qualitatively explained in the following way. YCrO$_3$ is a ferroelectric of type ABO$_3$ with transition temperature $T_c = 450$ K. The occurrence of spontaneous polarization $P_s$ is determined by the relative displacement of $Y$- and Cr- ions. On the other hand, the magnitude of the symmetric and antisymmetric exchange interaction depends on the distance between the magnetic ions in Cr-O-Cr bonds. The relative displacement of $Y^{3+}$- and Cr$^{3+}$- ions, which are responsible for the occurrence of spontaneous polarization, modulate the exchange interactions. If we designate the displacement of Cr ion towards its equilibrium state in the paraelectric phase with „u”, expand the vector of Dzyaloshinskii-Moriya $\mathbf{D}^{Cr-cr}_{ij}$, with respect to the „u” displacements, we get:

$$-\sum_{ij} \mathbf{D}^{Cr-cr}_{ij} \cdot [\mathbf{S}^C_r \times \mathbf{S}^C_r] \approx -\sum_{ij} \mathbf{D}^{Cr-cr}_{ij} \cdot [\mathbf{S}^C_r \times \mathbf{S}^C_r] - \lambda' \sum_{ij} (\mathbf{P}_3 \times \mathbf{e}^{Cr-cr}_{ij}) \cdot [\mathbf{S}^C_r \times \mathbf{S}^C_r] ,$$

(1)

where $\lambda' = \lambda/\epsilon$, $\lambda$ is the spin–lattice interaction which is a consequence of the relativistic spin–orbit interaction, $\epsilon$ the Born ionic charge and $P_3 = e^* < u >$ is the spontaneous polarization.

Analogically we expand isotropic exchange interaction $J^{Cr-cr}_{ij}$ regarding to the displacement „u” of Cr ions. Then we get:

$$-\gamma' \sum_{ij(nn)} |\mathbf{P}_3|^2 (\mathbf{S}^C_r \cdot \mathbf{S}^C_r) - \gamma \sum_{ij(nn)} |\mathbf{P}_3|^2 (\mathbf{S}^C_r \cdot \mathbf{S}^C_r)$$

(2)

where $\gamma' = \gamma/\epsilon$. $\gamma$ and $\gamma'$ are the second derivatives of $J^{Cr-cr}_{ij}$ and $J^{Cr-cr}_{ij}$ from the polar displacements „u”.

In the Hamiltonian appears an additional term of the form $-\lambda' \sum_{ij} (\mathbf{P}_3 \times \mathbf{e}^{Cr-cr}_{ij}) \cdot [\mathbf{S}^C_r \times \mathbf{S}^C_r]$. Comparing this term with the conventional DM interaction we conclude that the spontaneous polarization induces a DM interaction with the vector $\mathbf{D}^{Cr-cr}_{ind} = \lambda' (\mathbf{P}_3 \times \mathbf{e}^{Cr-cr}_{ij})$. This term is formally similar to the Peierls-type spin-phonon interaction. Note that the spontaneous polarization $P_3$ is not a consequence of the magnetic phase transition. Instead of that $P_3$ causes a change in the hybridization of the magnetic Cr-O-Cr and Cr-O-O-Cr bonds so that below $T_N$ the G-type structure is affected by the spontaneous polarization. We can define the temperature-dependent effective DM vector whose value increases when the temperature decreases below $T_N$. Analogically the terms in Eq. (2) make the isotropic super-exchange interactions $J_1$ and $J_2$ also temperature-dependent $J^{Cr-cr}_{1(2)} = J^{Cr-cr} + \gamma |P|^2$. The expressions in (1) and (2) determine in natural way the coupling between the two subsystems: magnetic and ferroelectric one.

