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Theory of magnetic resonance as an orbital state probe

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It is demonstrated that magnetic resonance in a magnetically ordered state is a sensitive indirect method for the investigation of the orbital ground state. This idea is illustrated for two perovskite titanates: $LaTiO_3$ and $YTiO_3$. In contrast to the spin-wave energy spectra, antiferromagnetic resonance spectra in an external magnetic field reveal clear dependence on the orbital state and it can distinguish the state with strong orbital fluctuations from the static orbital order. Our theoretical analysis is based on the model, which explicitly takes into consideration the strong correlation among lattice, orbital, and magnetic degrees of freedom.

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I. INTRODUCTION

The interaction of spin and orbital degrees of freedom in transition-metal (TM) oxides has attracted enormous attention for a long time.[1] But in spite of 20 years of efforts, multiple fundamental properties of these compounds are still a subject of the discussion. Among those phenomena, which attract the main interest, there is the superexchange driven orbital-spin phase diagram of perovskite titanates and vanadates.[2–6]

It is known that in wide temperature range and for different R=rare-earth element or Y titanates with general formula $RTiO_3$ possess orthorhombic crystal structure with *Pnma* space group, often called "quasicubic"[7,8] (see Fig. 1). The $GdFeO_3$-type distortions (T_{1g} distortions), which are present in these crystals, are believed to control magnetic structure and properties of the compounds through the influence on their orbital ground state.[1,5,6]

Generally there are two schemes for the description of titanates orbital and magnetic properties: strong crystal-field scheme and strong superexchange scheme. The first one implies the arrangement of orbital structure in a $3d$ perovskite, which is a well-known phenomenon[9,10] and is due to full lifting of $3d$ ion orbital state degeneracy by the crystal field (H_{cf}). In this case magnetic interactions are formed mainly by the superexchange interaction (H_{ex}) of $3d$ electrons in the ground state and the relation $H_{\mathrm{cf}} \gg H_{\mathrm{ex}}$ holds well. We will call this case "the static orbital order." If one reduces the crystal field, which lifts the degeneracy, H_{ex} will admix upper electronic states to the ground states. Superexchange interaction has dynamic origin (it is produced by virtual hoppings of electrons[11]), that is why such an admixture is often called "the orbital fluctuations." The case of extremely strong orbital fluctuations takes place when $H_{\mathrm{cf}} \ll H_{\mathrm{ex}}$ (the second scheme). When H_{cf} tends to zero, $3d$ orbital states become degenerate and H_{ex} becomes the only essential interaction in the system. In some specific cases [e.g., $J_H=0$ (Ref. 2)] the latter may lead to the formation of "orbital liquid" state which is just the absence of orbital order.

In this context, La and Y titanates are believed to be of special interest for investigators because these two ions stand at the opposite ends of rare earths and Y series of ionic radii. T_{1g} distortions in $YTiO_3$ with "smaller" Y are much greater of these in $LaTiO_3$, which has the biggest radius of R ion in the whole series. This gives strong argument to suppose that the ratio of H_{cf} and H_{ex} might be different for La and Y compounds because of the difference in crystal field which affects the Ti^{3+} ions in them. One more feature which makes these two crystals even more interesting is the difference of their magnetic ground states: lanthanum titanate is antiferromagnetic[8] with strong isotropic superexchange $J \approx 15.5$ meV,[12] whereas yttrium titanate is ferromagnetic with $J \approx -2.75$ meV.[13] Moreover, almost isotropic superexchange couplings (both in $LaTiO_3$ and its sister compound) are in contrast with the situation in manganites and cuprates, which have pronounced superexchange anisotropy.

The hot discussion was started by Khaliullin and Maekawa,[2] who proposed the superexchange model with dynamical quenching of local orbital moments in a simple cubic lattice of the Ti^{3+} ions. This model gives no static orbital order with fixed magnetic arrangement in contrast to the usual Goodenough-Kanamori picture. This approach, based on the Kugel-Khomskii method,[10] perfectly explains unusual reduction in the Ti^{3+} spin[13,14] and anomalous isotropic spin-wave spectra[12,13] found experimentally in $LaTiO_3$ and $YTiO_3$, but it contradicts NMR (Refs. 15 and 16) and x-ray absorption spectroscopy[17] experiments and some crystal-field[5,6,18–20] and density-functional[21,22] calculations.

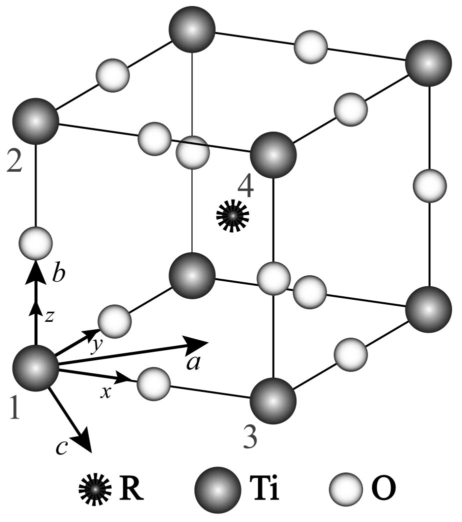

FIG. 1. $RTiO_3$ crystal structure. *Pnma* ($\mathbf{a},\mathbf{b},\mathbf{c}$) and pseudocubic ($\mathbf{x},\mathbf{y},\mathbf{z}$) axes are shown. Numbers denote Ti sublattices.

