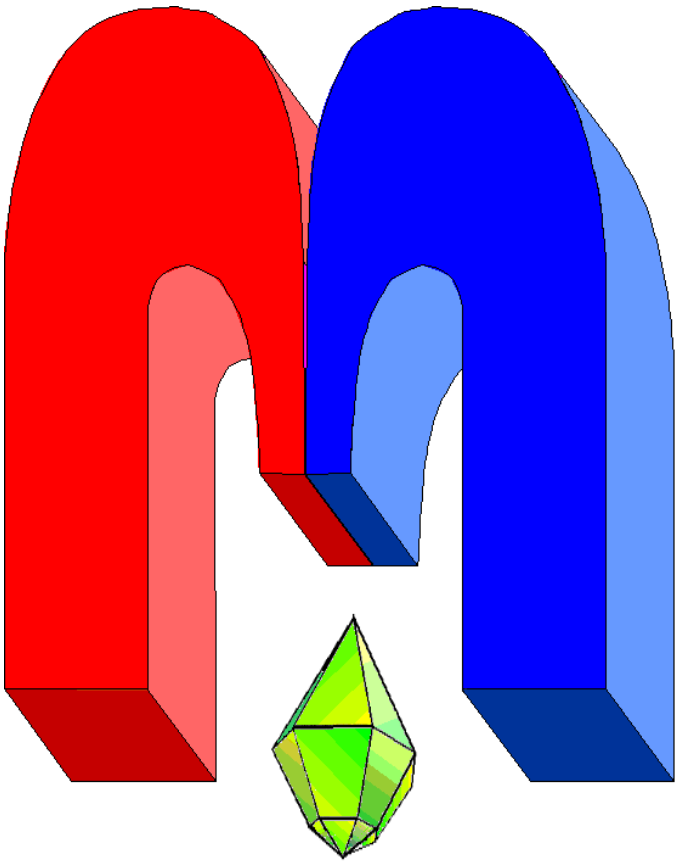
ISSN 2072-5981
doi: 10.26907/mrsej



# Magnetic Resonance in Solids

Electronic Journal

*Volume* ***21***
*Special Issue* ***3***
*Paper No* ***19303***
*1-6 pages*
***2019***
doi: **10.26907/mrsej-19303**

http://mrsej.kpfu.ru
http://mrsej.ksu.ru

Established and published by Kazan University
Endorsed by International Society of Magnetic Resonance (ISMAR)
Registered by Russian Federation Committee on Press (#015140), August 2, 1996
First Issue appeared on July 25, 1997



"***Magnetic Resonance in Solids. Electronic Journal***" (**MRS*ej***) is a peer-reviewed, all electronic journal, publishing articles which meet the highest standards of scientific quality in the field of basic research of a magnetic resonance in solids and related phenomena.

Indexed and abstracted by
*Web of Science* (*ESCI*, Clarivate Analytics, from 2015), *Scopus* (Elsevier, from 2012), *RusIndexSC* (*eLibrary*, from 2006), *Google Scholar*, *DOAJ*, *ROAD*, *CyberLeninka* (from 2006), *SCImago Journal & Country Rank*, etc.





* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

# Magnetoelectric coupling in noncollinear ferrimagnets

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(Received March 30, 2019; accepted March 31, 2019; published April 19, 2019)

The analytical expressions for the energy coupling of exchange coupled spins with electric field, induced by odd crystal field has been derived in the third order perturbation theory, combining the action of electric field, spin-orbit and exchange interactions. The magnetoelectric coupling due to the partial replacement of the $Cu^{2+}$ positions by $Li^{+}$ in $LiCuVO_4$ has been discussed.

**PACS:** 77.80.-e, 76.30.Fc.

**Keywords:** multiferroics, $LiCuVO_4$, incommensurate magnetic structure.

*In honor of Professor Boris Ivanovich Kochelaev*

## 1. Introduction

The materials, which simultaneously exhibit a long-range magnetic order and a spontaneous electric polarization, have attracted a great attention due to their potential applications in promising electronic devices as well as the source of fundamental knowledge of the nature of spins and electric field coupling [1–3]. Recent reviews of such kind materials and possible microscopic mechanisms are presented in Refs. [4–7]. Among most relevant mechanisms are magnetostriction and the so called inverse Dzyaloshinskii-Moriya (DM) mechanism [8, 9]. Currently the suggested expressions of spin-electric field coupling have a phenomenological status since the estimated parameters of suggested spin-Hamiltonian parameters are still do not to correspond those which determined experimentally [10]. Moreover, in particular for $LiCuVO_4$ and $LiCu_2O_2$ the inverse Dzyaloshinskii-Moriya (DM) mechanism [11, 12] fails to reproduce the direction of spontaneous electric polarization induced by spin order at $T < T_N$. Therefore, the phenomenological expressions for spin-electric field coupling should be revised as well.

