Ion doping effects in multiferroic MnWO$_4$

Safa Golrokh Bahoosh[1] and J. M. Wesselinowa[2,a)]
[1]*Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany*
[2]*University of Sofia, Department of Physics, Blvd. J. Bouchier 5, 1164 Sofia, Bulgaria*

We have studied the ion doping effects in multiferroic MnWO$_4$ proposing a microscopic model. It is shown that the exchange interaction constants can be changed due to the different ion doping radii. This leads to reduction of the magnetic phase transition temperature T_N by doping with non-magnetic ions, such as Zn, Mg, whereas T_N is enhanced by doping with transition metal ions, such as Fe, Co. The different behavior of the temperature T_1 (where up-up-down-down collinear spin structure appears) by Fe and Co doping could be explained taking into account the single-ion anisotropy. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4703913]

I. INTRODUCTION

There has been increasing recent interest in magneto-electric (ME) multiferroics,[1–3] which are materials that show spontaneous magnetic and electric ordering in the same phase. From a technological point of view the possibility to control magnetic properties by electric fields and, vice versa, ferroelectric order by magnetic fields, is very desirable. The coupling between dielectric and magnetic properties is of not only fundamental importance, but also of significant interest for application in magnetic storage media and "spintronics."[3] There exist several different microscopic mechanisms which cause multiferroic (MF) behavior,[4] for example a strong spin-lattice coupling,[5,6] coupled magnetic and electric domains.[7] The magnetic phase control by an electric field is discussed in Ref. [8]. The properties of the MF compounds are very sensitive to different ion doping.[9]

The aim of the present paper is to study the ion doping effects on different transition temperatures in the MF compound MnWO$_4$ based on a microscopic model. MnWO$_4$ undergoes three magnetic phase transitions under zero magnetic field below a temperature of 14 K.[10] With decreasing temperature MnWO$_4$ first transforms from a paramagnetic state to a collinear spin sinusoidal state (AF3) at a Neel temperature T_N of ~13.5 K, then to a tilted elliptical spiral spin state (AF2) at $T_2 \sim 12.3$ K, and eventually to an up-up-down-down collinear spin structure (AF1) at $T_1 \approx 8$ K. The loss of inversion symmetry due to the helical spin ordering at T_2 makes MnWO$_4$ exhibit ferroelectric polarization in the AF2 state, which can be controlled by an external magnetic field, and so T_2 is also the ferroelectric critical temperature, $T_2 = T_C$.[11]

Tuning of the magnetic exchange interactions and, consequently, the MF properties by partial substitution of different ions, such as Mg, Co, Zn, Fe, Ni, was achieved recently.[12–17] The effects of non-magnetic ions, such as Zn and Mg, are studied in Refs. [12–14], which cause a reduction of T_N and T_C with increasing of the doping concentration. Fe and Co substitution is opposite to the results on T_N of Zn and Mg substitution.[14–17] Moreover, there is a different behavior

of T_1 by the ion doping with Co and Fe.[14,17] The Fe substitution stabilizes the AF1 order, whereas the Co doping suppresses this AF1 state and stabilizes the spin-spiral AF2 magnetic structure. Chaudhury *et al.*[15] proposed a simple mean-field model, including nearest- and next-nearest-neighbor interactions, spin anisotropy and external magnetic field, to explain the observed phase diagram in Fe-doped MnWO$_4$. It was speculated that the lack of ferroelectricity (at zero magnetic field) in Mn$_{0.9}$Fe$_{0.1}$O$_4$ is due to the increase in the uniaxial anisotropy.

II. MODEL AND METHOD

Similar to the orthorhombic multiferroics,[18] the Hamiltonian for MnWO$_4$ could be written as

$$H = H^e + H^m + H^{me}. \quad (1)$$

H^e is the Hamiltonian of the transverse Ising model (TIM) for the electric subsystem,

$$H^e = -\Omega \sum_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z, \quad (2)$$

where S_i^x, S_i^z are the spin-1/2 operators of the pseudo-spins, J_{ij} denotes the nearest-neighbor pseudo-spin interaction, Ω is the tunneling frequency.

Blinc and de Gennes[19] proposed the TIM for the description of order-disorder KDP-type ferroelectrics (FE). Further the TIM is applied to displacive type FE, such as BaTiO$_3$ (BTO),[20,21] too. In the case of a tunneling frequency very small with respect of the interaction constant one may use the TIM as a model for order-disorder FE without tunneling motion (e.g., for NaNO$_2$, TGS). Therefore the TIM can be applied to describe the electric polarization in all types of FE. MnWO$_4$ is one of the representative materials that exhibit ferroelectricity induced by spiral spin structure together with the perovskite RMnO$_3$ (R = Tb and Dy) compounds. The ferroelectric polarization P of MnWO$_4$ appears in the spiral-spin state AF2. Here, we propose in our model for MnWO$_4$ that the tunneling frequency can be neglected and that the polarization P might be connected with an octahedral tilting in a

a)Author to whom correspondence should be addressed. Electronic mail: julia@phys.uni-sofia.bg. Tel.: 003592-8161-470.

