Coupling of spins with an electric field in FeV$_2$O$_4$

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The microscopic mechanism of the interaction of exchange-coupled Fe and V spins in a FeV$_2$O$_4$ ferrimagnet with the electric field has been described. The derived effective energy operator makes it possible to calculate the electric polarization vector using the information about the magnetic structure. The calculated electric polarization is consistent with the available experimental data.

I. INTRODUCTION

The materials which simultaneously exhibit long-range magnetic order and a spontaneous electric polarization (multiferroics) have attracted much attention due to their potential applications in promising electronic devices as well as a source of fundamental knowledge of the nature of spins and electric field coupling [1–3]. Recent reviews of such materials and possible microscopic mechanisms are provided in Refs. [4–6]. The most celebrated mechanisms are magnetostriction and the so-called inverse Dzyaloshinskii-Moriya (DM) mechanism [7,8]. In recent years, the number of discovered multiferroics has increased essentially. It is natural that a few new problems arose in understanding the nature of the magnetoelectric coupling. A number of multiferroics display the electric polarization, the origin of which cannot be explained within the current mechanisms of the magnetoelectric coupling. Among them are LiCuVO$_4$, LiCu$_2$O$_2$, Cu$_2$OSeO$_3$, noncollinear ferrimagnets with a spinel structure (FeCr$_2$O$_4$, FeV$_2$O$_4$), etc. In this Rapid Communication, we focus on a specific compound, FeV$_2$O$_4$.

The FeV$_2$O$_4$ compound has interesting physical properties. The structural and magnetic phase transitions occur in it as the temperature decreases. At a temperature of ∼140 K, the cubic symmetry of the lattice is changed into tetragonal, at $T \sim$ 110 K the symmetry of the lattice becomes orthorhombic, and at the same time the collinear ordering of spins appears. The tetragonal phase is restored at $T < 70$ K and the antiferromagnetic ordering of Fe and V spins becomes noncollinear. The spontaneous electric polarization P builds up simultaneously with the last two transitions reaching a P value of ∼63 mC/m^2 at ∼30 K [9]. The origin of the electric polarization and its connection to the features of spin ordering of iron and vanadium ions remains unclear. An analytical expression that would have made it possible to calculate the electric polarization in the magnetically ordered state is absent.

II. EFFECTIVE HAMILTONIAN OF THE INTERACTION OF 3d ELECTRONS WITH THE ELECTRIC FIELD

The electrically active ion in FeV$_2$O$_4$ is the Fe^{2+} ion. It is located in the center of a tetrahedron formed by oxygen ions.

The electric field mixes the ground electronic configuration $3d^6 L$ with the states of the excited configurations of opposite parity. The important role of this mixing was not noted in previous papers [4–8]. The lowest-energy configurations are $3d^5 4p L$ and $3d^7 L^{-1}$. Here, $3d^7 L^{-1}$ denotes the so-called charge-transfer configuration, in which an oxygen electron (from the $2p$ or $2s$ shell) is carried into the iron $3d$ shell. The operator describing the coupling of orbital states for a $3d$ electron with the electric field can be written as follows [10,11],

$$H_E = \sum_{p,t,k} \{E^{(1)} U^{(k)}\}_t^{(p)} \sum_j d^{(1k)p}(R_j)(-1)^t C_{-t}^{(p)}(\vartheta_j \varphi_j). \quad (1)$$

The curly brackets denote the Kronecker product of the spherical tensor of the electric field with the unit irreducible tensor operator acting on $3d$ electron states. The spherical coordinates $R_j, \vartheta_j, \varphi_j$ denote the positions of the lattice ions, the same as in the crystal field theory, and $C_{-t}^{(p)}(\vartheta_j \varphi_j) = \sqrt{4\pi/(2p+1)} Y_{p,-t}(\vartheta_j \varphi_j)$ the components of the spherical tensors. The quantities $d^{(1k)p}(R_j)$ are calculated in the local coordinate system with the z axis along the $3d$-ion ligand direction. They contain two contributions,

$$d^{(1k)p}(R_j) = d_{\text{cf}}^{(1k)p}(R_j) + d_{\text{cov}}^{(1k)p}(R_j). \quad (2)$$