On the base of the above considerations, the occurrence of a temperature-dependent SR transition in RCrO$_3$ can be qualitatively explained as follows: the induced antisymmetric interaction between Cr$^{3+}$ ions leads to appearance of an additional effective field favouring the rotation of Cr$^{3+}$ spins from $z$ -axis to $x$ -axis in $xz$ -plane. When the temperature decreases, the effective field increases because spontaneous polarization increases.
At a given temperature, when the energy of interaction of Cr$^{3+}$ spins with this effective field equals with the anisotropy energy of the Cr$^{3+}$ ions over the z-axis, conditions for spin-reorientation are created. In addition, the induced DM interaction determines an effective field on x-axis. Thus, the effective field on z-axis compensates the magnetic anisotropy and the effective field on x-axis rotates Cr-spin in the zxy-plane (Fig. 2).

In order to prove our hypothesis we define the following Hamiltonian which describes the multiferroic properties of RCrO$_3$ compounds with R non-magnetic ion (R = Y, La, Lu and Eu):

$$H = H_s + H_m + H_{me}.$$  

The first term in Eq. (3) describes the behaviour of the ferroelectric subsystem in on the base of the transverse Ising model with pseudo-spin $B = 1/2$:

$$H_e = -\Omega \sum_i B_i^z - \frac{1}{2} \sum_{ij} A_{ij} B_i^z B_j^z - \mu \sum_i \vec{E} \cdot \vec{B},$$  

where $B_i^z$ and $B_j^z$ are the components of pseudo-spins, $A_{ij}$ is the exchange pseudo-spin interaction, $\Omega$ is the tunneling frequency and $\vec{E}$ is the external electric field. The spontaneous polarization in pseudo-spin presentation has the following form:

$$\vec{P}_z = \left[ \frac{1}{N} \sum_i B_i^z; 0; \frac{1}{N} \sum_i B_i^x \right].$$  

The second term in Eq. (3) defines the magnetic behavior on the base of modified Heisenberg’s Hamiltonian including the antisymmetric exchange interaction and the magnetic anisotropy in the single-ion approximation:

$$H_m = -\sum_{ij} J_{ij} (\vec{S}_i \cdot \vec{S}_j) - \sum_{<ij>} J_{il} (\vec{S}_i \cdot \vec{S}_l) - \sum_{ij} \vec{B}_{ij} \cdot (\vec{S}_i \times \vec{S}_j) - K \sum_i (\vec{S}_i^z)^2 - g \mu_B \sum_i \vec{H} \cdot \vec{S}_i^z,$$  

where $\vec{S}_i$ is the spin of Cr$^{3+}$ ion, $J_{ij}$ and $J_{il}$ are the symmetric exchange interactions between the nearest-neighbours (nn) along the Cr–O–Cr bond and the next-nearest-neighbours (nnn) along the Cr–O–O–Cr bond, respectively. $\vec{B}_{ij}$ represents the DM vector characterizing the antisymmetric spin’s exchange interaction. The DM vector depends of the geometry of the Cr-O-Cr bonds and crystal structure. It is responsible for the weak ferromagnetism. The fourth term gives the single-ion (easy axis) anisotropy (SIA) along z-axis. The magnetization of the system is defined from $M = \frac{1}{N} \sum_i < S_i^z >$.

Third term in Eq. (3) defines the ME interaction between the magnetic and ferroelectric subsystems:

$$H_{me} = -\lambda' \sum_{ij} \left( \vec{P}_S \times \vec{e}_{ij} \right) \cdot (\vec{S}_i \times \vec{S}_j) - \gamma \sum_{ij(\text{nn})} (\vec{P}_S \times \vec{S}_i) \cdot (\vec{S}_j \times \vec{S}_j) - \gamma' \sum_{ij(\text{nnn})} (\vec{P}_S \times \vec{S}_i) \cdot (\vec{S}_j \times \vec{S}_j).$$  

