Crystal field, spin-orbit coupling and magnetism in a ferromagnet YTiO$_3$

R. J. Radwanski
Center of Solid State Physics, S$^{\text{st}}$Filip 5, 31-150 Krakow, Poland,
Institute of Physics, Pedagogical University, 30-084 Krakow, Poland

Z. Ropka
Center of Solid State Physics, S$^{\text{st}}$Filip 5, 31-150 Krakow, Poland

Magnetic properties of stochiometric YTiO$_3$ has been calculated within the single-ion-based paradigm taking into account the low-symmetry crystal field and the intra-atomic spin-orbit coupling of the Ti$^{3+}$ ion. Despite of the very simplified approach the calculations reproduce perfectly the value of the magnetic moment and its direction as well as temperature dependence of the magnetic susceptibility $\chi(T)$. It turns out that the spin-orbit coupling is fundamentally important for 3d magnetism and magnetic properties are determined by lattice distortions.

PACS numbers: 75.25.+z, 75.10.Dg
Keywords: Crystalline Electric Field, 3d oxides, magnetism, spin-orbit coupling, YTiO$_3$

INTRODUCTION

YTiO$_3$ is a unique 3d ferromagnet - the most of oxides are antiferromagnetic. In combination with a rather simple perovskite structure and Ti$^{3+}$ ions expected to have one electron in the incomplete 3d shell, YTiO$_3$ is regarded to be very good exemplary system for studying basic interactions in 3d oxides. Despite this simplicity its properties are not understood yet. In fact, there is going on at present a hot debate on description of its magnetic and electronic properties. In fact, there is going on at present a hot debate on description of its magnetic and electronic properties.

The local octahedra in YTiO$_3$ are tilted and rotated, what causes the need for consideration a larger elementary cell, with four Ti ions instead of one as in the simple perovskite structure. Thanks it other three Ti ions get a crystallographic freedom. As a result of rotations, tilts and other atom displacements there are four short Ti-O bonds and two long Ti-O bonds.

The orthorhombic lattice in the Pbnm structure results from that of an ideal cubic perovskite by setting $a_o = \sqrt{2}$ and $c_o = 2a_c$, where $a_c$ denotes the lattice parameter of the simple cubic perovskite. $a_c$ is of order of 400 pm. In the Pnma structure used by some authors the doubling occurs along the $b$ direction. The $c$, $a$, and $b$ axis in the Pnma structure becomes the $a$, $b$ and $c$ axis in the Pbnm structure, respectively. Independently of the used Pbnm or Pnma space group the derivation of the local surroundings must be, of course, the same.

THEORETICAL OUTLINE

We consider exactly stechiometric YTiO$_3$. From this and the insulating ground state we infer that all Ti ions are in the trivalent state according to the charge distribution $\text{Y}^{3+}\text{Ti}^{3+}\text{O}_3^{2-}$. The relevant charge transfer occurs during the formation of the compound. In the perovskite-based structure of YTiO$_3$ the Ti$^{3+}$ ion is surrounded by six oxygen ions forming distorted octahedron. There are still some Ti ions at the surface, for instance, with a reduced symmetry, but they are generally neglected, because we are interested in intrinsic properties of YTiO$_3$.

The aim of this paper is to present results of single-ion considerations that the lattice surroundings of the Ti ion in YTiO$_3$ is predominantly octahedral with a slight
RESULTS AND DISCUSSION

The electronic structure of the Ti$^{3+}$ ion with one d-electron under the action of the crystal-field interactions $H_{CF}$ and in the presence of the intra-atomic spin-orbit coupling $H_{s-o}$ we calculated with the use of the single-ion-like Hamiltonian often used in description of 3d impurity states in the Electron Paramagnetic Resonance (EPR). We accept also for a solid, where 3d atom is the full part of the crystallographic structure:

$$H_d = H_{CF} + H_{s-o} = B_4(O_4^1 + 5O_4^2) + \lambda_{s-o}L \cdot S + B_o^2O_2^0 + \mu_B(L + g_e S) \cdot B_{ext}.$$ (1)

The calculated electronic structure is presented in Fig. 1. The crystal field has been divided into the cubic part, usually dominant in case of compounds containing 3d ions, and the off-octahedral distortion written by the second-order leading term $B_o^2O_2^0$. The last term, Zeeman term, allows calculations of the influence of the external magnetic field. $g_e$ amounts to 2.0023. The Zeeman term is necessary for calculations, for instance, of the paramagnetic susceptibility - in fact the paramagnetic susceptibility is customarily calculated [25] as the magnetization in an external field of, say, 0.1 T applied along different crystallographic directions.