However, it is supported by recent Raman scattering experiments,[23] which revealed orbital excitations and made possible some orbital fluctuations at the ground state. Now there is no doubt that static orbital order is present in titanates, as it was shown by several authors in different approaches,[5,6,17–23] but the strength of possible orbital fluctuations and their influence on magnetic properties of compounds were not considered and thus, is not clear yet.

All above-mentioned facts and contradictions indicate a puzzling situation: on the one hand, the system has already been studied in many aspects; on the other hand, it is not clear yet, how to combine all reliably established facts and explain them in one consistent model. To solve the problem, the definite model of a titan perovskite oxide is developed by authors using particular examples of La and Y compounds.

Our target is to analyze the spin waves, which exist in both compounds and experimental studies of which have given rise to the discussion of titanates. We suggest these magnetic excitations to be a field for the discussion of two different experimental situations: neutron-scattering study of spin-wave energy spectra and resonance study of spin waves in the center of the Brillouin zone. These two techniques are often called "the spin-wave study" (it gives energy spectra) and "the magnetic resonance study" (which is often associated with external magnetic field spectra). Although the latter is just a special case of the former, these methods are completely different experimentally in realization and applications. As discussed below, the resonance method provides much more accurate information on magnetic interactions, and, what is surprising, on the orbital state of the compound. The main idea of this paper is that this method can serve as a referee between opposite orbital states: static structure and liquid. It also indicates intermediate state with orbital fluctuations in ordered phase. Thus, this method can give strong arguments for adequateness of one of two theoretical schemes.

Solving the problem of the description of spin waves, we focus on the mechanisms of orbital and magnetic ground states formation, not only revealing the fact that crystal structure predetermines electronic and magnetic properties (this is acknowledged by many authors), but also pointing out *how* it happens.

The rest of the paper is organized in the following way. Section II analyzes the formation of orbital state with the help of vibronic Hamiltonian (VH) and compares the present electronic structure calculations with other studies. The orbital state obtained here is used then for extracting the superexchange parameters. This extracting is carried out within the usual Kugel-Khomskii method and is described in Sec. III. A linear approximation for spin-wave energy spectra as well as magnetic resonance field spectra is given for both LaTiO$_3$ and YTiO$_3$ in Sec. IV. In this section we also compare two different orbital states and their evidences in spin waves and magnetic resonance. We present a brief summary of the paper in Sec. V.

II. ORBITAL GROUND STATE

We start from the low-energy spectrum of the crystal-field Hamiltonian with explicit electron-lattice interaction, which is VH (Ref. 24):

$$\begin{aligned} H_{\mathrm{vib}} = H_{\mathrm{lin}} + H_{QQ} + H_R = {} & [V_e(Q_\theta X_\theta + Q_\epsilon X_\epsilon) \\ & + V_t(Q_\xi X_\xi + Q_\eta X_\eta + Q_\zeta X_\zeta)] + \{V_a(Q_x^2 + Q_y^2 + Q_z^2)X_{A1} \\ & + V_b[(2Q_z^2 - Q_x^2 - Q_y^2)X_\theta + \sqrt{3}(Q_x^2 - Q_y^2)X_\epsilon] \\ & + V_c(Q_yQ_zX_\xi + Q_xQ_zX_\eta + Q_xQ_yX_\zeta)]\} + \{V_e^R(Q_\theta^R X_\theta \\ & + Q_\epsilon^R X_\epsilon) + V_t^R[(Q_{\xi,1}^R + Q_{\xi,2}^R)X_\xi + (Q_{\eta,1}^R + Q_{\eta,2}^R)X_\eta + (Q_{\zeta,1}^R \\ & + Q_{\zeta,2}^R)X_\zeta]\}. \end{aligned} \tag{1}$$

Here Q_θ, Q_ϵ, Q_ξ, Q_η, Q_ζ, Q_x, Q_y, Q_z and Q_θ^R, Q_ϵ^R, Q_ξ^R, Q_η^R, Q_ζ^R are symmetrized shifts of oxygen ions which form an octahedron and of R ions forming a cube.[25] Oxygen and R ions are the nearest and next-nearest Ti^{3+} neighbors correspondingly. Their shifts are obtained from accurate crystal structure data for LaTiO$_3$ (Ref. 8) and YTiO$_3$.[7] X_Γ are symmetric orbital operators, acting on the $3d$-t_{2g} triplet, and V_α $(\alpha=e,t,a,b,c)$ and V_α^R $(\alpha=e,t)$ are electron-lattice coupling constants.[26,27] The expressions in the first two square brackets, which are H_{lin} and H_{QQ}, represent interactions of the Ti^{3+} $3d$-t_{2g} electron with the linear and quadratic symmetrized shifts of the oxygen octahedron correspondingly, and H_R (the third expression) is responsible for this electron and a cube of R ions shifts coupling.

The electron-lattice coupling constants V_α may be obtained as Q_Γ and Q_Γ^R derivatives of energy (1).[26,27] For each constant V_α any of the above-mentioned Qs with appropriate Γ may be used. For example, V_e is equal to $\partial\langle H_{\mathrm{vib}}\rangle / \partial Q_\theta$ and also to $\partial\langle H_{\mathrm{vib}}\rangle / \partial Q_\epsilon$. To obtain these coupling constants one does not need to know the actual (experimental) values of Q_Γ and Q_Γ^R: only the opportunity to vary the energy of a cluster with respect to symmetrized shifts of this cluster is important.