### III. METHOD AND NUMERICAL RESULTS

A Following [27,28] for the extraordinary polarization below $T_N$ we find:

$$\Delta P_\phi^\alpha = \lambda' \sum_{ij} [\vec{e}_{ij} \times (\vec{S}_i \times \vec{S}_j)]^\alpha;$$  

$$\Delta P_{\phi S}^\alpha = \gamma \sum_{ij} (\vec{e}_{ij})^\alpha (\vec{S}_i \times \vec{S}_j) + \gamma' \sum_{ij(\text{nn})} (\vec{e}_{ij})^\alpha (\vec{S}_i \times \vec{S}_j),$$

where $\alpha = x, y, z$. $\Delta P_\phi^\alpha$ in Eq. (8) determines the emergence of polarization due to the strong interaction between ferroelectricity and frustrated magnetism due to the DM interaction (so called spin-current model). $\Delta P_{\phi S}^\alpha$ in Eq. (9)
determines the magnetostrictive mechanism which causes polarization in systems where a magnetic arrangement breaks the centrosymmetry of the structure. For calculation of the extraordinary polarization, we define for a given spin and DM vector their components as follows:

1/ For the magnetic configuration $\Gamma$;

$$\vec{S}(S_f^x; S_i^y; S_i^z); \quad \vec{D}_{ij} (D_{ij}^x; D_{ij}^y; D_{ij}^z).$$

(10)

For convenience, we assume that the weak ferromagnetism is always in the direction of the z-axis independently of the magnetic configuration. In the case of $\Gamma$, we rotate the coordinate system along the y-axis as $z \rightarrow x$ and $x \rightarrow z$. Thus, the weak ferromagnetism in the new coordinate system is along the z-axis.

2/ For the magnetic configuration $\Gamma_2$ we have the following coordinate transformation:

$$\left( S_f^x; S_f^y; S_f^z \right) \rightarrow \vec{S}_i \left(-S_i^x; S_i^y; S_i^z \right); \quad \vec{D}_{ij} (D_{ij}^x; D_{ij}^y; D_{ij}^z) \rightarrow \vec{D}_{ij} (-D_{ij}^x; D_{ij}^y; D_{ij}^z).$$

(11)

Here, we should note that for each position of the spins in the unit cell, for the calculations is necessary to take into account the corresponding sign of the component of the spins and the DM vector. We determine the sign and direction of the vector of the DM interaction from Eq. (27) in [21] which determines the relationship between $\vec{D}$ and the coordinates of the Cr-ions in the unit cell at a given Cr-O-Cr bond.

For the calculation of extraordinary polarization $\Delta P$ from Eqs. (8) and (9) of particular importance is the point group symmetry of the crystal. Following the rules of influences of individual elements of symmetry on the direction and size of the DM interaction defined in [29] and [30] and the influence of symmetry on canted-spin-caused electric dipole [31] for the extraordinary polarization below $T_K$ we get:

$$\Delta P_{\text{ex}} = 2\lambda \Sigma_{ij} \langle S_f^i S_f^j \rangle;$$

$$\Delta P_{\text{ex}} = 0.$$

(12)

(13)

From a symmetrical point of view, we have proven that a magnetostrictive mechanism in RCrO$_3$ when R is non-magnetic does not form extraordinary polarization as in the case when R is magnetic [32]. From the theoretical calculations we can conclude that the expressions (12) and (13) are valid for two spin configurations $\Gamma_1$ and $\Gamma_2$ where the direction of the extraordinary polarization is along the y-axis for both of them. Instead of the $x, y, z$ components of the vectors $\vec{S}, \vec{B}$ and $\vec{D}$ we introduce the following operators:

$$S_i^+ = \frac{1}{\sqrt{2}} (S_i^x \pm iS_i^y); \quad S_i^- = S_i^z;$$

$$B_i^+ = \frac{1}{\sqrt{2}} (B_i^x \pm iB_i^y); \quad B_i^- = B_i^z;$$

$$D_{ij}^+ = \frac{1}{\sqrt{2}} (D_{ij}^x \pm iD_{ij}^y); \quad D_{ij}^- = D_{ij}^z.$$