TH-2012-58

perovskite (for example, WO_6 or/and MnO_6 octahedron in $MnWO_4$).[8]

In the ordered phase we have the mean values $\langle S^x \rangle \neq 0$ and $\langle S^z \rangle \neq 0$, and it is appropriate to choose a new coordinate system rotating the original one used in (2) by the angle θ in the xz plane. The rotation angle θ is determined by the requirement $\langle S^{x'} \rangle = 0$ in the new coordinate system. The exchange interaction constant J_{ij} (and later for the magnetic subsystem A) depends on the distance between the pseudospins, i.e., on the lattice parameters, on the symmetry, and on the number of nearest neighbors. By ion doping due to the different radii between the doping ions and the host ions there appear different strains, which lead to changing of the exchange interaction constants. We denote them in the defect sites with the index d. In dependence of the strain - tensile or compressive - they can be smaller or greater compared to the case without strain, without ion doping or defects.

H^m is the Heisenberg Hamiltonian for the magnetic subsystem,

$$H^m = -\frac{1}{2}\sum_{ij} A(i,j)\mathbf{B}_i \cdot \mathbf{B}_j - \sum_i D_i (B_i^z)^2, \qquad (3)$$

where $\mathbf{B}$ is the Heisenberg spin operator, the exchange integral A represents the coupling between the nearest neighbors, D is the single-ion anisotropy. In the case without defects, Eq. (3) describes the interaction between the Mn-ions in $MnWO_4$. By replacing some of the Mn-ions with different doping ions, the situation would be similar to a ferrimagnet with two sublattices, so (3) describes the interaction between the Mn-ions in the new strained lattice, then we must add a Heisenberg term which describes for example the interaction between the Co ions, and a term for the description of the interaction between the Mn-Co ions.

H^{me} gives the coupling between the magnetic and the electrical subsystems in $MnWO_4$ which we assume to be linear,

$$H^{me} = -g\sum_{ij}\sum_k S_k^z \mathbf{B}_i \cdot \mathbf{B}_j. \qquad (4)$$

Here g is the coupling constant between the magnetic and the electric order parameters. The ME coupling in the MF orthorhombic $RMnO_3$ and $MnWO_4$ should be invariant with respect to spatial inversion. Therefore the actual coupling mechanism is more complicated and is proportional, e.g., to some vector, but the resulting coupling can be modeled by the form (4) where the coupling constant g is a pseudoscalar. In the phenomenological treatment as done by Mostovoy[22] this was taken by introducing one more vector in the ME coupling term, i.e., the coupling is not $S^z\mathbf{BB}$, but rather $\mathbf{P.M}(\mathbf{\Delta \cdot M})$ in the notation of the author. In our model the spins $\mathbf{B}$ are even, but polarization, or pseudo-spins S are odd under reflection, i.e., S should change sign. For the total coupling term to be invariant, the coupling constant g should change sign, i.e., it should be a pseudoscalar.

It must be noted here that the orthorhombic perovskite $RMnO_3$ and the hexagonal $RMnO_3$ are in very different classes of magnetoelectrics. The use of the TIM and biquadratic coupling between the pseudospins and magnetic moments implies that the magnetic and ferroelectric orderings have independent mechanisms. In particular, this generally leads to different transition temperatures for the two subsystems, $T_C \gg T_N$, and the ME coupling is small, for example in hexagonal $RMnO_3$ and $BiFeO_3$. In the orthorhombic perovskite $RMnO_3$ the leading ME interaction term is linear in the electrical dipole moment, due to the improper nature of its ferroelectricity, i.e., when ferroelectricity occurs as a secondary effect or concomitantly with some other kind of ordering (such as spin ordering, in particular). The same applies to RMn_2O_5, which is also an improper ferroelectric. In these MFs the transition temperatures are nearly of the same order, $T_N \geq T_C$, and the ME coupling is stronger compared to the biquadratic case. Moreover, magnetically-driven improper FE, such as $TbMnO_3$ or $MnWO_4$, are materials in which a spontaneous polarization arises due to symmetry-breaking by a spin instability. These materials naturally have a strong coupling between magnetism and the polarization, but the polarization is too small for device applications. In known MF materials with a large electrical polarization, such as $BiFeO_3$, the ferroelectricity is proper, originating from a zone-center polar lattice instability, as in the prototypical perovskite ferroelectric $PbTiO_3$. However, except in a few special cases that satisfy restrictive symmetry criteria, the polar instability in a proper ferroelectric does not break the right symmetries to turn on a nonzero magnetization and therefore does not satisfy the criteria of the only known mechanism that enables the electric field switching of the magnetization. It is desirable to identify a more general mechanism-applicable to a large class of materials, for example, the ABO_3 perovskites - whereby ferroelectricity and ferromagnetism are induced by the same lattice instability. Octahedron rotations, ubiquitous in perovskites and related materials, are natural candidates for this lattice instability as they are known to strongly couple to magnetic properties.[23]