The first term is associated with the odd crystal field. It can be calculated using the expression for the operator of the electric dipole transitions in optical spectroscopy [10],

$$d_{\text{cf}}^{(1k)p}(R_j) = 2|e| \frac{\varepsilon' + 2}{3} \frac{(2k+1)\langle r \rangle_{ll'}}{|\Delta_{ll'}|\sqrt{(2p+1)}} (l \| C^{(1)} \| l')$$
$$\times (l' \| C^{(p)} \| l) \begin{Bmatrix} 1 & k & p \\ l & l' & l \end{Bmatrix} a^{(p)}(R_j). \quad (3)$$

Here, we assume that l and l' refer to $3d$ and $4p$ shells, respectively, ε' is the relative permittivity, which is about 26 for FeV$_2$O$_4$ [9], $|\Delta_{ll'}| = 70\,000$ cm^{-1} is the energy gap between the $3d^5 4p$ and $3d^6$ configurations [12], and $(l' \| C^{(p)} \| l)$ is the reduced matrix element. The quantities $a^{(p)}(R_j)$ are the so-called intrinsic crystal field parameters of the odd crystal field Hamiltonian

$$H_{\text{cf}} = \sum_{p,t} B_t^{(p)} C_t^{(p)}. \quad (4)$$

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In the superposition model the crystal field parameters $B_t^{(p)}$ are evaluated as

$$B_t^{(p)} = \sum_j a^{(p)}(R_j)(-1)^t C_{-t}^{(p)}(\vartheta_j \varphi_j). \quad (5)$$

In the exchange charge approximation, the quantities $a^{(p)}(R_j)$ can be estimated similar to those which are present in the even crystal field theory [13,14], i.e., as follows,

$$a^{(p)}(R_j) = -\frac{Z_j e^2}{R_j^{p+1}} \langle r^3 \rangle_{ll'} + \frac{(2p+1)G_{pd}e^2}{(l\|C^{(p)}\|l')R_j}$$

$$\times \sum_\rho (-1)^{l-m} \begin{pmatrix} l & p & l' \\ -m & 0 & m \end{pmatrix} S_{lm,\rho} S_{\rho,l'm}. \quad (6)$$

The first term in Eq. (6) accounts for the electrostatic field from electric charges of lattice ions. The second term takes into account the effects of overlapping between electronic shells (l, l') of iron and the ρ state $(2pm, 2sm)$ of oxygen ions, $S_{lm,\rho}$ are overlap integrals, and G_{pd} is the exchange charge parameter.

The second term in Eq. (2) is due to the asymmetry in the overlap of $3d$ electron states with the shells ($2p$ and $2s$) of the surrounding oxygen ions [11] and as well to the asymmetry in the amplitudes of probabilities of the virtual transfer of electrons from the ligands to the $3d$ shell, which we have taken into account. It is calculated as follows:

$$d_{\text{cov}}^{(1k)p}(R_j) = |e|\frac{\varepsilon' + 2}{3} \sum_q (-1)^q \sqrt{(2p+1)}$$

$$\times \begin{pmatrix} 1 & k & p \\ -q & q & 0 \end{pmatrix} d_q^{(k)}(R_j), \quad (7)$$

where

$$d_q^{(k)}(R_j) = (2k+1) \sum_{m,m'} (-1)^{l-m} \begin{pmatrix} l & k & l \\ -m & q & m' \end{pmatrix}$$

$$\times \langle lm|rC_q^{(1)}|lm'\rangle, \quad (8)$$

$$\langle lm|rC^{(1)}|lm'\rangle = \lambda_{lm,\rho}\langle \rho|rC_q^{(1)}|\rho'\rangle \lambda_{\rho',lm'}$$

$$- 2\langle lm|rC_q^{(1)}|\rho\rangle \lambda_{\rho,lm'}. \quad (9)$$

Here, for brevity, as usual [15] we denote $\lambda_{lm,\rho} = \gamma_{lm,\rho} + S_{lm,\rho}$. $\gamma_{lm,\rho}$ are the so-called covalency parameters and $S_{lm,\rho}$ are overlap integrals. In Eq. (7) k are even numbers 2 and 4, and p are odd 1, 3, and 5.