For the numerical calculations the expression for the extraordinary polarization finally we get:

$$\Delta P_{\text{ex}} = i\sqrt{2}\lambda \Sigma_{ij} \left[ \langle S_i^+ S_f^+ \rangle - \langle S_i^- S_f^- \rangle \right].$$

(14)

For the theoretical calculations we using the method of retarded Green’s functions (GF) [32]. This method is widely used for investigation of manybody complex systems whose subsystems are interacted intensive. This leads to occurrence of nonlinear interactions in which absent the small coupling parameter. Green’s functions are universal approach to calculate the static and dynamic characteristics of the different systems. Formalism is very convenient because is not used operators but complex functions which have simple analytical properties. GF allows a single solution of all quantum statistical problems of many systems. The obtained expressions are in analytical form and they are convenient for numerical calculations.

In order to calculate the spontaneous polarization, magnetization and extraordinary polarization we will use retarded Green’s function in Heisenberg’s presentation:

$$G_{AB} = \langle \hat{A}(t); \hat{B}(t) \rangle = -\theta(t-t') < [\hat{A}(t); \hat{B}(t')]_\tau > .$$

(15)

We define the following Green’s function in the energetic presentation:

$$G_{1 g}^{(ex)} = \langle S_f^+, S_g^- \rangle_E ;$$

$$G_{1 g}^{(ps)} = \langle B_f^+, B_g^- \rangle_E .$$

After Fourier transformation, the equations of motion are:

$$Eg_{1 g}^{(ex)} = \frac{i}{2\pi} < [S_f^+, S_g^-] > + \langle [S_f^+/H]; S_g^- \rangle,$$

$$Eg_{1 g}^{(ps)} = \frac{i}{2\pi} < [B_f^+, B_g^-] > + \langle [B_f^+/H]; B_g^- \rangle .$$

(16)
From the pole of the Green’s function, we obtain in the random phase approximation the energy $E_i$ of the $i$th spin and the energy $\omega_i$ of the $i$- pseudo-spin taking into account the transverse correlation functions, whereas the longitudinal ones are decoupled. The correlation functions are calculated from the spectral theorem [32]. Then for $<S_1^z>$, $<B_1^z>$ and $<B_1^z>$ we get:

\[
\begin{align*}
< S_1^z > &= \left( S + \frac{1}{2} \right) \text{coth} \left( \frac{1}{2} \frac{E_i}{k_B T} \right) - \frac{1}{2} \frac{E_i}{k_B T} ; \\
< B_1^z > &= \frac{1}{2} \frac{A_{\text{eff}}}{\omega_i} \frac{\omega_i}{k_B T} ; \\
< B_1^z > &= \frac{1}{2} \frac{B_{\text{eff}}}{\omega_i} \frac{\omega_i}{k_B T} ,
\end{align*}
\]

where:

\[
A_{\text{eff}} = \sum_i \left[ A_{ij} + 4 \gamma \sum_{kl} < (\vec{S}_k \cdot \vec{S}_l) > + \gamma \sum_{<kl>} < (\vec{S}_k \cdot \vec{S}_l) > \right] \delta_{ij} < B_i^z > + \frac{\gamma^2}{2} \sum_{kl} < (\vec{S}_k \times \vec{S}_l)^2 > ;
\]

\[
\Omega_{\text{eff}} = \Omega + \frac{\gamma^2}{2} \sum_{kl} < (\vec{S}_k \times \vec{S}_l)^2 > ;
\]

\[
J_{ij} = \sqrt{\left( J_{ij} \right)_{\text{eff}}^2 + \left( D_{ij} \right)_{\text{eff}}^2} \quad \left( J_{jj} \text{eff} = J_{ij} + \gamma P_S^2 \right) ;
\]

\[
J_{ij} \text{eff} = J_{ij} + \gamma P_S^2 ;
\]

\[
\omega_i = \sqrt{A_{\text{eff}}^2 + \Omega_{\text{eff}}^2} ;
\]

\[
E_i = \frac{2}{N} \sum_j \left( \bar{J}_{ij} + J_{ij} \text{eff} \right) < S_j^z > - \frac{2}{N} \sum_j \left( \sqrt{\left( J_{ij} \right)^2 + \left( D_{ij} \right)^2_{\text{eff}} + J_{ij}^2} \right) < S_j^z > + 2K_i < S_i^z > + g \mu_B h .
\]

