Supplementary Material to the article "The relationship of the magnetoelectric effect with local magnetic and electric moments in paramagnetic terbium langasite"

Let us consider the details of the theoretical approach and simulation of the magnetic and magnetoelectric properties of langasite $(La_{0.95}Tb_{0.05})_3Ga_5SiO_{14}$ doped with magnetic Tb^{3+} ions (TbLGS). The Tb^{3+} ions occupy 3*e* sites of C_2 symmetry in the crystal with a local axis coinciding with one of the three crystallographic axes of the 2nd order (*a*, *b*, -*a*-*b*). They remain in the paramagnetic state up to lowest temperatures. The random distribution of Ga/Si in the 2*d* sites, as in other rare-earth langasites [1, 2], can lead to distortions of the crystal field on the rare-earth ion and violation of its local symmetry C_2. The crystal field V_{cf} splits the ground multiplet $^7F_6$ of the non-Kramers ion Tb^{3+}+ into $2J + 1$ = 13 singlets. At low temperatures, the magnetic properties of the rare earth ion are mainly determined by the two lower energy levels (quasi-doublet) with the splitting value Δ_{cf}.

To describe the magnetic and magnetoelectric properties of TbLGS, we took into account the influence of external magnetic $\boldsymbol{H}$ and electric $\boldsymbol{E}$ fields on the Tb^{3+} ion in the perturbation operator

$$\hat{V} = -\hat{\mathbf{d}}\mathbf{E} + \mu_B g_L \hat{\mathbf{J}}\mathbf{H}, \tag{S1}$$

where the first term accounts for the interaction of the effective dipole moment $\boldsymbol{d}$ of the rare earth ion with the electric field, and the second one - the Zeeman interaction with the external magnetic field $\boldsymbol{H}$, μ_B and g_L = 3/2 are the Bohr magneton and the Lande factor, respectively.

Spin-Hamiltonian. Projecting the Hamiltonian $H = \hat{V}_{cf} + \hat{V}$ onto the subspace of the two lower singlets of the Tb^{3+} ion, one can obtain a 2x2 matrix (in the second order of perturbation theory in *V*) [3]:

$$\langle l|\hat{H}|m\rangle = \frac{1}{2}(-1)^l E_{lm} + \langle l|\hat{V}|m\rangle - \sum_{k\neq 1,2} \frac{\langle l|\hat{V}|k\rangle\langle k|\hat{V}|m\rangle}{E_k - (E_l - E_m)/2}, \tag{S2}$$

where l, m = 1, 2 denote the wave functions |1> and |2> of the ground quasidoublet, and k = 3…13 are excited crystal field states E_k, whose admixture result in a downward displacement of the ground doublet as a whole (the Van Fleck contribution to magnetization), as well as the interaction of the electric dipole moment with the magnetic field thus determining magnetoelectric coupling. The effective spin-Hamiltonian can be represented in terms of Pauli matrices (Eq. (3) in the main text).

The energy levels of the Tb^{3+} ground quasidoublet in the *q* site, found by diagonalizing the Hamiltonian, are

$$E_{\boldsymbol{q}}^{\pm} = \pm\varepsilon_q - \varepsilon_{VV}^{(q)} \equiv \pm\left(\left(\boldsymbol{\mu}_q\mathbf{H} + \mathbf{E}\hat{g}_{ME}^{(q)}\mathbf{H}\right)^2 + \Delta_{cf}^2\right)^{1/2} - ½\mathbf{H}\hat{\chi}_{VV}^{(q)}\mathbf{H}\,, \tag{S3}$$

and they allow to determine the free energy

$$\Phi(\mathbf{H}, \mathbf{E}, T) = -k_B T \sum_q n_{Tb}^q \left[ln\left(2cosh\frac{\varepsilon_q}{k_B T}\right) - \varepsilon_{VV}^{(q)}\right]\;, \tag{S4}$$

where n_{Tb}^q is the number of Tb^{3+} ions in the *q* site, k_B is the Boltzmann constant and *T* is the temperature.