In the present communication we study the effect of an electric field, induced by an odd crystal field, on a system of exchange-coupled spins. It is known that odd crystal field plays a key role in the theory of electric field effect in electron paramagnetic resonance [13] and in the theory of induced electric dipole transitions in optical spectroscopy [14]. Recently it was found that its role is important for explanation of the peculiarity of magnetoelectric coupling in $FeCr_2O_4$ ferrimagnet [15]. The ground state of $Fe^{2+}$ in $FeCr_2O_4$ possesses the orbital degree of freedom. In present communication we study the exchange coupled systems like $LiCuVO_4$ and $LiCu_2O_2$ in which the ground states of magnetic ions are nondegenerate and assume that the energy intervals between ground and excited states are much larger with respect to exchange interactions.

## 2. Matrix elements of electric field enhanced by odd crystal field

The energy operator of interaction of an electron with applied electric field is written as follows:

$$V = \sum D^{(1)}_{q'} a^{+}_{\eta} \left( \eta \right| C^{(1)}_{q'} \left| \xi \right) a_{\xi} \,, \tag{1}$$

where $C^{(k)}_{q'} = \sqrt{4\pi/(2k+1)}\, Y_{kq}$ are the spherical tensor components, $D^{(1)}_{q'}$ are quantities related to the applied electric field components; $D^{(1)}_{0} = |e|\, r\varepsilon_z E_z$, $D^{(1)}_{\pm 1} = \mp |e|\, r \left(\varepsilon_x E_x \mp i\varepsilon_y E_y\right)/\sqrt{2}$, $\varepsilon_x, \varepsilon_y, \varepsilon_z$ are dielectric permittivity parameters. For the case of the isotropic medium $\varepsilon_x = \varepsilon_y = \varepsilon_z = (\varepsilon + 2)/3$.

The energy operator corresponding to the odd crystal field acting on the magnetic ions can be written in the same form:

$$H_{\rm cr} = \sum B_q^{(k)} a_\eta^+ \left(\eta\right| C_q^{(k)} \left|\xi\right) a_\xi \,. \tag{2}$$

The odd crystal field leads to the admixture of the opposite-parity excited $3d^{n-1}4p$ states to the ground states of the $3d^n$ electron configuration. As a result, it induces the effect of the applied electric field on the orbital degrees of freedom of $3d$-electrons.

The effective operator describing the coupling of orbital states for $3d$-electrons with enhanced electric field is derived in the second order of perturbation theory. Using second quantization technique one has

$$\begin{aligned} H_E &= -\frac{1}{\Delta_{pd}} \sum B_q^k D_{q'}^{(1)} a_\eta^+ \left(\eta\right| C_q^{(k)} \left|\xi'\right) a_{\xi'} \, a_\xi^+ \left(\xi\right| C_{q'}^{(1)} \left|\eta'\right) a_{\eta'} + \text{h.c.} \\ &= \sum E_q^{(k)} D_{q'}^{(1)} a_\eta^+ \left[ \left(\eta\right| C_q^{(k)} \left|\xi\right) \left(\xi\right| C_{q'}^{(1)} \left|\eta'\right) + \left(\eta\right| C_{q'}^{(1)} \left|\xi\right) \left(\xi\right| C_q^{(k)} \left|\eta'\right) \right] a_{\eta'} \\ &= \sum a_\eta^+ \left(\eta\right| H_E \left|\eta'\right) a_{\eta'}. \end{aligned} \tag{3}$$