Following [11] in order to prove the existence of an SR transition, we will define three types of Hamiltonians. The first - corresponding to the magnetic configuration $\Gamma_1$ and having the type defined in Eq. (3). The second - corresponding to the magnetic configuration $\Gamma_4$, which is obtained by replacing in Eq. (3) the components of the spin vectors and the DM vector as defined in Eq. (11). The third Hamiltonian describes the magnetic configuration (denoted by $\Gamma_{42}$) when Cr spins rotate in the zx-plane. Because of this, we introduce an angle $\phi$, which determines the deviation of spins from the z-axis. According to Fig. 2 (b), the Cr-spin components for a given angle $\phi$ for $\Gamma_{42}$ will be defined as follows:

\[
\vec{S}_i (\Gamma_{42}) (S_i^z \sin \phi - S_i^x \cos \phi; S_i^x \sin \phi + S_i^z \cos \phi) .
\]

Substituting the last expressions into the Hamiltonian of the orthochromites Eq. (3), we observe a new expression for the Hamiltonian which describes the temperature dependent SR transition. This Hamiltonian already depends on the angle $\phi$: $H = H(\phi)$. We suspect that the transition of the system from $\Gamma_4$ to $\Gamma_2$ passes through a series of equilibrium states with fixed angle which define a specific spin orientation. Then at a given temperature exist such $\phi(T)$ angle for which the system has a minimum of the energy $E_{\text{tot}} = <H>$. The value of $\phi$ at a given temperature is calculated from the following equation:

\[
\frac{\partial <H(\phi)>}{\partial \phi} = 0 .
\]

Finally, the total energy of the system for the three magnetic configurations is calculated numerically as function of the temperature. From the intersection points of the curves which determine the dependence of $E_{\text{tot}}(\Gamma_4)$, $E_{\text{tot}}(\Gamma_4)$ and $E_{\text{tot}}(\Gamma_{42})$, from $T$ we will prove the existence and nature of SR transition (rotational or abrupt).

For the numerical calculations we use the following model parameters appropriated for YCrO$_3$: $A = 575.12 \text{ cm}^{-1}$; $\Omega = 21.35 \text{ cm}^{-1}$; $J_1 = -13.58 \text{ cm}^{-1}$; $J_2 = -3.45 \text{ cm}^{-1}$; $D = 4.25 \text{ cm}^{-1}$; $\lambda = 1.43 \text{ cm}^{-1}$; $\gamma_1 = 3.43 \text{ cm}^{-1}$; $\gamma_2 = 1.56 \text{ cm}^{-1}$ and $K = 0.087 \text{ cm}^{-1}$. A detailed description of the methodology for determining model parameters for the system is discussed in [11]. Fig. 3 presents the temperature dependence of $E_{\text{tot}}$ for the three magnetic configurations. For temperatures greater than $T_1$, but less than $T_{\text{cr}}$, the magnetic configuration $\Gamma_4$ has the lowest energy. For temperatures from $T_2$ to 0 K the lowest energy has the magnetic configuration $\Gamma_2$. This unambiguously suggests that when the temperature decreases a transition from $\Gamma_4$ to $\Gamma_2$ occurs, i.e. temperature-dependent spin reorientation transition in YCrO$_3$ is proven. In the temperature interval between $T_1$ and $T_2$ the magnetic configuration is stable when with decreasing of the temperature, the angle $\phi$ continuously increases (Fig. 2). This means that the SR transition is continuous. The numerical calculations show that this SR transition performed in a temperature interval from 64 K to 25 K. As a result this coincides with the experimentally observed anomaly in the magnetic specific heat capacity in YCrO$_3$ [22].
Fig. 3. Temperature dependence of $E_{\text{tot}}(T)=\langle H(T) \rangle$ in YCrO$_3$ with $E_{\text{tot}}(\Gamma_4)$ (green line), $E_{\text{tot}}(\Gamma_{42})$ (red line) and $E_{\text{tot}}(\Gamma_2)$ (black line). $T_1$ is the SR temperature between the phases $\Gamma_4$ and $\Gamma_{42}$ whereas $T_2$ is between $\Gamma_{42}$ and $\Gamma_2$.