All coupling constants were calculated this way within the cluster method, which is realized in the GAMESS package.[28,29] We used $[\mathrm{TiO}_6]^{9-}$ and $[\mathrm{TiO}_6R_8]^{15+}$ clusters in the environment of 90 point charges. The basis sets we used were CRENBS ECP (Ref. 30) and CRENBL ECP (Ref. 31) for the Ti^{3+} and O^{2-} ions, correspondingly. Electronic cores of both ions were substituted by the effective core potentials (ECP). The particular method of electronic calculation was multiconfigurational self-consistent field method with correlation corrections in molecular orbital (as a linear combination of atomic orbitals, MO LCAO) approach for open shells. Also correlation corrections were introduced by considering the second order of Möller-Plesset perturbation theory (MP-2).

A detailed analysis of different advantages and limitations of the electronic structure description with the help of VH can be found elsewhere.[32] For our purposes it is enough to know that this Hamiltonian counts in both electronic and lattice degrees of freedom explicitly that is why it describes their interplay effectively and in a simple manner. It is also important that the parameters of VH (namely, coupling constants) are calculated *ab initio*.

The Hamiltonian (1) diagonalization gives the three lowest atomic states of the Ti^{3+} (see Table I). The ground state appears to possess *static orbital structure* of the form predicted by Mochizuki and Imada,[5,6] which are the following wave functions ($3d$-t_{2g} cubic basis set): $\psi_{1,2}(\mathrm{La}) = \psi_{3,4}(\mathrm{La})$

TABLE I. The three lowest Ti^{3+} atomic orbitals in $\mathrm{LaTiO_3}$ and $\mathrm{YTiO_3}$ for the Ti ion no. 1. The $3d$-t_{2g} atomic basis set is used, that is (ξ,η,ζ).

R	Energy (eV)	Function
	0	(−0.61, −0.45, 0.65)
La	0.181	(0.79, −0.26, 0.56)
	0.213	(0.08, −0.85, −0.51)
	0	(−0.58, 0.28, 0.76)
Y	0.172	(0.70, −0.30, 0.64)
	0.284	(0.42, 0.91, −0.02)

$\approx 1/\sqrt{3}(\mp\xi\mp\eta+\zeta)$, in $\mathrm{LaTiO_3}$ and $\psi_{1,2}(\mathrm{Y})\approx 1/\sqrt{2}(\mp\xi+\zeta)$, $\psi_{3,4}(\mathrm{Y})\approx 1/\sqrt{2}(\mp\eta+\zeta)$—in $\mathrm{YTiO_3}$.

Table I shows the results, which are similar to other calculations,[5,6,17–22,33] but we have irrefutable argument for reproducing results of previous LDA-based[17,21,22] and point-charge[5,6,18–20] studies by using Eq. (1). All those studies have their disadvantages: either they were based on oversimplified model[5,6] (giving unlikely structure parameters) or they did not reveal the mechanisms of the ground-state formation.[17–22] The present calculation, based on VH, reveals that H_R plays a crucial role in the formation of solitary orbital singlet with its segregation at ≈ 0.20 eV in $\mathrm{LaTiO_3}$ and ≈ 0.15 eV in $\mathrm{YTiO_3}$. About half of these gaps are produced by the crystal field of R ions which are the next-nearest neighbors to the Ti^{3+} (see Table II). This mechanism of the strong orbital order formation was not mentioned in previous publications containing microscopic calculations, although it was counted in there. Thus, the Mochizuki and Imada[5,6] hypothesis about R-ion crystal field is now explicitly manifested.

The influence of the remainder of the crystal on the Ti^{3+} orbital state is negligible. To estimate this influence we compared the VH spectra with coupling constants calculated for clusters surrounded by point charges from many coordination spheres (from 8 to about 15 000 charges). The resulting t_{2g} splittings varied within the limits of 10% and orbital functions were also almost unchangeable. Considering the Ti^{3+} orbital state interactions with nearest and next-nearest neighbors shifts only, we obtained results very close to these published by Schmitz *et al.*,[18–20] who used Ewald summation method to take account of the main long-range effect—the Coulomb interaction—in the whole crystal. This finding of the weak influence of remote neighbors on the Ti^{3+} low-energy spectrum is also supported by other calculations.[17,21,22]

TABLE II. Oxygen and R-ion environment contributions to the three lowest Ti^{3+} orbital energies in $\mathrm{LaTiO_3}$ and $\mathrm{YTiO_3}$. The energies are given in eV.

	Oxygen ($H_{\mathrm{lin}}+H_{QQ}$)	R ions (H_R)	Total (H_{vib})
	0	0	0
La	0.046	0.086	0.181
	0.121	0.152	0.213
	0	0	0
Y	0.072	0.103	0.172
	0.257	0.256	0.284

TABLE III. Single crystal g factors of $\mathrm{LaTiO_3}$ and $\mathrm{YTiO_3}$. Static orbital order is assumed. The *Pnma* coordinate system is used.