Here for short we have introduced the quantities $E_q^{(k)} = -B_q^{(k)} / \left|\Delta_{pd}\right|$, where $\Delta_{pd}$ is the energy interval between excited $3d^{n-1}4p$ and ground $3d^n$ states. We have calculated the expressions for the matrix elements in the basis of wave functions $|3dm_l\rangle$ which are given below:

$$\begin{aligned} \langle 2| H_E |2\rangle &= \langle -2| H_E |-2\rangle = \frac{\sqrt{6}}{35} \left( E_1^{(3)} D_{-1}^{(1)} + E_{-1}^{(3)} D_1^{(1)} \right) - \frac{2}{5} \left( E_1^{(1)} D_{-1}^{(1)} + E_{-1}^{(1)} D_1^{(1)} \right), \\ \langle 2| H_E |1\rangle &= -\frac{1}{7}\sqrt{\frac{3}{5}} E_2^{(3)} D_{-1}^{(1)} - \frac{\sqrt{3}}{35} E_1^{(3)} D_0^{(1)} - \frac{3\sqrt{2}}{35} D_1^{(1)} E_0^{(3)} \\ &\quad + \frac{\sqrt{2}}{5} \left( E_1^{(1)} D_0^{(1)} + D_1^{(1)} E_0^{(1)} \right), \\ \langle 2| H_E |0\rangle &= \frac{1}{5} E_1^{(3)} D_1^{(1)} + \frac{2}{7}\sqrt{\frac{1}{5}} E_2^{(3)} D_0^{(1)} + \frac{1}{7}\sqrt{\frac{3}{5}} E_3^{(3)} D_{-1}^{(1)} - \frac{2}{5}\sqrt{\frac{2}{3}} D_1^{(1)} E_1^{(1)}, \\ \langle 2| H_E |-1\rangle &= -\frac{3}{7}\sqrt{\frac{1}{5}} E_3^{(3)} D_0^{(1)} - \frac{3}{7}\sqrt{\frac{3}{5}} E_2^{(3)} D_1^{(1)}, \\ \langle 2| H_E |-2\rangle &= \frac{6}{7}\sqrt{\frac{2}{5}} E_3^{(3)} D_1^{(1)}, \end{aligned} \tag{4}$$

$$\begin{aligned} \langle 1| H_E |1\rangle &= \frac{1}{5} \left( 2E_0^{(1)} D_0^{(1)} - E_1^{(1)} D_{-1}^{(1)} + E_{-1}^{(1)} D_1^{(1)} \right) - \frac{6}{55} E_0^{(3)} D_0^{(1)} \\ &\quad - \frac{2\sqrt{6}}{55} \left( E_1^{(3)} D_{-1}^{(1)} + E_{-1}^{(3)} D_1^{(1)} \right), \\ \langle 1| H_E |0\rangle &= \frac{1}{5}\sqrt{\frac{1}{3}} \left( E_0^{(1)} D_1^{(1)} + E_1^{(1)} D_0^{(1)} \right) + \frac{\sqrt{2}}{5} E_1^{(3)} D_0^{(1)} \\ &\quad + \frac{4\sqrt{3}}{35} E_0^{(3)} D_1^{(1)} + \frac{1}{7}\sqrt{\frac{2}{5}} E_2^{(3)} D_{-1}^{(1)}, \\ \langle 1| H_E |-1\rangle &= -\frac{2}{5} E_1^{(1)} D_1^{(1)} - \frac{4\sqrt{6}}{35} E_1^{(3)} D_1^{(1)} - \frac{2}{7}\sqrt{\frac{6}{5}} E_2^{(3)} D_0^{(1)}, \\ \langle 1| H_E |-2\rangle &= \frac{3}{7}\sqrt{\frac{3}{5}} E_2^{(3)} D_1^{(1)} + \frac{3}{7}\sqrt{\frac{1}{5}} E_3^{(3)} D_0^{(1)}, \end{aligned} \tag{5}$$

$$
\begin{aligned}
\langle 0|\, H_E\, |0\rangle &= \frac{2}{15}\left(4E_0^{(3)}D_0^{(1)} - E_1^{(1)}D_{-1}^{(1)} - E_{-1}^{(1)}D_1^{(1)}\right) + \\
&+ \frac{12}{35}E_0^{(1)}D_0^{(1)} + \frac{2\sqrt{6}}{55}\left(E_1^{(3)}D_{-1}^{(1)} + E_{-1}^{(3)}D_1^{(1)}\right), \\
\langle 0|\, H_E\, |-1\rangle &= -\frac{1}{5}\sqrt{\frac{1}{3}}\left(E_0^{(1)}D_1^{(1)} + D_0^{(1)}E_1^{(1)}\right) - \frac{\sqrt{2}}{5}E_1^{(3)}D_0^{(1)} \\
&- \frac{4\sqrt{3}}{35}E_0^{(3)}D_1^{(1)} - \frac{1}{7}\sqrt{\frac{2}{5}}E_2^{(3)}D_{-1}^{(1)}, \\
\langle 0|\, H_E\, |-2\rangle &= -\frac{2}{5}\sqrt{\frac{2}{3}}E_1^{(1)}D_1^{(1)} + \frac{1}{5}E_1^{(3)}D_1^{(1)} + \frac{1}{7}\sqrt{\frac{3}{5}}E_3^{(3)}D_{-1}^{(1)} + \frac{2}{7}\sqrt{\frac{1}{5}}E_2^{(3)}D_0^{(1)},
\end{aligned}
\tag{6}
$$