Fig. 4. Temperature dependence in YCrO$_3$ of the a/ magnetization $M$ and b/ extraordinary polarization $\Delta P$ for a poling field $E = 1.5$ kV/cm and different h-values 1/ $h = 10$ kOe; 2/ $h = 100$ Oe.

In Fig. 4 are presented the numerical calculations of the $M$ dependence and the extraordinary polarization $\Delta P$ from the temperature. The obtained results show that the microscopic model proves the existence of additional polarization $\Delta P$ in the RCrO$_3$ compounds when R is a non-magnetic ion. The results obtained show good qualitative coincidence with the experimental results reported in [12,22].

Fig. 5 shows the dependence of $\Delta P$ on the magnitude of the constant of the antisymmetric exchange interaction $D$. It is clear that with the increase of the intensity of the DM interaction the value of the additional polarization increases. This is another important proof of the adequacy of the built-up microscopic model. It is well known that for systems in which polarization occurs as a result of magnetic phase transition within the so-called spin-current model, the antisymmetric DM interaction stabilizes the multiferroic phase [27].
Fig. 5. The extraordinary polarization $\Delta P$ in YCrO$_3$ as a function of the constant of the antisymmetric exchange interaction $D$ for a poling field $E = 1.5$ kV/cm and different $T/T_N$ values 1/2 $T/T_N = 0.5$; 2/2 $T/T_N = 0.6$.

As we noted above, a remarkable feature of multiferroic compounds is the possibility to control the magnetization by an external electric field and with an external magnetic field to be controlled the polarization. This is a consequence of the ME interactions defined by the Eq. (7). The dependence of the magnetization of the system on an external electric field $E$. With the increase of $E$, the magnetization decreases. This result can be qualitatively explained as follows: with the increase of the electric field, the spontaneous polarization $P_S$ increases, which results in an increase in the value of the vector of DM interaction. The reason for this is that the arrangement of the electrical dipoles induces an additional antisymmetric exchange interaction $D_{ind}^{Cr-Cr} = \lambda'(\vec{P}_S \times \vec{e}_{ij}^{Cr-Cr})$. Increasing the magnitude of DM interaction results in an increase of the weak ferromagnetism. Also, with increasing $E$, the value of a symmetric exchange interaction $J_{eff}^{Cr-Cr} + \gamma P^2$ increases. $J_{eff}^{Cr-Cr}$ seeks to orient spins antiferromagnetically by reducing their deviation from the ideal collinear structure. Both mechanisms are in competition - the symmetrical exchange interaction prevails over antisymmetric one and as a result the macroscopic magnetization decreases. The dependence of the magnetization on the electric field is in qualitative coincidence with the experimental results reported in [34-36].

Fig. 6. The dependence of the magnetization $M$ in YCrO$_3$ from external electric field $E$ at $T/T_N = 0.5$ for: 1/2 $h = 10$ kOe and 2/h = 100 Oe.