In the local coordinate system (Fig. 1), the Hamiltonian of the odd crystal field acting on $3d$ electrons of Fe ions is written as $H_{\text{cf}} = B_2^{(3)}(C_2^{(3)} + C_{-2}^{(3)})$. The parameter $B_2^{(3)}$ is mainly determined by the nearest oxygen ions,

$$B_2^{(3)} = \frac{2}{3}\frac{e^2\sqrt{10}}{R}\left[\frac{2\langle r^3 \rangle_{3d,4p}}{R^3} + \frac{7G_{pd}}{\sqrt{15}}\begin{pmatrix} S_{3d0,2p0}S_{2p0,4p0} \\ + S_{3d0,2s}S_{2s,4p0} \\ -\frac{2}{\sqrt{3}}S_{3d1,2p1}S_{2p1,4p1} \end{pmatrix}\right]. \quad (10)$$

The value $\langle r^3 \rangle_{3d,4p} = 3.26$ a.u. was estimated in Ref. [11] using the Hartree-Fock wave functions of $3d$ and $4p$ electrons [16] of the Fe^{3+} ion, and R is the oxygen-iron distance which
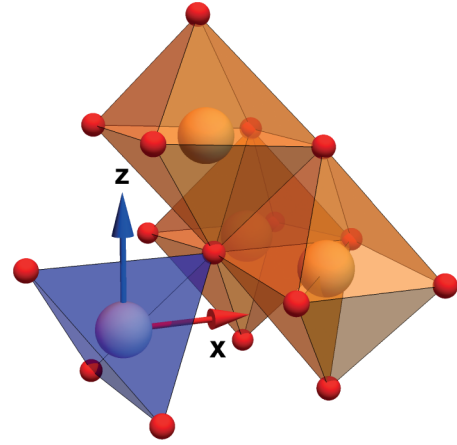

FIG. 1. Fragment of the FeV_2O_4 crystal structure. The iron ion is in the center of the tetrahedron. Vanadium ions are in the centers of the octahedra. The bridging oxygen ion is located at the top of the tetrahedron. Its coordinates are $(R\sqrt{2/3}, 0, R/\sqrt{3})$.

is about 1.98 Å. The values of the overlap integrals are $S_{3d0,2p0} = -0.071$, $S_{3d0,2s} = -0.068$, $S_{3d1,2p1} = 0.051$, and $S_{4p0,2s} = -0.073$, $S_{4p0,2s} = -0.043$, $S_{4p1,2p1} = 0.036$. The wave functions for the $2p$ and $2s$ electron shells of the oxygen ion are taken from Ref. [17]. Assuming that the G_{pd} value is approximately the same as the G_{dd}, i.e., the same as that for the even crystal field acting on the state of the $3d$ electron, we have $G_{pd} = G_{dd} = 2.5$ and therefore $B_2^{(3)} = B_{-2}^{(3)} \cong 2 \times 10^4$ cm^{-1}, and then using Eq. (3) the evaluated quantities are

$$d_{\text{cf}}^{(12)3} = 0.026|e|\langle r \rangle_{3d,4p}\frac{\varepsilon' + 2}{3} \cong 0.13 \text{ a.u.},$$

$$d_{\text{cf}}^{(14)3} = 0.184|e|\langle r \rangle_{3d,4p}\frac{\varepsilon' + 2}{3} \cong 0.94 \text{ a.u.} \quad (11)$$

The value $\langle r \rangle_{3d,4p} = 0.55$ a.u. was taken from Ref. [11]. Analogously, using Eqs. (7)–(9) and the Hartree-Fock wave functions from Refs. [16,17], we have

$$d_{\text{cov}}^{(12)3} \cong -1.08 \text{ a.u.},$$

$$d_{\text{cov}}^{(14)3} = 1.37 \text{ a.u.} \quad (12)$$

The covalency parameters $\gamma_{3d0,2p0}$, $\gamma_{3d1,2p1}$, and $\gamma_{3d0,2s}$ were taken as -0.1, 0.08, and -0.02, respectively [18,19], and $\langle r \rangle_{2p,2s} = -1.20$ a.u.

Finally, the effective Hamiltonian of the electric field acting on $3d$ electrons of Fe^{2+} in a tetrahedral coordination is written as follows,

$$H_E = \frac{4}{3}\sqrt{\frac{5}{6}}d^{(12)3}\left\{E_z\left(U_2^{(2)} + U_{-2}^{(2)}\right)\right.$$

$$+ \sqrt{2}\left(E_{-1}^{(1)}U_{-1}^{(2)} + E_1^{(1)}U_1^{(2)}\right)\right\} + \frac{4}{3}\sqrt{\frac{5}{6}}d^{(14)3}$$

$$\times \left\{\begin{array}{c} -E_z\left(U_2^{(4)} + U_{-2}^{(4)}\right) + \frac{1}{2}\left(E_{-1}^{(1)}U_{-1}^{(4)} + E_1^{(1)}U_1^{(4)}\right) \\ + \frac{1}{2}\sqrt{\frac{7}{3}}\left(E_1^{(1)}U_{-3}^{(4)} + E_{-1}^{(1)}U_3^{(4)}\right) \end{array}\right\}. \quad (13)$$

Comparing (11) and (12), it can be seen that the contributions to the $d^{(1k)p}$ parameters caused by mixing of the $3d^5 4p L$ and

$3d^6 L^{-1}$ configurations to the ground one are of the same order of magnitude.