The detailed form of the Hamiltonian (1) is written down in the LS space that is the 10 dimensional spin-orbital space $[L_S L_z S_z]$. The $L$ and $S$ quantum numbers for one 3d electron are equal to $L=2$ and $S=1/2$ (here, for 3d$^1$ configuration, lower $l$ and $s$ could be also used). The Hamiltonian (1) is customarily treated by perturbation methods owing to the weakness of the s-o coupling for the 3d ions in comparison to the strength of the crystal-field interactions. We have accepted the weakness of the s-o coupling, what is reflected by the sequence of terms in the Hamiltonian (1), but we have performed direct calculations treating all shown terms in the Hamiltonian (1) on the same footing. The separate figures, if presented, are shown for the illustration reasons.

Diagonalization have been performed for physically relevant values of $\lambda_{s-o}$ of +220 K ($= 150$ cm$^{-1}$) found for the Ti$^{3+}$ ion [21]. The cubic CEF parameter $B_4$ is taken as +240 K (results are not sensitive to its exact value provided $B_4 > +50$ K). The positive sign of $B_4$ comes from ab initio point charge calculations of octupolar interactions of the Ti$^{3+}$ ion with the octahedral oxygen (negative charges) surroundings. Such value of $B_4$ yields the $T_{2g}-E_g$ splitting of 2.5 eV. A splitting of 2.15-2.5 eV has been observed for Ti$^{3+}$ ions in Al$_2$O$_3$, where the similar oxygen octahedron exists. In LaCoO$_3$ we derived value of $B_4$ of 280-320 K [26].

In Fig. 2 we show detailed calculations of the influence of the spin-orbit coupling on the three lowest states $t_{2g}$ ($=2T_{2g}$) of the 3d$^1$ configuration for the elongated (c/a>1) and stretched (c/a<1) tetragonal off-octahedral distortion. The right hand states correspond to the three lowest states shown in Fig. 1d and 1e. The splitting due to the tetragonal off-octahedral distortion of $B_{2g}^1 = +10$ K (c/a>1); e) the splitting due to compressing tetragonal distortion of $B_{2g}^1 = -10$ K (c/a<1, apical oxygens become closer). Figs c, d and e are not to the left hand energy scale - the splitting of the three lowest states on Figs c, d and e amounts to 333 K, 368 K and 372 K, respectively.

Fig. 2: The calculated spin-orbit coupling $\lambda$ dependence of the three lowest states $t_{2g}$ ($=2T_{2g}$) of the 3d$^1$ configuration for the elongated (c/a>1) and stretched (c/a<1) tetragonal off-octahedral distortion. The right hand states correspond to the three lowest states shown in Fig. 1d and 1e. Analyzing the effect of the sign of the tetragonal distortion lead us to a conclusion that the magnetic moment lies along the tetragonal axis for the $z$-axis stretching. For the elongation case the moment lies perpendicularly
FIG. 3: The calculated temperature dependence of some properties of YTiO₃. a) The temperature dependence of the three lowest states (t₂g states) of the Ti³⁺-ion in YTiO₃ in the magnetically-ordered state below Tₖ = 30.6 K; in the paramagnetic state the electronic structure is temperature independent unless we do consider a changing of the CEF parameters, for instance, due to the thermal lattice expansion. The used parameters: B₁ = +240 K, B₂ = ±50 K, B₃ = -10 K, λ = -10 K and λₘ₋₋ = -220 K and nₙ₋₋ = 69 T/μᵢ. The splitting of the Kramers doublets should be noticed in the ferromagnetic state. Excited states are at 377, 645, 28843 and 29447 K. (b) the temperature dependence of the Ti³⁺-ion magnetic moment in YTiO₃. At 0 K the total moment m₀, of 0.84 μᵢ is built up from the orbital mₒ and spin mₛ moment of -0.06 and 0.90 μᵢ, respectively. c) The calculated temperature dependence of the 3d contribution c₅(T) to the heat capacity of YTiO₃. The λ-type peak marks Tₖ.