The Eq. (7) for ME interaction also determines the ability spontaneous polarization $P_S$ to be controlled by the external magnetic field. This expression can be seen as a kind of feedback. The dependence of spontaneous polarization $P_S$ in YCrO$_3$ on the external magnetic field. This dependence is calculated for two different directions of $h$ - [0,0,1] and [1,0,0]. As the magnitude of the field increases in the direction of the $z$-axis, spontaneous polarization $P_S$ increases reaching saturation (Fig. 7 (a)). When the field is applied in the direction of the $x$-axis, $P_S$ decreases (Fig. 7 (b)). The qualitative explanation of this behaviour is determined by the fact that the tunnelling frequency $\Omega$ and the exchange pseudo interaction $A$ are renormalized by the appearance of weak ferromagnetism under $T_N$. The theoretical calculations for the renormalized tunnelling frequency and exchange interaction give the following expressions:

$$\Omega_{eff} = \Omega + 4\lambda \sum_i \frac{\Psi_i(|\Psi_i\varphi_i h_i < S_i^z |)}{(2\gamma_{ij} h_i)^2};$$  \hspace{1cm} (21)

$$A_{eff} = A + 4\gamma \sum_i (< S_i^z >)^2;$$  \hspace{1cm} (22)

where: $\Psi_i = 4 \sum_j (J_{ij eff} + J'_{ij eff}) < S_j^z >$. 
Fig. 7. The spontaneous polarization $P_S$ as a function of the external magnetic field in the direction a/ $h_{[0,0,1]}$ and b/ $h_{[1,0,0]}$ for 1/ $T/ T_N = 0.5$ and 2/ $T/ T_N = 0.6$.

At a given temperature when an external magnetic field is applied to the $z$-axis ($h_{[0,0,1]}$) from Eq. (21) follows that the tunneling frequency does not change until the symmetric exchange pseudo-spin interactions increases (Eq. (22)) because $< S_i^z >$ increases. Increasing $\Delta_{eff}$ leads to an increase in $P_S$ [33]. Saturation of spontaneous polarization at large magnetic field values is naturally explained by the fact that spin is oriented entirely in the $z$-axis direction.

Applying an external magnetic field in the direction of the $x$-axis ($h_{[1,0,0]}$), when $h$ increases the tunneling frequency increases, whereas $\Delta_{eff}$ decreases due to the decrease of $< S_i^z >$ with the increase of the magnetic field. This reduces the value of spontaneous polarization $P_S$ [33]. In the case of a critical value of the magnetic field along the $x$-axis $h^C_{[1,0,0]}$ due to the increase of the tunneling frequency, the spontaneous polarization in the system must be disappear, i.e. $P_S = 0$. Numerical calculations show that for $T/ T_N = 0.5$ $h^C_{[1,0,0]} = 166$ kOe, and for $T/ T_N = 0.6$ $h^C_{[0,0,1]} = 98$ kOe. A similar dependence of $P_s$ on the direction of the magnetic field was observed in BiFeO$_3$ [37,38]. The numerical calculations show that in both orientations that with increasing of the external magnetic field $h$ the width of the temperature interval $\Delta T_{SR} = T_1 - T_2$ decreases (Fig. 8). There are different reasons for this and they can qualitatively be explained by the balance of energy between DM interaction, magnetic anisotropy and the interaction of spins with the external magnetic field.
As we already noted, when h is in the direction of z-axis (the axis of the easy magnetization) the induced antismetric interaction between Cr$^{3+}$ ions lead to appearance of additional effective field, which favours the rotation of Cr$^{3+}$ spins from z-axis to x-axis in zx-plane. When the temperature decreases, the effective field increases because the spontaneous polarization increases. At a given temperature, when the energy of interaction of Cr$^{3+}$ spins with this effective field becomes equal to the sum of the energy of the magnetic anisotropy of Cr$^{3+}$ ion and the energy of interaction of Cr$^{3+}$ ion with the external magnetic field on the z-axis are created conditions for spin reorientation. Increasing the value of the magnetic field leads to an increase in the value of energy $\sum_i \vec{S}_i^2 h_z$. This determines the need for a higher value of the effective energy which is a consequence of the DM interaction in order to compensate the other two – by the anisotropy and by the magnetic field. This is possible at a higher value of $\vec{D}_{ij}^{Cr-Cr}$, i.e. at a greater value of the spontaneous polarization. The increase of $P_s$ in these compounds becomes with decrease of the temperature. This means that the SR transition will start at a lower temperature with an increase of the external magnetic field, i.e. $T_1$ decreases with the increase of the h$_{[0,0,1]}$. At the moment when the balance of the above mentioned energies on the z-axis becomes zero, the induced DM interaction determining an effective field along x-axis will begin the rotation of Cr$^{3+}$ spins. As far as only DM interaction is responsible for the rotation, the end of the SR transition is occurred at the same temperature $T_2$ in which a magnetic field is absent (Eq. 21). It is clear that this picture causes reduction of the $\Delta T_{SR}$ with the increase of the external magnetic field on the z-axis. When h is in the direction of the x-axis to the energy of interaction of the external magnetic field with Cr spin is added the energy of the effective field which determines by the induced DM interaction on the x-axis. This results in a faster rotation of the spins from z-axes to x-axes. This means that at a higher value of $T_2$ the SR transition will end. $\Delta T_{SR}$ will decrease as the external magnetic field increases along the x-axis. The experimental results published in [39] confirm the theoretical predictions reported by us.