III. THE BASIC FRAGMENT OF THE CRYSTAL STRUCTURE AND A SET OF WAVE FUNCTIONS

Figure 1 shows a fragment of the crystal structure FeV_2O_4 [20–22]. In order to indicate the most effective channel of the exchange coupling of the iron ion with vanadium ions via the intermediate (bridging) oxygen ion, we rotate the local coordinate axis of the Fe^{2+} ion by 45° with respect to the crystallographic axes. It is clear that in this case the most effective exchange channel is through the d_{xz} state. The basis of the wave functions of $Fe^{2+}d^6(^6D)$ with $M_S = 2$ in the hole representation is written as follows,

$$|^5E\zeta, 2\rangle = \left\{\begin{matrix} + & + & + & + \\ \varepsilon & \eta & \vartheta & \xi \end{matrix}\right\}, \quad |^5E\vartheta, 2\rangle = \left\{\begin{matrix} + & + & + & + \\ \varepsilon & \eta & \xi & \zeta \end{matrix}\right\},$$

$$|^5T\eta, 2\rangle = \left\{\begin{matrix} + & + & + & + \\ \zeta & \vartheta & \xi & \varepsilon \end{matrix}\right\}, \quad |^5T\xi, 2\rangle = \left\{\begin{matrix} + & + & + & + \\ \varepsilon & \vartheta & \eta & \zeta \end{matrix}\right\},$$

$$|^5T\varepsilon, 2\rangle = \left\{\begin{matrix} + & + & + & + \\ \xi & \zeta & \eta & \vartheta \end{matrix}\right\}. \tag{14}$$

Here, we have used the determinantal product states in the strong crystal field representation, $\eta = d_{xz}$, $\xi = d_{yz}$, $\varepsilon = d_{x^2-y^2}$, $\zeta = d_{xy}$, $\vartheta = d_{3z^2-r^2}$.

IV. THE ORIGIN OF THE COUPLING OF Fe AND V SPINS WITH THE ELECTRIC FIELD IN FeV_2O_4

According to Refs. [21–23], at $T < 70$ K the ^5E_g state of the Fe^{2+} ion splits into $^5E_\vartheta$ and $^5E_\zeta$ states. In the total momentum representation $L = 2$ and the lowest orbital state in the crystallographic coordinate system is $(|-2\rangle + |2\rangle)/\sqrt{2}$. In the rotated coordinate system (Fig. 1), it is the $|^5E_\zeta\rangle = i(|-2\rangle - |2\rangle)/\sqrt{2}$ state. The energy gap between the $^5T_\eta$ ($^5T_\xi$) and ^5E states is about $\Delta_{\eta\zeta}(\Delta_{\xi\zeta}) \cong 4000$ cm^{-1} [23]. The V^{3+} ions are in the octahedral positions. At $T < 70$ K the octahedra are also distorted [20–22]. The orbital triplet $^3T_{1g}$ of the V^{3+} ion splits. A simple calculation using the crystal field theory yields that the ground state of vanadium ions at $T < 70$ K is orbitally nondegenerate.

In the third-order perturbation theory, as explained in Fig. 2, for the effective energy interaction operator of Fe spins and three V spins (see Fig. 1) with the external electric field, we derive the following expression,

$$H_{\text{eff}}^{(x)} = \frac{\lambda_{\text{Fe}}\langle \zeta|d_x|\xi\rangle}{|\Delta_{\zeta\xi}|^2} \sum_V J_{\xi V}[\mathbf{S}_{\text{Fe}} \times \mathbf{S}_V]_y E_x, \tag{15}$$

where $\lambda_{\text{Fe}} \simeq -103$ cm^{-1} is the spin-orbit coupling parameter, and the matrix element of the x component of the effective electric dipole moment is

$$\langle^5E_\zeta|d_x|^5T_\xi\rangle = \langle \zeta|d_x|\xi\rangle = \frac{2}{3}\sqrt{\frac{2}{7}}d^{(12)3} + \frac{16}{9}\sqrt{\frac{5}{42}}d^{(14)3}. \tag{16}$$

Note that the matrix elements $\langle \zeta|H_E^a|\vartheta\rangle$ and $\langle \zeta|H_E^a|\varepsilon\rangle$ are zero.