$$
\begin{aligned}
\langle -1|\, H_E\, |-1\rangle &= \langle 1|\, H_E\, |1\rangle\,, \\
\langle -1|\, H_E\, |-2\rangle &= -\frac{\sqrt{2}}{5}\left(E_0^{(1)}D_1^{(1)} + E_1^{(1)}D_0^{(1)}\right) + \frac{3\sqrt{2}}{35}E_0^{(3)}D_1^{(1)} \\
&+ \frac{1}{7}\sqrt{\frac{3}{5}}E_2^{(3)}D_{-1}^{(1)} + \frac{3\sqrt{2}}{35}E_0^{(3)}D_1^{(1)}, \\
\langle -2|\, H_E\, |-2\rangle &= \langle 2|\, H_E\, |2\rangle\,.
\end{aligned}
\tag{7}
$$

Combining these matrix elements with those which are allowed for spin-orbit and exchange interaction between magnetic ions one can calculate the coupling energy of the spins with electric field, using third order perturbation theory.

## 3. Effective Hamiltonian for interaction of exchange coupled spins with electric field

Let us consider two magnetic ions ($a$ and $b$) with one electron (hole) per each site. The wave function of the ground state in second quantization representation is written as

$$|n\rangle = a_\rho^+ b_\varphi^+ |0\rangle\,, \tag{8}$$

where Greek symbols denote occupied orbital states. Quantum numbers of spins are dropped for short. The states, when the electron at site $a$ ($b$) occupies the excited state $\tau$ ($\mu$) are

$$|n'\rangle = a_\tau^+ b_\varphi^+ |0\rangle\,, \qquad |n''\rangle = a_\rho^+ b_\mu^+ |0\rangle\,. \tag{9}$$

Below, in contrast to Ref. [15], we consider the cases when the energy intervals between excited and ground state are larger with respect to spin-orbit and exchange interactions. Those energy intervals are formed by even crystal fields.

Two types of terms can be selected in third order perturbation theory. The first one is that when matrix elements of operators $H_E(a)$ and $H_{\rm so}(a)$ are nondiagonal, whereas the exchange coupling operators $H_{\rm ex}(\tau\varphi) = J_{\tau\varphi}(\mathbf{s}_a\mathbf{s}_b)$ and $H_{\rm ex}(\rho\mu) = J_{\rho\mu}(\mathbf{s}_a\mathbf{s}_b)$ are diagonal, i.e. they are acting within the equal energy states. One can speculate about the effect of the exchange coupling of magnetic ion with another one in excited state. The second type term of virtual excitation process is that when the matrix elements $\langle\rho|\, H_E(a)\, |\rho\rangle$ and $\langle\mu|\, H_E(b)\, |\mu\rangle$ are diagonal. These matrix elements can be interpreted as a result of electric polarisation of the ions in their excited states.

Therefore we can discuss two possible mechanisms of the spins and electric field coupling. The effective spin-Hamiltonian, which corresponds to the first case, is written as