R	La	Y
$\mathbf{g}_i$	$\begin{pmatrix} 1.93 & -0.07 & 0.02 \\ -0.07 & 1.92 & -0.00 \\ 0.02 & -0.00 & 1.86 \end{pmatrix}$	$\begin{pmatrix} 1.85 & -0.01 & 0.04 \\ -0.01 & 1.96 & -0.05 \\ 0.04 & -0.05 & 1.93 \end{pmatrix}$

III. SUPEREXCHANGE PARAMETERS

Using the low-energy spectrum obtained from VH diagonalization, we exploit common Kugel-Khomskii (KK) method within the Hubbard model[10] and arrive at isotropic superexchange. Then, one can use Moriya's approach[34] for treating antisymmetric terms and g factors[35] of the effective S-$\frac{1}{2}$ spin Hamiltonian (ESH) introduced below:

$$H_{\mathrm{eff}} = J_{ij}(\mathbf{S}_i\cdot\mathbf{S}_j) + \mathbf{D}_{ij}(\mathbf{S}_i\times\mathbf{S}_j) + S_i^{\alpha}A_{ij}^{\alpha\beta}S_j^{\beta} + H^{\alpha}g_i^{\alpha\beta}S_i^{\beta}, \quad (2)$$

where J_{ij} stands for isotropic superexchange between the ith and the jth magnetic ions, $\mathbf{D}_{ij}$ is Dzyaloshinskiy-Moriya vector, $\mathbf{A}_{ij}$ is symmetric anisotropy tensor, $\mathbf{g}_i$ is g factor of the ith Ti^{3+} ion, and $\mathbf{H}$ represents external magnetic field.

The Hubbard model parameters: energy of electron hopping from the mth orbital on one site to the nth orbital on the neighboring one t_{mn} $(m,n=\xi,\eta,\zeta)$, on-site Coulomb repulsion of a pair of electrons U and intra-atomic electronic exchange interaction J_H were extracted from the LDA-based calculation.[21] For $\mathrm{LaTiO_3}$ $U\approx 3.20$ eV, J_H was not considered and for $\mathrm{YTiO_3}$ $U\approx 3.45$ eV, $J_H\approx 0.62$ eV. The values of t_{mn} are discussed further. All interactions in ESH, which result from these parameters, are listed in Tables III and IV.

We emphasize that the low-energy spectra of the Ti^{3+} ion in $\mathrm{LaTiO_3}$ and $\mathrm{YTiO_3}$, obtained with the help of VH, are fixed now and remain unchanged in all subsequent calculations. Calculating the ground state and considering superexchange interactions are the two successive steps of classical superexchange theory by Anderson.[11]

This calculation of superexchange couplings, although it is not something new, is to be reproduced because of extreme sensitivity of these interactions to the orbital state. This well-known feature of the KK treatment should be considered because (in comparison with previous studies[5,6,17–22,33,36]) we have obtained different $\psi_i(\mathrm{La})$ and $\psi_i(\mathrm{Y})$, $i=1\ldots3$ for each of four centers in the cell.

By using the ESH (2) one can obtain magnetic ground state as well as magnetic excitations in both compounds. The magnetic structure code for both crystals is (A_x,F_y,G_z) with major G component in $\mathrm{LaTiO_3}$ (G-type magnetic structure) and F-component in $\mathrm{YTiO_3}$ (F-type magnetic structure, see

TABLE IV. Magnetic interactions (meV) in $\mathrm{LaTiO_3}$ and $\mathrm{YTiO_3}$. Static orbital order is assumed. The *Pnma* notations are used.

R	J_{12}	J_{13}	$\mathbf{D}_{12}$	$\mathbf{D}_{13}$	$\mathbf{A}_{12}$	$\mathbf{A}_{13}$
La	12.66	15.75	$\begin{pmatrix} 0.33 \\ 0 \\ -1.58 \end{pmatrix}$	$\begin{pmatrix} -0.42 \\ -0.34 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0.19 & 0 & -0.58 \\ 0 & 0.30 & 0 \\ -0.58 & 0 & 0.10 \end{pmatrix}$	$\begin{pmatrix} 0.32 & 0.30 & 0 \\ 0.30 & -0.14 & 0 \\ 0 & 0 & 0.59 \end{pmatrix}$
Y	−0.21	−3.31	$\begin{pmatrix} 1.84 \\ 0 \\ -0.62 \end{pmatrix}$	$\begin{pmatrix} -0.99 \\ -0.11 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0.22 & 0 & -0.14 \\ 0 & 0.22 & 0 \\ -0.14 & 0 & -0.10 \end{pmatrix}$	$\begin{pmatrix} 0.31 & -0.02 & 0 \\ -0.02 & -0.14 & 0 \\ 0 & 0 & 0.15 \end{pmatrix}$

Fig. 2), in excellent agreement with neutron-scattering experiments.[13,14] Here we should emphasize two special features in J_{ij} which are crucial for obtaining the correct magnetic structure. The first is considering Hund's coupling. Its contribution into J_{ij} is smaller by a factor of J_H/U than "common" superexchange,[11] which is proportional to t^2_{mn}/U. The latter value is believed to be only slightly renormalized by the Hund's coupling, that is why J_H/U terms are often neglected in J_{ij}. This is true for $\mathrm{LaTiO_3}$, but not for $\mathrm{YTiO_3}$, in which delicate balance between competing antiferromagnetic and ferromagnetic contributions into superexchange energy makes necessary such weak interactions as J_H to be taken into consideration. The second feature, which should be considered in J_{ij}, is the explicit introduction of the Ti–O–Ti bond angle (φ) dependence of t_{mn} (Ref. 37) (see below).