Magnetization. Differentiating (S4) by **H**, we obtain the total magnetization:

$$\boldsymbol{M}(\mathbf{H},T) = -\frac{\boldsymbol{\partial}\Phi}{\boldsymbol{\partial}\mathbf{H}}|_{E=0} \approx \sum_q n_{Tb}^q\ \boldsymbol{\mu}_q(\boldsymbol{\mu}_q\mathbf{H})\chi_q + \hat{\chi}_{vv}\mathbf{H} \tag{S5}$$

where $\chi_q = \tanh(\varepsilon_q/k_BT)/\varepsilon_q$ is the effective local susceptibility and the last term is the Van Fleck contribution to the magnetization determined by the susceptibility $\hat{\chi}_{vv} = \sum_q n_{Tb}^q \hat{\chi}_{VV}^{(q)}$, which is independent on temperature at $T < 100$ K.

The magnetization in the basal plane is rapidly saturated (at $\mu_0 H \approx 1$ T) and has a slight slope in the saturation region (Fig. 1). Simulation of field dependences shows that this behavior is due to a small value of the crystal field quasi-doublet splitting $\Delta_{cf} \lesssim 0.7$ K. When describing the magnetization along the b^* and c axes, we additionally took into account the deviation of the ion behavior from the Ising one due to the contribution to the quasi- doublet splitting Δ_{cf} (Eq.(3)) of a higher order terms in H [2], which leads to a larger slop in the magnetization in a field directed perpendicular to the Ising axes.

To determine the orientation of the Ising axes, we simulated the angular dependences of the magnetization at $\mu_0 H = 5$ T and T = 1.9 K. In the saturation region ($\boldsymbol{\mu}_q\mathbf{H} >> \Delta_{cf}$, k_BT), the magnetization along the field is $M_H = \sum_q |n_{Tb}^q \boldsymbol{\mu}_q \mathbf{H}| + \mathbf{H}\hat{\chi}_{vv}\mathbf{H}/H$. When the magnetic field rotates in the ab^* plane, the maximum magnetization is reached at $H||a$ and 60° anisotropy is observed (Fig. 2a). This indicates the orientation of the local magnetization axes $\boldsymbol{n}_q$ along the second order axes a, b, $-a$-b (Fig. 5). At the same time, the magnetization in the ac and b^*c planes is proportional to $|\sin\theta_H|$, where θ_H is the angle of field deviation from the c axis, which is also consistent with the dependences observed in the experiment (Fig. 2b,c). The nonzero value of the magnetization at $H || c$ may be due to the presence of a small (~0.25%) number of distorted positions having the projection of the local easy Ising axis onto the c axis and not perfect orientation of the sample. The contribution to polarization from distorted positions is small and was omitted.

Thus, in TbLGS, the effect of local symmetry distortions on values of quasidoublet splitting in the crystal field and the orientation of the Ising axes is weak, therefore, a simple model is used, which assumes that the local symmetry is not broken, and the Ising axes are directed along three second order axes (Fig. 5). In this case, the number of Tb^{3+} ions in the q site $n_{Tb}^q = x_{Tb}N/3$, where x_{Tb} is their total concentration, $N = 1/V_0 = 1/a^2 c \sin 60° \approx 3.5\ 10^{27}$ m^{-3}is the total number of rare earth ion positions per unit volume ($a \approx 8.06$ Å and $c \approx 5.06$ Å - unit cell parameters [4]).

The magnetic susceptibility obtained in the framework of the model at $\boldsymbol{\mu}_q\mathbf{H} << \Delta_{cf}$ has a temperature dependence of $\sim T^{-1}$ (inset in Fig. 1) up to 100 K, where contributions from the overlying levels (above 250 K) is appeared.

In addition to crystal field splitting of the ground quasidoublet, consistent modeling of the field and temperature dependences of magnetization made it possible to determine its magnetic moment $\mu_{Tb} = (8.25 \pm 0.02)\mu_B$. The obtained characteristics of the magnetic subsystem are then used to simulate magnetic field-induced polarization.