IV. CONCLUSION

A microscopic theory of magnetoelectric effects in multiferroic RCrO$_3$ compounds, where R is a non-magnetic ion (R = Y, La, Lu and Eu) is presented. For the theoretical calculations temperature-dependent retarding functions of Green and the procedure of Tyablikov for splitting of the higher Green’s functions were used. In these calculations, the Ising model in transverse field for a pseudo-spin $B = 1/2$ was used. ME interaction between the magnetic and the ferroelectric subsystems is described by biquadratic term with respect to spin and pseudo-spin operators $-\gamma \sum_{ij} (\vec{P})^2 (\vec{S}_i \cdot \vec{S}_j) - \gamma' \sum_{ij} (\vec{P})^2 (\vec{S}_i \times \vec{S}_j)$ and an antisymmetric term describing induced DM interaction from the polar displacements of R ions to Cr $-\lambda' \sum_{ij} (\vec{P} \times \vec{e}_{ij}) \cdot (\vec{S}_i \times \vec{S}_j)$. This model makes it possible to describe and qualitatively explain the occurrence of a temperature-dependent spin-reorientation transition and the occurrence of extraordinary polarization below the temperature of the magnetic phase transition. It was theoretically found that the antisymmetric ME interaction renormalizes the tunnelling frequency while the biquadratic ME interaction renormalizes the pseudo-spin exchange interaction under $T_N$. This makes it possible to qualitatively explain the dependence of the spontaneous polarization $P_s$ from the magnitude and direction of the external magnetic field. It has been established that when applied h along the axis of the easy magnetization (z-axis), with the increase of the magnetic field, $P_s$ increases, reaching saturation. When h is applied to the x-axis, i.e. perpendicularly to the axis of the easy magnetization, $P_s$ decreases as the magnetic field increases, as at a given critical value of the external field $h_{[1,0,0]}$, the spontaneous polarization becomes equal to zero. It has been established that the width of the temperature interval $\Delta T_{SR}$ in which SR transition occurs, decreases with the increase in the value of the external magnetic field. When h is along the z-axis, with the increase of field $T_1$ decreases, i.e. the beginning of SR transition starts at a lower temperature. When h is applied along the x-axis $T_2$ increases with the increasing of the field.

Fig. 8. Dependence of the temperature interval $\Delta T_{SR} = T_1 - T_2$ in which the continuous spin reorientation transition exist from the external magnetic field is performed: a/h$_{[0,0,1]}$ and b/h$_{[1,0,0]}$. 

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i.e. the SR transition ends at a higher temperature. There are good qualitative coincidences with the experimental results.

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