to the tetragonal axis. Taking into account that in YTiO₃ the ordered moment lies along the c direction (in the Pbnm structure) and our long-lasting studies of CEF effects we came to values for B₁ = ±50 K and B₃ = -10 K which reproduce the magnetic moment value, its direction and (some) thermodynamics. The

calculated ground-state eigenfunction (the z component of L and S are shown)

\[ ψ_{GS±} = 0.690|±2, \mp \frac{1}{2}\rangle - 0.678|±2, \mp \frac{1}{2}\rangle - 0.253|±1, \mp \frac{1}{2}\rangle - 0.020|±1, \mp \frac{1}{2}\rangle \]

where the sign ± refers to two conjugate Kramers states. This state has S_z = ±0.44 and L_z = ±0.10. The resultant moment m_z = ±0.78 μᵢ cancels each other in the paramagnetic state as is denoted in Fig. 3a.

Making use of the |xy, ±\rangle function extended for the spin component, as |xy, ±\rangle = \sqrt{1/2} (|2, ±\frac{1}{2}\rangle - |2, ±\frac{3}{2}\rangle) (also functions |xz\rangle, |yz\rangle, |x² - y²\rangle and |z²\rangle) one can write the ground state ψ_{GS±} function approximately as:

\[ ψ_{GS±} = 0.967|xy, ±\rangle + 0.0085|x² - y², ±\rangle - 0.186|xz, ±\rangle - 0.172|yz, ±\rangle - \ldots \]

In the magnetic state the ground state ψ_{GS±} Kramers doublet function becomes polarized as a molecular field is self-consistently settled down and the function

\[ ψ_{GS+} = 0.695|+2, -\frac{1}{2}\rangle - 0.686|-2, -\frac{1}{2}\rangle - 0.215|+1, +\frac{1}{2}\rangle - 0.016|-1, +\frac{1}{2}\rangle \]

is obtained as the ground state. The higher conjugate state is calculated to be described by

\[ ψ_{GS-} = 0.665|+2, +\frac{1}{2}\rangle - 0.682|-2, +\frac{1}{2}\rangle - 0.303|-1, -\frac{1}{2}\rangle + 0.026|+1, -\frac{1}{2}\rangle \]
Below $T_c$ there opens, as is seen in Fig. 3a, a spin-like gap that amounts at $T = 0$ K to 59.7 K ($-1 = 41.4$ cm$^{-1} = 5.15$ meV). The spin-like gap is associated with the splitting of the Kramers doublet ground state in the ferromagnetic state. The magnetic ground state $\psi_{GS+}$ has $S_z = -0.45$ and $L_z = +0.06$ and the resultant moment amounts to $0.84 \mu_B$. The appearance of the magnetic state is calculated self-consistently. It appears in the instability temperature ($T_c$) in the temperature dependence of the CEF paramagnetic susceptibility when

$$\chi_{CF}^{-1} = n_{d-d} \tag{6}$$

as is illustrated in Fig. 4 for different crystallographic directions. With decreasing temperature this equality is reached the first for the $c$ direction pointing the preferred magnetic arrangement axis. The magnetic state is calculated self-consistently by adding to the Hamiltonian Eq. (1) the inter-site magnetic (spin-dependent) interactions instead of the last Zeeman term $29$

$$H_{d-d} = n_{d-d} \left( -m_d \cdot m_d + \frac{1}{2} \langle m_d^2 \rangle \right) \tag{7}$$

where $n_{d-d}$ is the molecular-field coefficient.

Having eigenvalues in a function of temperature we calculate the free energy $F(T)$. From $F(T)$ using well-known statistical formulae we calculate all thermodynamics like temperature dependence of the magnetic moment, of the additional $c_d$ heat capacity, of paramagnetic susceptibility, of the 3$d$-shell quadrupolar moment and many others. The present calculations are similar to those performed for FeBr$_2$ $30$ and CoO $31$.

CONCLUSIONS

We have calculated consistently a value of the magnetic moment of 0.84 $\mu_B$ and its direction (along the $c$ axis in the Pbnm structure) in YTiO$_3$ as well as temperature dependence of the paramagnetic susceptibility in very good agreement with experimental observations.

This remarkable reproduction of so many physical properties has been obtained within the localized-electron approach taking into account lattice off-octahedral distortions and the intra-atomic spin-orbit coupling $27$. Although the spin-orbit coupling is weak, it amounts to only 1.2 % of the octahedral CEF splitting, it has enormous influence on the low-energy electronic structure and low-temperature magnetic and electronic properties. The spin-orbit coupling binds the orbital moment to the spin moment being the reason for the spin-lattice and spin-phonon coupling. The suggested energy (QUASST) $32$, if applied to YTiO$_3$, is related to our long-lasting systematic studies, despite of discrimination and inquisition, of the spin-orbit coupling and crystal-field interactions in 3$d$ compounds and in study of the region, where the spin-orbit coupling and off-octahedral lattice distortions are of the comparable strength.