Polarization. Similarly to magnetization, differentiating the free energy (S5) by the electric field vector, we calculated the macroscopic electric polarization:

$$\mathbf{P} = \tfrac{x_{Tb}N}{3}\textstyle\sum_q \mu_{Tb}(\mathbf{n}_q\mathbf{H})\hat{g}_{ME}^{(q)}\mathbf{H}\chi_q, \tag{S6}$$

where the magnetoelectric interaction tensor, for local symmetry C_2, has five components:

$$\hat{g}_{ME}^{loc} = \begin{pmatrix} g_{XX} & 0 & 0 \\ 0 & g_{YY} & g_{YZ} \\ 0 & g_{ZY} & g_{ZZ} \end{pmatrix} \tag{S7}$$

The local coordinate system at position "1" coincides with the crystallographic one: $X \parallel C_{2a}$, $Z \parallel c$, Y axis is orthogonal to X, Z and forms the right-handed basis. Local coordinate systems at "2", "3" sites are connected to site "1" by rotation operations $\hat{\boldsymbol{C}}_{\boldsymbol{3}}^{\pm}$ around the trigonal axis by ±120°: $\hat{\boldsymbol{g}}_{\boldsymbol{ME}}^{(\boldsymbol{2/3})} = \left(\hat{\boldsymbol{C}}_{\boldsymbol{3}}^{\pm}\right)^{-\boldsymbol{1}} \hat{\boldsymbol{g}}_{\boldsymbol{ME}}^{\boldsymbol{loc}} \hat{\boldsymbol{C}}_{\boldsymbol{3}}^{\pm}$.

Using the definition of the polarization (S5) and introducing combination of effective local susceptibilities $\chi = (\chi_1 + \chi_2 + \chi_3)/3$, $\chi_{123} = (2\chi_1 - \chi_2 - \chi_3)/3$ and $\chi_{23} = \sqrt{3}(\chi_2 - \chi_3)/3$ with components of the magnetic field $\mathbf{H}$, the resulting expression for the polarization P_a:

$$\begin{aligned}\frac{P_a}{x_{\mathrm{Tb}} N \mu_{\mathrm{Tb}}} = \chi &\left(-\tfrac{g_{YZ}}{2} H_{b^*} H_c + \tfrac{(g_{XX}-g_{YY})}{4}\left(H_a^2 - H_{b^*}^2\right)\right) \\ &+ \tfrac{g_{YZ}}{4}\left(\chi_{123} H_{b^*} H_c - \chi_{23}(-H_a H_c)\right) \\ &+ \tfrac{(g_{XX}+g_{YY})}{8}\left(\chi_{123}\left(H_a^2 - H_{b^*}^2\right) - \chi_{23}(-2H_a H_{b^*})\right) \\ &+ \tfrac{g_{XX}}{4}\chi_{123}\left(H_a^2 + H_{b^*}^2\right)\end{aligned} \tag{S8}$$

where the effective susceptibility χ provides a total response of the magnetic system to an external magnetic field. It remains a non-zero at $H = 0$ and decreases with increasing magnetic field due to a saturation of magnetic moments. The susceptibilities $\chi_{123} = \chi_{23} = 0$ at $H = 0$, but due to the different magnetization of ions in in non-equivalent sites, they increase with increasing field and then decrease with a saturation of magnetic moments. The expression written in this way allows us to explicitly separate the contributions to polarization in high and weak magnetic fields and determine the components of the magnetoelectric tensor $\hat{g}_{ME}^{loc}$.