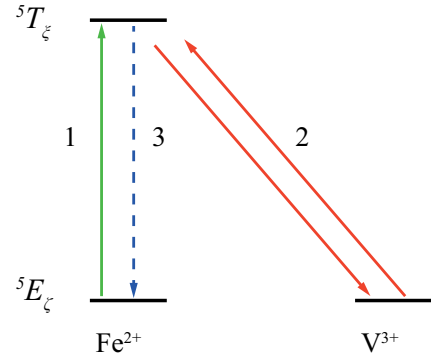The operator of the interaction of the electric field with exchange-coupled Fe and three V spins via the bridging

FIG. 2. Example of virtual excitation scheme. Line 1 corresponds to the excitation under the action of the electric field (the operator H_E), 3 refers to the transition due to the spin-orbit interaction, and double line 2 to the superexchange interaction $H_{\text{ex}} = J_{\xi V}(\mathbf{S}_{\text{Fe}}\mathbf{S}_V)$ of the V^{3+} ion with the Fe^{2+} ion in the *excited state*.

oxygen in the position $(-R/\sqrt{2}, 0, R/\sqrt{2})$ is determined by the expression similar to Eq. (15).

It is clear (Goodenough-Kanamori-Anderson rule) that the excited $^5T_\xi$ state of iron is the most active for the superexchange coupling with other six vanadium ions via oxygen ions in positions $(0, \pm R/\sqrt{2}, -R/\sqrt{2})$. In this case, we have

$$H_{\text{eff}}^{(y)} = \frac{\lambda_{\text{Fe}}\langle \zeta|d_y|\eta\rangle}{|\Delta_{\zeta\eta}|^2} \sum_V J_{\eta V}[\mathbf{S}_{\text{Fe}} \times \mathbf{S}_V]_x E_y, \tag{17}$$

where $\langle \zeta|d_y|\eta\rangle = \langle \zeta|d_x|\xi\rangle$.

Note that FeV_2O_4 is a compound with the geometrical frustration. There are two types of FeO_4 tetrahedra in the crystal lattice, which are tilted with respect to each other by 90° around the c axis of the crystal [20–22]. In this regard, it is necessary to consider the fragments of the structure in which the bridging oxygen ions between the Fe and V ions are located not along the x axis as in Fig. 1, but along the y axis. The calculation similar to that performed above shows that for tetrahedra of the second type, the sum of expressions (15) and (17) remains unchanged.

The presence of the vector product of spins in operators (15) and (17) resembles the so-called inverse Dzyaloshinskii-Moriya mechanism for the magnetoelectric coupling [7,8]. However, there is a fundamental difference. In the Dzyaloshinskii-Moriya interaction, the spin-orbit interaction appears in the combination with the exchange integrals that are nondiagonal in orbital quantum numbers (for details, see, e.g., Ref. [24]). The presence of the Dzyaloshinskii-Moriya interaction itself, in the general case, is not necessary.

At $T > 75$ K, according to the study of the Mössbauer spectra [23,25,26], the directions of the Fe^{2+} ($S = 2$) and V^{3+} ($S = 1$) spins are antiparallel. In this case, the vector products in Eqs. (15) and (17) are equal to zero. This observation corresponds to the fact that there is no electric polarization in the collinear ferrimagnetic phase of FeV_2O_4. At $T < 75$ K, as the temperature decreases, the canting angle between the iron and vanadium spins builds up and, accordingly, the vector product of spins increases in the absolute value, reaching $[\mathbf{S}_{\text{Fe}} \times \mathbf{S}_V] = S_{\text{Fe}}S_V \sin(111°) = 1.86$. This behavior of the

canting angle explains the smooth increase in the electric polarization observed in [9] at $T < 75$ K.

To estimate the exchange interaction parameter J_{FeV} in order of magnitude, we use the expression from the exchange channel model [27],

$$J_{ab} = \frac{1}{4 S_a S_b} \sum_{\gamma a, \gamma b} j_{\gamma a, \gamma b}, \quad (18)$$

where $j_{\gamma a, \gamma b}$ are contributions of the pairs of one-electron orbitals of magnetic ions a and b. Using $J_{MnV} \cong 18$ K in MnV_2O_4 [28] and $J_{MnCr} \cong 16$ K in $MnCr_2O_4$ [29], we find $J_{\xi V} \cong J_{\eta V} \cong J_{FeV} \cong 14$ K. Indeed, it is clear from the wave functions given by Eq. (14) that the dominating channel $j_{\xi, V}$ ($j_{\eta, V}$) is present for the ground $^5E_\zeta$ state and for the excited $^5T_\xi$ ($^5T_\eta$) state of the Fe^{2+} ion.