$$
\begin{aligned}
H_{\text{eff}}^{(1)} &= i\frac{\lambda_a J_{\rho\varphi}}{2\Delta_{\rho\tau}^2}\left\{\langle\rho|\, l_a^{(\alpha)}\,|\tau\rangle\,\langle\tau|\, H_E(a)\,|\rho\rangle + \text{h.c.}\right\}[\mathbf{s}_a\times\mathbf{s}_b]_\alpha \\
&+ i\frac{\lambda_b J_{\varphi\rho}}{2\Delta_{\varphi\mu}^2}\left\{\langle\varphi|\, l_a^{(\alpha)}\,|\mu\rangle\,\langle\mu|\, H_E(b)\,|\varphi\rangle + \text{h.c.}\right\}[\mathbf{s}_b\times\mathbf{s}_a]_\alpha \\
&- i\frac{\lambda_a J_{\tau\varphi}}{2\Delta_{\rho\varphi}^2}\left\{\langle\rho|\, l_a^{(\alpha)}\,|\tau\rangle\,\langle\tau|\, H_E\,|\rho\rangle - \text{h.c.}\right\}[\mathbf{s}_a\times\mathbf{s}_b]_\alpha \\
&- i\frac{\lambda_b J_{\rho\mu}}{2\Delta_{\mu\varphi}^2}\left\{\langle\varphi|\, l_b^{(\alpha)}\,|\mu\rangle\,\langle\mu|\, H_E(b)\,|\varphi\rangle - \text{h.c.}\right\}[\mathbf{s}_b\times\mathbf{s}_a]_\alpha.
\end{aligned}
\tag{10}
$$

Here the index $\alpha \equiv x, y, z$; $\lambda_a$ and $\lambda_b$ are spin-orbit coupling parameters, $\Delta_{\rho\tau}$ and $\Delta_{\mu\varphi}$ are the energies of excitations at the sites $a$ and $b$, respectively.

The spin-Hamiltonian, containing electric polarization of the ground and excited states is

$$
\begin{aligned}
H_{\text{eff}}^{(2)} &= i\frac{\lambda_a\,\langle\rho|\, H_E(a)\,|\rho\rangle}{2\Delta_{\tau\rho}^2}\left\{\langle\rho|\, l_a^{(\alpha)}\,|\tau\rangle\, J_{\tau\varphi,\rho\varphi} + \text{h.c.}\right\}[\mathbf{s}_a\times\mathbf{s}_b]_\alpha \\
&+ i\frac{\lambda_b\,\langle\varphi|\, H_E(b)\,|\varphi\rangle}{2\Delta_{\mu\varphi}^2}\left\{\langle\varphi|\, l_b^{(\alpha)}\,|\mu\rangle\, J_{\mu\rho,\varphi\rho} + \text{h.c.}\right\}[\mathbf{s}_b\times\mathbf{s}_a]_\alpha \\
&- i\frac{\lambda_a\,\langle\tau|\, H_E(a)\,|\tau\rangle}{2\Delta_{\tau\rho}^2}\left\{\langle\rho|\, l_a^{(\alpha)}\,|\tau\rangle\, J_{\tau\varphi,\rho\varphi} - \text{h.c.}\right\}[\mathbf{s}_a\times\mathbf{s}_b]_\alpha \\
&- i\frac{\lambda_b\,\langle\mu|\, H_E(b)\,|\mu\rangle}{2\Delta_{\mu\varphi}^2}\left\{\langle\varphi|\, l_b^{(\alpha)}\,|\mu\rangle\, J_{\mu\rho,\varphi\rho} - \text{h.c.}\right\}[\mathbf{s}_b\times\mathbf{s}_a]_\alpha.
\end{aligned}
\tag{11}
$$

Note that deriving the expression (11) we used the exchange coupling operators as follows:

$$
\begin{aligned}
H_{\text{ex}}(\rho\tau) &= J_{\rho\varphi,\tau\varphi}a_\rho^+ a_\tau b_\varphi^+ b_{\varphi'} + \text{h.c.}, \\
H_{\text{ex}}(\varphi\mu) &= J_{\varphi\rho,\tau\varphi}b_\varphi^+ b_\mu a_\rho^+ a_{\rho'} + \text{h.c.}
\end{aligned}
\tag{12}
$$

As one can see from (10) and (11), both expressions vanish if the direction of spins at site $a$ and $b$ states are parallel. The vector product of spins reminds those which enter in the inverse Dzyaloshinskii-Moriya mechanism [8,9]. However, quantities which stay in front of components $[\mathbf{s}_b\times\mathbf{s}_a]_\alpha$ have different nature and values. Moreover, the expressions (10), (11) do not vanish for number of noncollinear spin systems in which the Dzyaloshinskii-Moriya interaction is absent.