In weak magnetic fields $\boldsymbol{\mu}_q\mathbf{H} << \Delta_{\mathrm{cf}}, k_B T$ the effective susceptibilities become the same $\chi_q \approx \tanh(\Delta_{\mathrm{cf}}/k_B T)/\Delta_{\mathrm{cf}}$ resulting in only non-zero first terms with χ in Eq. (S8), and the polarization P_a is determined by the quadratic magnetoelectric susceptibilities $\alpha_{1,2}(T)$ (Eq.(1)), which are determined by the tensor $\hat{g}_{ME}^{loc}$ components

$$\begin{aligned}\alpha_1(T) &= -g_{YZ} \tfrac{\mu_0 x_{\mathrm{Tb}} N}{2\Delta_{\mathrm{cf}}} \tanh \tfrac{\Delta_{\mathrm{cf}}}{k_{\mathrm{B}} T} \\ \alpha_2(T) &= (g_{XX} - g_{YY}) \tfrac{\mu_0 x_{\mathrm{Tb}} N}{4\Delta_{\mathrm{cf}}} \tanh \tfrac{\Delta_{\mathrm{cf}}}{k_{\mathrm{B}} T}\end{aligned} \tag{S9}$$

The $\alpha_{1,2}$ remain finite at $T \to 0$ and with increasing temperature (up to 100 K) they are proportional to T^{-1} (Fig.3d). When describing the polarization above 100 K, the population of Tb^{3+} excited states is taken into account in its partition function. Thus, the polarization P_a is determined by the total response of three sites q, whose susceptibilities in weak fields are equal, and the magnitude of the polarization is determined by the three components of the magnetoelectric interaction tensor g_{XX}, g_{YY}, g_{YZ}.

In a saturation regime for magnetic moments ($\boldsymbol{\mu}_q\mathbf{H} >> \Delta_{\mathrm{cf}}, k_B T$), additional contributions from χ_{123} and χ_{23} appear (see (S8)), and the dependence $P_a(H)$ becomes quasi-linear and has the form for actual field directions:

$$\begin{aligned}P_a(H_a) &\approx \frac{x_{\mathrm{Tb}} N}{6}(g_{XX} - 3g_{YY}) H_a, \\ P_a(H_{b^*}) &\approx -\frac{\sqrt{3} x_{\mathrm{Tb}} N}{6}(g_{XX} - g_{YY}) H_{b^*}, \\ P_a(H_{a45b^*45c}) &\approx \frac{x_{\mathrm{Tb}} N}{4}\left(2g_{XX} - 4g_{YZ} - \sqrt{3}(g_{XX} - g_{YY})\right) H_{a45b^*45c}\end{aligned} \tag{S10}$$

Such polarization dependence on magnetic field is in a good agreement the experiment (see, for example, the inset in Fig. 3a) and allows to determine the values of the derivatives

$dP_a/dH_a \approx$ -(3.7±0.1)μC/m^{2}T, $dP_a/dH_{b*} \approx$(2.1±0.1)μC/m^{2}T, $dP_a/dH_{a45b^*45c} \approx$(1.6±0.1) μC/m^{2}T to find the components of the magnetoelectric tensor $\hat{g}_{ME}^{loc}$. As a result, by a consistent simulation of the magnetic field dependences of $P_a(H,T)$ for different field orientations and at various temperatures, the following components of $\hat{g}_{ME}^{loc}$ are determined:

$g_{XX} \approx 0$, $g_{YY} \approx (4.30 \pm 0.23)\times 10^{-32}$ (C × м/T) and $g_{YZ} \approx -(0.68 \pm 0.14)\times 10^{-32}$ (C × м/T) .

Since g_{XX} is negligible within an experimental accuracy, this means that a local polarization occurs in the plane orthogonal to the Ising axis of Tb^{3+} ions (Fig. 5) as well as the relation $P_a(H_a) \approx -\sqrt{3}P_a(H_{b*})$ takes place (Fig. 3). We note also that the measurement of polarization at *H* || *a45 °b*45* °c is a more complex experimental task, so its value has a larger error compared to the geometries *H*||*a and H*|| *b** (Fig.3c).