Further, we discuss the role of virtual excitation processes containing matrix elements,

$$\langle \xi | H_E | \xi \rangle = \left(\frac{2}{3} \sqrt{\frac{2}{7}} d^{(12)3} + \frac{8}{9} \sqrt{\frac{5}{42}} d^{(14)3} \right) E_z,$$

$$\langle \eta | H_E | \eta \rangle = -\langle \xi | H_E | \xi \rangle = \langle \xi | d_z | \xi \rangle E_z. \quad (19)$$

These matrix elements can be interpreted as the energy of the electric polarization of the iron excited states. They induce the electric polarization component along the z axis. The operator of the binding energy of the iron and vanadium spins with the electric field is written in the form

$$H_{eff}^{(z)} = \frac{\lambda_{Fe} \langle \xi | d_z | \xi \rangle}{|\Delta_{\zeta \xi}|^2} \sum_V J_{\zeta \xi, V} [\mathbf{S}_{Fe} \times \mathbf{S}_V]_y E_z$$

$$+ \frac{\lambda_{Fe} \langle \eta | d_z | \eta \rangle}{|\Delta_{\zeta \eta}|^2} \sum_V J_{\zeta \eta, V} [\mathbf{S}_{Fe} \times \mathbf{S}_V]_x E_z. \quad (20)$$

The parameters of the iron-vanadium exchange coupling in Eq. (20) are nondiagonal in terms of the orbital quantum numbers of the iron ion, i.e., the same as it appears in the microscopic theory of the antisymmetric exchange interaction [24]. One of the relevant virtual excitation schemes is shown in Fig. 3. It can be seen from the wave functions (10) and (11) that $J_{\zeta \xi, V} \cong J_{\zeta \eta, Y} \cong J_{Fe, V}$.

The electric polarization was measured on polycrystalline samples in Ref. [9], therefore, the direction of the polarization vector remains uncertain. In the absence of magnetic fields, the measured value is $|P| \cong 63 \ \mu C/m^2$. If one assumes that the electric polarization is oriented along the z axis, Eq. (20)
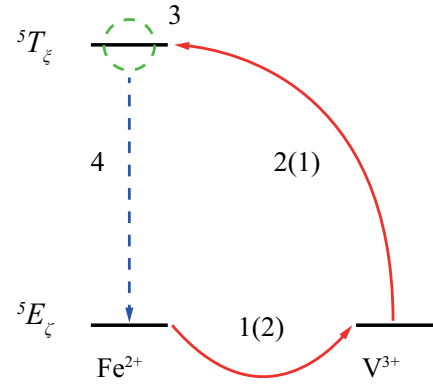

FIG. 3. One of the virtual excitation schemes. Lines 1 and 2 correspond to the excitation of the iron ion via the nondiagonal superexchange interaction $H_{ex} = J_{\zeta \xi, V} (\mathbf{S}_{Fe} \mathbf{S}_V)$ of Fe and V ions, 3 to the electric polarization of the excited state, and 4 refers to the transition caused by the spin-orbit coupling.

yields $P_z \cong 47 \ \mu C/m^2$. If it is assumed that the electric polarization is oriented along the x axis, Eq. (15) yields $P_x \cong 85 \ \mu C/m^2$. According to Ref. [9], the applied magnetic field reduces the electric polarization value. Qualitatively, it can be interpreted as follows. According to Eqs. (15), (17), and (20), the electric polarization sets up when the vector product of Fe and V spins is nonzero (a noncollinear ferrimagnet). The magnetic aligns the spins in parallel, and thus reducing the value of the vector product of spins.

V. CONCLUDING REMARKS

In this Rapid Communication, we contribute to the current microscopic theory of magnetoelectric coupling [6–8]. Focusing on FeV_2O_4, we have tested in detail the microscopic mechanism of the interaction of exchange-coupled Fe and V spins with the electric field. Simple analytical expressions for magnetoelectric coupling energy are derived. The calculated electric polarization is consistent with the experimental value [9] in order of magnitude. The proposed mechanism of the interaction of the electric field with exchange-coupled spins is applicable to a wide class of noncollinear ferrimagnets with magnetic ions located in positions without the inversion symmetry.

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