Because of the modulation of "hoppings" (t_{mn}) by the Ti–O–Ti bond angle, the isotropic superexchange interaction for a pair of $\mathrm{Ti^{3+}}$ ions becomes a function of φ. For example, the dependence of J_{ij} on φ in the **ac** plane (*Pnma*) reads as

$$J_{13} = J_0\left(1 - \frac{\sin^2\varphi}{2}\right), \tag{3}$$

where $J_0 = 17.56(-4.01)$ meV is the superexchange integral for strictly cubic geometry of the system with La(Y) ion. This integral depends on the particular $\mathrm{Ti^{3+}}$ orbital state, on U, J_H, and t^c_{mn}. The latter values are not the transfer integrals for a real crystal. These are the transfer integrals for a strictly cubic system. Some notes on t^c_{mn} should clarify the matter: (i) t^c_{mn} are those parts of transfer integrals, which are related only to the Ti–O–Ti processes, but not to the Ti–R–Ti hoppings; (ii) t^c_{mn} depend on the Ti–Ti distance and do not depend on the superexchange angle φ; (iii) $t^c_{mn} \neq 0$ only for $m = n$ because exdiagonal hoppings are forbidden by the symmetry of the pair[38] (in cubic system); (iv) for $\mathrm{LaTiO_3}$ $t^c_{mm} \approx 0.25$ eV and for $\mathrm{YTiO_3}$ $t^c_{mm} \approx 0.25$ eV, although these values are slightly different for the perovskite axis (**b**) and the plane (**ac**).[21] These parameters are introduced to show the explicit φ dependence of J_{ij}. For lanthanum titanate the Ti–O–Ti bond angle φ is about 153° and for $\mathrm{YTiO_3}$ it is approximately 142°.

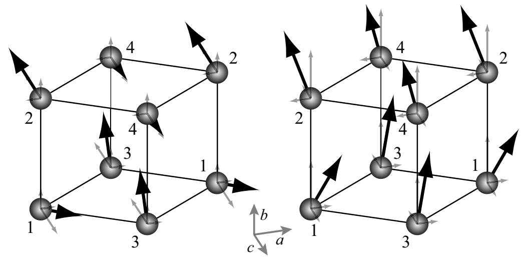

FIG. 2. Schematic magnetic structures of $\mathrm{LaTiO_3}$ (left) and $\mathrm{YTiO_3}$ (right). Gray arrows denote magnetization projections (*Pnma*).

Assuming strictly cubic symmetry of the system [the violation of which by the crystal field appears in $\varphi \neq 180°$ in Eq. (3)], it is impossible to obtain the correct orbital structure. That is why Khaliullin and Maekawa[2] have not obtained it for $\mathrm{LaTiO_3}$. Also one cannot obtain experimentally observed magnetic structure in both compounds simultaneously without analyzing the influence of J_H on J_{ij}.[11,18–20] This is perfectly shown in the Fig. 3. This figure gives an example of the dependence of J_{ij} on the assumed lowest orbital state of the $\mathrm{Ti^{3+}}$ ion in $R\mathrm{TiO_3}$. For simplicity the orbital state is represented in terms of orbital angles ($3d$-t_{2g} atomic basis set is used): $(\xi, \eta, \zeta) = (\sin\Theta\cos\Phi, \sin\Theta\sin\Phi, \cos\Theta)$ and only one superexchange interaction is shown ($J_{12} = J_z$). The dependencies are calculated with Hubbard model parameters for $\mathrm{LaTiO_3}$ including J_H and without J_H. It is clear that for the

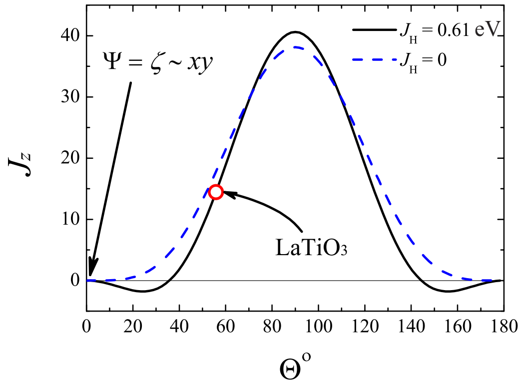

FIG. 3. (Color online) Orbital dependence of J_{12} in $\mathrm{LaTiO_3}$. Orbital angles are used to represent $3d$-t_{2g} atomic basis set: $(\xi, \eta, \zeta) = \sin\Theta\cos\Phi, \sin\Theta\sin\Phi, \cos\Theta$. Calculations for $J_H = 0$ (solid line) and for $J_H = 0.61$ eV (Ref. 21) are shown.

TABLE V. Single crystal g factors of $LaTiO_3$ and $YTiO_3$. Strong orbital fluctuations are assumed. The *Pnma* coordinate system is used.

R	La	Y
$\mathbf{g}_i$	$\begin{pmatrix} 2.00 & 0 & 0 \\ 0 & 2.00 & 0 \\ 0 & 0 & 2.00 \end{pmatrix}$	$\begin{pmatrix} 2.00 & 0 & 0 \\ 0 & 2.00 & 0 \\ 0 & 0 & 2.00 \end{pmatrix}$

case $J_H=0$ no ferromagnetic sign of J_{ij} may be reproduced whatever orbital state is assumed.