## 4. The origin of spin-electric field coupling in $LiCuVO_4$

The nature of spin-electric field coupling in $LiCuVO_4$ has been discussed in number of papers [16–20]. In this compounds copper spins ($S = 1/2$) build up the chains along the $b$ axis. Below Neel temperature ($T_N = 2.4\,K$), spiral structures in Cu-O chins are set due to the competition between the nearest neighbor ferromagnetic and next-nearest neighbor antiferromagnetic exchange interactions along the chain. Simultaneously, an electric polarization appears along the $a$ axis [16,17].

The symmetry analysis of crystal structure rules out the presence of Dzyaloshinskii-Moriya interaction [18,19]. Authors of Ref. [20] suggested to take into account the non-stoichiometry of $LiCuVO_4$. Indeed, the ionic radius of $Li^+$ and $Cu^{2+}$ ions are very close to each other. As a result even the best samples of $LiCuVO_4$ show up the non-stoichiometry and structural defects [21,22]. The model of the structural defect considered in Ref. [20] is that when the

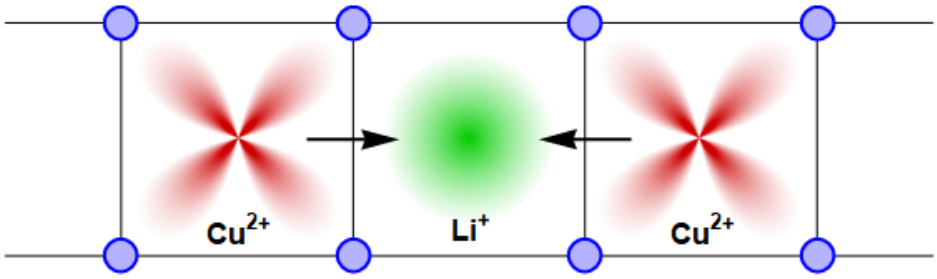


**Figure 1.** Fragment of Cu-O chain with $Li^+$. Arrows illustrate the direction of odd crystal fields on copper ions.

$Li^+$ position is occupied by $Cu^{2+}$ ion (out-of-chain $Cu^{2+}$ centers). Here we focus on the other relevant model of the structural defect in $LiCuVO_4$, which is schematically shown in Fig. 1; i.e. $Li^+$ sets instead $Cu^{2+}$ in Cu-chain.

As one can see there is strong odd crystal field action on $3d$-hole at $Cu^{2+}$ site neighboring to $Li^{1+}$ ion. In the coordinate system with the $y$ axis directed along the Cu-O bonds the ground state of $Cu^{2+}$ is the hole state $|xy\rangle = |\zeta\rangle$. The nearest excited state is $\left|x^2 - y^2\right\rangle = |\varepsilon\rangle$. The matrix element $\langle\zeta| l_z |\varepsilon\rangle = 2i$ is the largest one among others. On the other hand there is matrix element $\langle\varepsilon| H_E(a) |\zeta\rangle$ when electric field is oriented along the $a$ axis. This follows from the symmetry selection rule. Indeed, in this case the operator $H_E(a)$ contains the term which transforms as $y^3x$. Therefore one has the following contribution to the energy of spin-electric field coupling per one $Li^+$ defect position:

$$H_{\text{eff}}^{(1)} \cong -2i\frac{\lambda}{\Delta_{\varepsilon\zeta}^2} \langle\zeta| l_z^{(\alpha)} |\varepsilon\rangle \langle\varepsilon| H_E(a) |\zeta\rangle J_{\varepsilon\zeta}[\mathbf{s}_a \times \mathbf{s}_b]_z \cong p_x E_x [\mathbf{s}_a \times \mathbf{s}_b]_z. \tag{13}$$

Derived phenomenological form, of the expression (13) well corresponds to experimentally observed situation in $LiCuVO_4$ [16–18]. At $T < T_N$ the helical spin order sets in $xy$ plane and simultaneously electric polarization appears along the $a$ axis.

In conclusion, the analytical expressions for the energy coupling of exchange coupled spins with electric field, induced by odd crystal field has been derived in the third order perturbation theory, combining the action of electric field, spin-orbit and exchange interactions. As an example, I have analyzed the magnetoelectric coupling, caused by in-plane defects for $LiCuVO_4$ and found that the resulting expression for the binding energy of spins with an electric field corresponds, at least qualitatively, to the results of experimental studies.

## Acknowledgments

I am grateful to Kirill Vasin for his help. This work is partially supported by the Ministry of Science and Higher Education of the Russian Federation, project no. 3.6722.2017/8.9 for the Kazan Federal University.

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