Polarization along the trigonal axis P_c, in the general case, has the form

$$\frac{P_c}{x_{\text{Tb}} N \mu_{\text{Tb}}} = \frac{1}{2} g_{ZZ}\left(\chi_{23} H_{b^*} H_c - \chi_{123}(-H_a H_c)\right) + \\ + \frac{1}{4} g_{zy}\left(\chi_{23}\left(H_a^2 - H_{b^*}^2\right) - \chi_{123}(-2H_a H_{b^*})\right) \tag{S11}$$

Unlike the P_a and P_{b*} polarization components, the P_c does not depend on the total susceptibility χ and at low fields and high temperatures ($\boldsymbol{\mu}_q\mathbf{H}$) << k_BT, Δ occurs only starting from the fourth order in the magnetic field. Expanding of the local susceptibilities χ_q and their combinations χ_{123} and χ_{23} over the magnetic field **H** for ($\boldsymbol{\mu}_q\mathbf{H}$) << k_BT, Δ_{cf} , results for P_c the expression

$$P_c(H,T) \approx -\frac{x_{\text{Tb}} N g_{ZZ}}{12}\left(\frac{\mu_{Tb}}{k_B T}\right)^3 H_a H_c\left(H_a^2 - 3H_{b^*}^2\right) \\ -\frac{x_{\text{Tb}} g_{ZY}}{120}\left(\frac{\mu_{Tb}}{k_B T}\right)^5 H_a H_{b^*}\left(H_a^2 - 3H_{b^*}^2\right)\left(H_{b^*}^2 - 3H_a^2\right) + \cdots \tag{S12}$$

Thus, when the field deviates from the *ab** plane, the polarization is determined by only one microscopic parameter g_{ZZ}, it is proportional to H^4T^{-3} (Fig. 4a,b) and has a maximum at *H* ‖ *a*60º*c*.

At large magnetic fields $\boldsymbol{\mu}_q\mathbf{H}$ >> k_BT, Δ_{cf}, the field dependence of the P_c, as well as the P_a, has a quasi-linear character and at *H* || *a60*°c is equal to

$$P_c(H_{a60c}) \approx -\frac{1}{6} x_{\text{Tb}} N g_{ZZ} H_{a60c}. \tag{S13}$$

The g_{ZZ} component of the magnetoelectric tensor can be found directly from the slope $dP_c/dH_{a60c} \approx (2.0 \pm 0.1)$ μC/m^{2}T, which gives $g_{ZZ} \approx (6.89 \pm 0.28) \times 10^{-32}$ C × м/T.

According to (S10), the g_{ZY} component determines the P_c polarization when the magnetic field is oriented in the basal *ab** plane. Expansion of the susceptibilities χ_{123} and χ_{23} over **H** shows that the polarization P_c is proportional to H^6T^{-5} (S12), similar to HoLGS [3 36]. However, due to the high sensitivity of polarization to the magnetic field deviation from a given orientation and, probably, the low value of g_{ZY}, it was not possible to extract this component from P_c measurements against the background of parasitic contributions, therefore its value is assumed to be negligible.

The simulation of polarization within a framework of the proposed model and taking into account the field and temperature dependences of the susceptibilities χ, χ_{123} and χ_{23} (Fig. 3-4) shows that a set of three components of the magnetoelectric tensor g_{YY}, g_{YZ} and g_{ZZ} allows us to describe the entire set of experimental data in a wide range of magnetic fields and temperatures (see Table S1).

Table S1. Magnetic and magnetoelectric parameters of the proposed model: μ_{Tb} is the magnetic moment of the ground Tb^{3+} quas-doublet and its local easy direction $\mathbf{n}_q$, Δ_{cf} is the crystal field splitting of the ground quasidoublet, x_{Tb} - the concentration of Tb^{3+} ions, $\hat{g}_D^{loc}$is the tensor of the magnetoelectric interaction (S7) in D/T.

Parameter	Value
μ_{Tb}	$(8.25 \pm 0.1)\mu_B$
$\mathbf{n}_q$	$\parallel C_2$ (along a, b, and $-a$-b)
Δ_{cf}	$\lesssim 0.7$ K
x_{Tb}	5%
$\hat{g}_D^{loc}$	$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 1.3 \pm 0.07 & -0.2 \pm 0.04 \\ 0 & 0 & -2.1 \pm 0.07 \end{pmatrix} 10^{-2} \frac{\mathrm{D}}{\mathrm{T}}$

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