Finally, discussing the properties of the ESH, it is important to mention that both anisotropic terms of the ESH, namely Dzyaloshinskiy-Moriya interaction and symmetric anisotropy, should be considered in Eq. (2), otherwise the static magnetic order cannot exist.[39] This is not always kept by investigators.[12,13]

Actually, different pieces of the above results were obtained earlier by several authors.[5,6,18–22,24,25,33,36] Orbital structure, superexchange interactions, and magnetic ground state are reproduced here to illustrate the realistic model with reasonable parameters, and, what is more important, to uncover particular mechanisms of titanates orbital and magnetic ground states formation that has not been done before.

In order to understand how the orbital state influences magnetic dynamics of the compounds, we need to model superexchange interactions in a hypothetic state with strong orbital fluctuations. For this purpose we average J_{ij}, $\mathbf{D}_{ij}$, $\mathbf{A}_{ij}$, and $\mathbf{g}_i$ over the three lowest orbital states listed in Table I. When applying this averaging, the perturbation theory, which we use for calculation of anisotropic parameters[34] and g factors,[35] remains applicable. At the same time, the extreme case of strong orbital fluctuations is reproduced. We do not answer the questions, what are the reasons of orbital fluctuations (superexchange, phonons, etc.) and what is the actual strength of these fluctuations. We just take into account the orbital fluctuations, considering the extreme case of strong excitations.

The ESH parameters obtained in this way are listed in Tables V and VI. The parameters are not compared with those from other papers because in all cases they are the result of model calculations and their accuracy is very low: all such calculations should be accepted as evaluative only. Besides this, all previous model calculations did not consider the orbital fluctuations or were not aimed to obtain the ESH parameters. Finally, the codes and types of $LaTiO_3$ and $YTiO_3$ magnetic structures are the same in the present study and for example in Refs. 18–20, and in contrast to the calculated parameters, magnetic structure code and type are qualitative characteristics, which represent themselves as a convenient comparison tool for the different investigations results.

Our isotropic superexchange parameters for both cases of static orbital structure (Table IV) and strong orbital fluctuations (Table VI) are in qualitative agreement with experiments.[12,13] Considerable deviation of J_{12}, J_{13} for $YTiO_3$ from their isotropic form (when $J_{12} \approx J_{13}$) is the consequence of specific form of orbital structure obtained above. This orbital structure is similar to that reproduced by other investigators,[6,19–22] but it is still somewhat original. Superexchange interactions are extremely sensitive to the particular form of orbital structure[10,37] (see Fig. 3). That is why little divergence of two orbital structures may lead to a big difference of superexchange interaction values. By using some other set of the Hubbard model parameters we could fit the J_{ij} values reported by those authors,[12,13] but this was not our purpose. We are going to discuss those effects which are not the consequence of J_{ij} values, and at the same time, the qualitative picture is already reproduced. Moreover, it was proved for cuprates[40] and titanates[19] that while the isotropic couplings are not very accurate, the anisotropic ones can be accurate enough to reproduce spin excitation spectra. That is why for the investigation of spin waves and antiferromagnetic resonance spectra we use experimental values of J_{12} and J_{13}.

IV. SPIN WAVES AND ANTIFERROMAGNETIC RESONANCE

We now turn to the core idea of the paper, that is, drastic dependence of the particular kind of magnetic excitations on the orbital ground state. Using linear approximation, we consider magnetic excitations, namely, spin waves and antiferromagnetic/ferromagnetic resonance (AFMR/FMR) spectra, in $LaTiO_3$ and $YTiO_3$ compounds. Simulations (see Figs. 4 and 5) provide surprising results when comparing the

TABLE VI. Magnetic interactions (meV) in $LaTiO_3$ and $YTiO_3$. Strong orbital fluctuations are assumed. The *Pnma* notations are used.

R	J_{12}	J_{13}	$\mathbf{D}_{12}$	$\mathbf{D}_{13}$	$\mathbf{A}_{12}$	$\mathbf{A}_{13}$
La	8.47	7.17	$\begin{pmatrix} -1.53 \\ 0 \\ -0.86 \end{pmatrix}$	$\begin{pmatrix} 0.65 \\ -0.62 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 3.18 & 0 & 0.23 \\ 0 & 4.18 & 0 \\ 0.23 & 0 & 0.09 \end{pmatrix}$	$\begin{pmatrix} 5.56 & -4.45 & 0 \\ -4.45 & 4.17 & 0 \\ 0 & 0 & 0.76 \end{pmatrix}$
Y	−3.36	−1.26	$\begin{pmatrix} 0.96 \\ 0 \\ -0.31 \end{pmatrix}$	$\begin{pmatrix} -0.18 \\ 0.01 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0.18 & 0 & 0.03 \\ 0 & 0.86 & 0 \\ 0.03 & 0 & 0.28 \end{pmatrix}$	$\begin{pmatrix} 0.23 & -0.09 & 0 \\ -0.09 & 0.31 & 0 \\ 0 & 0 & 0.34 \end{pmatrix}$

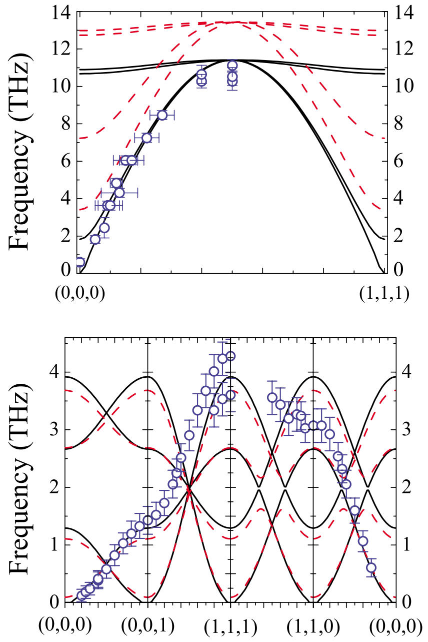

FIG. 4. (Color online) Spin-wave dispersions for $LaTiO_3$ (up) and $YTiO_3$ (bottom). Circles denote experimental data, taken from Ref. 12 for $LaTiO_3$ and from Ref. 13 for $YTiO_3$. Simulated curves are black for static orbital order and dashed red for orbitally fluctuating state.

real static orbital structure with hypothetical orbitally fluctuating state.