Acknowledgements. We are very grateful to all our opponents. Although we do not think that the discrimination and inquisition should take place in Physics at the XXI century their critics largely stimulated these, very natural for us studies. This discrimination is the best proof that the knowledge about the CEF and the role of the spin-orbit coupling in 3$d$ magnetism is rather poor. We are thankful to a numerous members of the International Committee of the Strongly-Correlated Electron Systems Conference in Vienna 2005 for the friendly support. We are convinced that Physics can develop only in the friendly atmosphere and in the open exchange of information.

* dedicated to John Van Vleck and Hans Bethe, pioneers of the crystal-field theory, to the 75$^{th}$ anniversary of the crystal-field theory, and to Pope John Paul II, a man of freedom and honesty in life and in Science.

* URL: [http://www.css-physics.edu.pl](http://www.css-physics.edu.pl) Electronic address: sfirawan@cyf-kr.edu.pl

1. J. E. Greedan, J. Less-Common Met. 111, 335 (1985).
2. D. A. MacLean, H. N. Ng, and J. E. Greedan, J. Solid State Chem. 30, 35 (1979); D. A. MacLean, K. Seto, and J. E. Greedan, J. Solid State Chem. 40, 241 (1981).
3. M. Tsubota, F. Iga, T. Takabatake, N. Kikutagava, T. Suzuki, I. Oguro, H. Kawanaka, and H. Bando, Physica 281/282, 622 (2000).
4. M. Itoh, M. Tsuchiya, H. Tanaka, and K. Motoka, J. Phys. Soc. Jap. 68, 2783 (1999).
5. M. Cwik, T. Lorenz, J. Baier, R. Muller, G. Andre, F. Bourée, F. Lichtenberg, A. Freimuth, R. Schmitz, E. Muller-Hartmann, and M. Braden, Phys. Rev. B 68,
[6] E. Pavarini, S. Biermann, A. Poteryaev, A. I. Lichtenstein, A. Georges, and O. K. Andersen, Phys. Rev. Lett. 92, 176403 (2004); cond-mat/0309102.

[7] G. Khalilullin and S. Okamoto, Phys. Rev. B 68, 205109 (2003); cond-mat/0309102.

[8] R. M. Eremina, M. V. Eremin, S.V. Iglamov, J. Hemberger, H.-A. Krug von Nidda, F. Lichtenberg, and A. Loidl, cond-mat/0407264.

[9] S. V. Streitsov, A. S. Mylnikova, A. O. Shorikov, Z. V. Pchelkina, D. I. Khomskii, and V. I. Anisimov, Phys. Rev. B 68, 205109 (2003); cond-mat/0510175.

[10] R. M. Eremina, M. V. Eremin, S.V. Iglamov, J. Hemberger, H.-A. Krug von Nidda, F. Lichtenberg, and A. Loidl, cond-mat/0407264.

[11] S. V. Streitsov, A. S. Mylnikova, A. O. Shorikov, Z. V. Pchelkina, D. I. Khomskii, and V. I. Anisimov, Phys. Rev. B 71, 245114 (2005); cond-mat/0504281.

[12] R. M. Eremina, M. V. Eremin, S.V. Iglamov, J. Hemberger, H.-A. Krug von Nidda, F. Lichtenberg, and A. Loidl, cond-mat/0407264.

[13] S. V. Streitsov, A. S. Mylnikova, A. O. Shorikov, Z. V. Pchelkina, D. I. Khomskii, and V. I. Anisimov, Phys. Rev. B 71, 245114 (2005); cond-mat/0504281.

[14] R. M. Eremina, M. V. Eremin, S.V. Iglamov, J. Hemberger, H.-A. Krug von Nidda, F. Lichtenberg, and A. Loidl, cond-mat/0407264.

[15] S. V. Streitsov, A. S. Mylnikova, A. O. Shorikov, Z. V. Pchelkina, D. I. Khomskii, and V. I. Anisimov, Phys. Rev. B 71, 245114 (2005); cond-mat/0504281.

[16] R. M. Eremina, M. V. Eremin, S.V. Iglamov, J. Hemberger, H.-A. Krug von Nidda, F. Lichtenberg, and A. Loidl, cond-mat/0407264.