Spin-wave spectra are found to exhibit almost no differences in two different orbital states for both crystals (Fig. 4). Little discrepancy in the simulations can be easily removed by the slight fitting of the Hubbard model parameters in anisotropic couplings calculations. This fitting is really possible within these parameters' calculation discrepancies in different approaches.[21,22,41] At the same time there is a significant change in AFMR spectra for both La and Y compounds (Fig. 5) with switching their orbital states. Orbital fluctuations show up in both compounds through raising the magnetic anisotropy. This produces typical handbook curves of AFMR field spectra with different anisotropic behavior. The lanthanum compound in hypothetic orbital fluctuating state demonstrates typical antiferromagnetic behavior with strong anisotropy. The large zero-field gap and almost field-independent AFMR frequencies prove this fact. The fluctuating state of yttrium titanate also produces antiferromagnetic curves instead of genuine ferromagnetic ones of its static antipode. In $YTiO_3$ without orbital fluctuations one can clearly see zero frequency at $H=0$ but one observes only "quasi-FMR region" in the case of orbital fluctuations when anisotropy is suppressed near $H\approx 65$ kOe. The spin-reorientational transition at ≈ 65 kOe is a qualitative feature of the spectrum, which could not be unnoticed experimentally, the more so since the lower AFMR branch can be observed at quite obtainable frequency range.

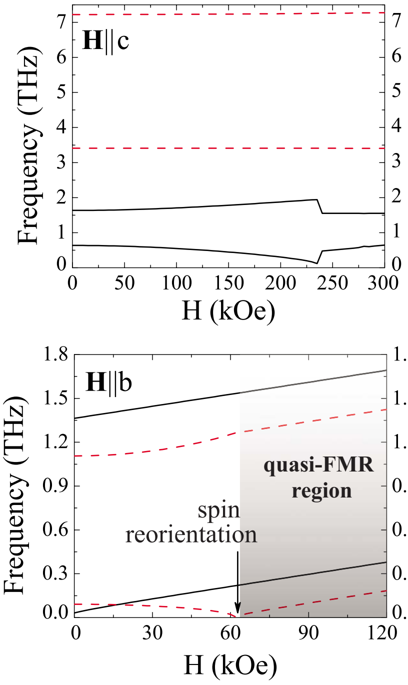

FIG. 5. (Color online) Field dependencies of AFMR frequencies in $LaTiO_3$ (up) and $YTiO_3$ (bottom). **H** is parallel to easy axes. Curves are black for static orbital order and dashed red for orbitally fluctuating state. Only the two lowest resonance curves, observable experimentally, are shown.

These results can be explained in the following way. In the static case the superexchange interaction is essential only for the ground orbitals whereas considering orbital fluctuations makes all three t_{2g} states on each Ti^{3+} ion in a pair equivalent. This results in nine equivalent contributions into isotropic superexchange. Averaging of these contributions gives $J_{12}(\mathrm{OF})\approx J_{13}(\mathrm{OF})$ and (by virtue of orbital states specificity) these are close to J_{12} and J_{13} of the static case. But the same nine contributions into anisotropic interactions are not equivalent because the spin-orbit coupling H_{so} excludes some of these contributions such as $\langle \mathrm{gs1}|Hso|\mathrm{gs1}\rangle\langle \mathrm{gs1}|Hex|\mathrm{gs2}\rangle$ term in Dzyaloshinskiy-Moriya interaction,[34] where "gs" labels "ground state," and 1 and 2 mark the Ti^{3+} ions. That is why the balance between different terms of averaging is violated in the calculation of anisotropic interactions and (again by virtue of orbital states specificity) it is shifted toward increasing the anisotropy. The modification of the form and the values of anisotropic magnetic interactions in the OF case produces another ground state of ESH (2), but since the signs of J_{12} and J_{13} remained the same as in the static (OO) case, the magnetic structure *types* also remain unchanged: *G* for $LaTiO_3$ and *F* for $YTiO_3$. All the peculiarities of SW and AFMR spectra in both orbital states are predetermined by the magnetic structure (see Figs. 4 and 5), and AFMR turned out to be more sensitive to the secondary components of the magnetic structure than the SW method.

Experimental studies of spin waves in $LaTiO_3$ (Ref. 12) and $YTiO_3$ (Ref. 13) were previously interpreted by their authors in terms of strong orbital fluctuations or even orbital liquid. But we showed now (following other authors,[18–20,42] but using a more accurate model for treating low-energy orbital spectrum of the Ti^{3+} ions) that these experiments can be successfully regarded as an evidence of static orbital order in both compounds (Fig. 4). AFMR studies do not suffer from the disadvantage of its ambiguous interpretation, clearly revealing the particular orbital state in qualitative level (Fig. 5). We should mention here that our investigation is intentionally made for opposite cases of orbitally ordered and orbitally fluctuating states to show their differences in a more clear way. One should understand that the veritable orbital state of $\mathrm{LaTiO_3}$ and $\mathrm{YTiO_3}$ is static orbital order with an admixture of orbital fluctuations. This admixture is not very big in real compounds because of large crystal-field splitting of the Ti^{3+} $3d$-t_{2g} levels in both of them. The central point of the discussion of titanates[2–8,12,13,15–25,33,36,42–44] is the question of what approach is more relevant as a starting point for these compounds description: “crystal-field” approach, when it is assumed that the crystal field is much stronger than superexchange interaction, $H_\mathrm{cf} \geqslant H_\mathrm{ex}$; or the ”orbital fluctuations” approach, when the opposite relation ($H_\mathrm{cf} \leqslant H_\mathrm{ex}$) is considered. From this point of view the present work is an investigation and a comparison of two models on the example of titanates rather than a study of some real compound properties. Although we adhere to use crystal-field approach in orbital structure calculation, superexchange interactions and macroscopic magnetic properties of La and Y titanates are also calculated for the states with strong orbital fluctuations (which states are hypothetic in our approach).

Antiferromagnetic resonance is much more accurate in spin-wave energy measurements than neutron scattering. Although it gives information on magnetic excitations in the center of the Brillouin zone only, and, thus is not convenient for the energy spectrum investigation. But if one is interested in isotropic and, especially, in weak anisotropic magnetic interactions (as $\mathbf{D}_{ij}$ and $\boldsymbol{\mathsf{A}}_{ij}$) or g factor measurements, the resonance method is much more informative than the scattering one. For example, experimental accuracy of neutron measurements for $\mathrm{YTiO_3}$ is ± 0.5 meV or worse,[13] whereas the precision of AFMR field spectrum data obtained by submillimeter spectrometer is about 8 GHz,[44] which is close to 0.03 meV and, at least, 1 order of magnitude better than neutron scattering usually gives.

So, at least for titanates, AFMR appears to have two advantages over the neutron scattering when investigating superexchange interactions: it has impressive sensitivity and high accuracy. Unfortunately, no serious attention was paid to this powerful and sensitive method of magnetic structure and magnetic couplings investigation so far. The only attempt to observe electron spin resonance (ESR) below the magnetic transition temperatures (that is AFMR or FMR) and above them (EPR) was made by Okubo *et al.*[44] But, first, in their investigation the AFMR signals for $\mathrm{LaTiO_3}$ were not obtained at all (probably, because of frequency limits of the equipment used). Secondly, Okubo *et al.* used only powder samples and thus all direction-dependent effects were wiped out. We cannot but mention that if powder samples are used, neither such an interesting field spectra as represented in Fig. 5 can be observed, nor the strong orbital state dependence of these spectra can be found.

Actually, peculiarities of magnetic resonance spectra are the consequence of the compounds’ magnetic structures. In the case of orbitally fluctuating state we find the following magnetic structures to be optimal: (G_x, C_y, A_z) with major G component for $\mathrm{LaTiO_3}$ and (F_x, A_y, C_z) with major F component for $\mathrm{YTiO_3}$. Generally speaking, all components of the magnetic structure can be measured in neutron-scattering experiments, but because of equipment limitations and the quality of samples used,[14] it is not always possible for the minor (not major) components. Usually, only the larges component of the magnetic structure is measured reliably, but for both compounds under consideration the major magnetic structure components are the same in two different orbital states (G for $\mathrm{LaTiO_3}$ and F for $\mathrm{YTiO_3}$). Besides this, some $R\mathrm{TiO_3}$ crystals possess high neutron absorption capacity[45] and, thus, the neutron-scattering method of magnetic structure investigation is not applicable to them. Antiferromagnetic resonance again turns out to be a more convenient method of orbital structure investigation than neutron-scattering measurements of magnetic structure. This is even more so because of less sensitivity of the AFMR to the sample quality.

V. SUMMARY

We have presented a detailed theoretical study of spin and orbital physics of titanates. This study is an improvement of many previous works on orbital state and superexchange interactions in titanates. On one hand, it deals with rather simple and well-known approaches, such as electron-lattice model Hamiltonian (1), Kugel-Khomskii method for superexchange interactions, and linear spin-wave approximation. On the other hand, in this paper we focused on revealing those tiny mechanisms that control orbital and magnetic properties of titanates and are often hidden under a thick layer of model assumptions and heavy calculations.

The presented study revealed that common spin-wave measurements are a very weak tool for investigating subtle features of orbital ground state. Our simulation points out that within the uncertainty in the Hubbard model parameters, spin-wave dispersion curves calculated for the different orbital states are in good agreement with one and the same neutron-scattering experiment. This holds for $\mathrm{LaTiO_3}$ and for its sister compound as well.

Finally, we argue that at present, magnetic resonance is the ultimate method to ascertain the actual orbital state of $3d$-t_{2g} perovskites as it gives qualitative discrimination of two opposite model cases: the static orbital order and the orbital order with extremely strong fluctuations. Having advantages over the magnetic structure measurements by neutron scattering and being more accessible than such investigations, AFMR/FMR experiments with single crystals should put a dot at the end of the discussion of the presence and the strength of orbital fluctuations in titanates, which represent a remarkable system with strong entanglement of lattice, spin, and orbital degrees of freedom.

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