[17] S. V. Streitsov, A. S. Mylnikova, A. O. Shorikov, Z. V. Pchelkina, D. I. Khomskii, and V. I. Anisimov, Phys. Rev. B 71, 245114 (2005); cond-mat/0504281.

[18] R. M. Eremina, M. V. Eremin, S.V. Iglamov, J. Hemberger, H.-A. Krug von Nidda, F. Lichtenberg, and A. Loidl, cond-mat/0407264.

[19] S. V. Streitsov, A. S. Mylnikova, A. O. Shorikov, Z. V. Pchelkina, D. I. Khomskii, and V. I. Anisimov, Phys. Rev. B 71, 245114 (2005); cond-mat/0504281.

[20] R. M. Eremina, M. V. Eremin, S.V. Iglamov, J. Hemberger, H.-A. Krug von Nidda, F. Lichtenberg, and A. Loidl, cond-mat/0407264.

[21] S. V. Streitsov, A. S. Mylnikova, A. O. Shorikov, Z. V. Pchelkina, D. I. Khomskii, and V. I. Anisimov, Phys. Rev. B 71, 245114 (2005); cond-mat/0504281.

[22] R. M. Eremina, M. V. Eremin, S.V. Iglamov, J. Hemberger, H.-A. Krug von Nidda, F. Lichtenberg, and A. Loidl, cond-mat/0407264.

[23] S. V. Streitsov, A. S. Mylnikova, A. O. Shorikov, Z. V. Pchelkina, D. I. Khomskii, and V. I. Anisimov, Phys. Rev. B 71, 245114 (2005); cond-mat/0504281.

[24] R. M. Eremina, M. V. Eremin, S.V. Iglamov, J. Hemberger, H.-A. Krug von Nidda, F. Lichtenberg, and A. Loidl, cond-mat/0407264.

[25] S. V. Streitsov, A. S. Mylnikova, A. O. Shorikov, Z. V. Pchelkina, D. I. Khomskii, and V. I. Anisimov, Phys. Rev. B 71, 245114 (2005); cond-mat/0504281.

[26] R. M. Eremina, M. V. Eremin, S.V. Iglamov, J. Hemberger, H.-A. Krug von Nidda, F. Lichtenberg, and A. Loidl, cond-mat/0407264.

[27] S. V. Streitsov, A. S. Mylnikova, A. O. Shorikov, Z. V. Pchelkina, D. I. Khomskii, and V. I. Anisimov, Phys. Rev. B 71, 245114 (2005); cond-mat/0504281.

[28] R. M. Eremina, M. V. Eremin, S.V. Iglamov, J. Hemberger, H.-A. Krug von Nidda, F. Lichtenberg, and A. Loidl, cond-mat/0407264.

[29] S. V. Streitsov, A. S. Mylnikova, A. O. Shorikov, Z. V. Pchelkina, D. I. Khomskii, and V. I. Anisimov, Phys. Rev. B 71, 245114 (2005); cond-mat/0504281.

[30] R. M. Eremina, M. V. Eremin, S.V. Iglamov, J. Hemberger, H.-A. Krug von Nidda, F. Lichtenberg, and A. Loidl, cond-mat/0407264.

[31] S. V. Streitsov, A. S. Mylnikova, A. O. Shorikov, Z. V. Pchelkina, D. I. Khomskii, and V. I. Anisimov, Phys. Rev. B 71, 245114 (2005); cond-mat/0504281.

[32] R. M. Eremina, M. V. Eremin, S.V. Iglamov, J. Hemberger, H.-A. Krug von Nidda, F. Lichtenberg, and A. Loidl, cond-mat/0407264.

[33] S. V. Streitsov, A. S. Mylnikova, A. O. Shorikov, Z. V. Pchelkina, D. I. Khomskii, and V. I. Anisimov, Phys. Rev. B 71, 245114 (2005); cond-mat/0504281.

[34] R. M. Eremina, M. V. Eremin, S.V. Iglamov, J. Hemberger, H.-A. Krug von Nidda, F. Lichtenberg, and A. Loidl, cond-mat/0407264.

[35] S. V. Streitsov, A. S. Mylnikova, A. O. Shorikov, Z. V. Pchelkina, D. I. Khomskii, and V. I. Anisimov, Phys. Rev. B 71, 245114 (2005); cond-mat/0504281.