Using the Green's function method we have calculated the polarization P, magnetization M, and the critical temperatures T_C and T_N as the temperatures where P and M vanish. For the relative polarization P we obtain

$$P - \frac{1}{2N}\sum_k \tanh\frac{E(\mathbf{k})}{2k_B T}. \qquad (5)$$

$E(\mathbf{k})$ is the transverse pseudo-spin wave energy,

$$\begin{aligned}
E(\mathbf{k}) &= 2\Omega\sin\theta + \frac{1}{2}P\cos^2\theta J_{eff} - \frac{1}{4}P\sin^2\theta J_{eff}(\mathbf{k}) \\
&\quad - \frac{1}{NP}\sum_q (\cos^2\theta J_{eff}(\mathbf{k}-\mathbf{q}) - \frac{1}{2}\sin^2\theta J_{eff}(\mathbf{q})) \\
&\quad < S_q^- S_q^+ >
\end{aligned} \qquad (6)$$

with $J_{eff} = J_0 + 2g(\langle B^- B^+ \rangle + \langle B^z B^z \rangle)$ and $\sin q = 4\Omega/(PJ_{eff})$.

The relative magnetization M for arbitrary spin value S is equal to

$$\begin{aligned}
M = \frac{1}{N}\sum_k \Bigg[&(S+0.5)\coth\left[(S+0.5)\frac{E_m(\mathbf{k})}{k_B T}\right] \\
&- 0.5\coth\left(0.5\frac{E_m(\mathbf{k})}{k_B T}\right) \Bigg].
\end{aligned} \qquad (7)$$

E_m is the spin-wave energy taking into account all correlation functions

$$E_m(\mathbf{k}) = \frac{1}{2\langle B^z \rangle} \frac{1}{N} \sum_q (A_{eff}(\mathbf{q}) - A_{eff}(\mathbf{k} - \mathbf{q}))(2\langle B_q^z B_{-q}^z \rangle$$
$$- \langle B_{k-q}^z B_{k-q}^+ \rangle) + 2D\langle B^z \rangle \qquad (8)$$

with the renormalized exchange interaction constant $A_{eff} = A + gP\cos\theta$.

It must be mentioned that the analytical expressions for the excitation energies in Eqs. (6) and (8) are obtained without any approximation, and the correlation functions are observed from the Spectral theorem. By the numerical calculations we have made the following approximation in J_{eff} and in Eq. (8): the longitudinal correlation function $\langle B^z B^z \rangle$ is decoupled to $\langle B^z \rangle \langle B^z \rangle$. It can be seen that J_{eff} is proportional to M^2, whereas A_{eff} is proportional to P suggested by the underlying model. The approximations are consistent with the strong ME coupling mechanism.

III. NUMERICAL RESULTS AND DISCUSSION

From the model presented in Sec. II we can obtain the properties around the magnetic and ferroelectric critical temperatures, T_N and T_C, and in the phase where magnetic and ferroelectric properties coexist. Moreover, taking into account the single-ion anisotropy it can be applied in the whole temperature interval and can describe the correct dependence of T_N, T_C, and T_1 on the Fe- and Co-ion doping concentration.

We have studied at first the influence of doping with the non-magnetic ions Zn^{2+} and Mg^{2+}. Their radii (0.88 and 0.86 Å, respectively) are larger compared to the ion radius of Mn^{2+} (0.81 Å). This leads to tensile strain and to smaller magnetic and electric exchange interaction constants $A_d < A$, $J_d < J$. The results for the critical temperatures T_N (curve 1) and T_C (curve 2) for $Mn_{1-x}Zn_xWO_4$ are shown in Fig. 1. It can be seen that they decrease with increasing Zn-concentration x. This is in agreement with the experimental

data of Chaudhury et al.[12] and Meddar et al.[13] For Mg-doping the behavior is comparable.

By the Fe and Co-doping we observe the opposite result for the magnetic transition temperature T_N. The ionic radii of Fe^{2+} and Co^{2+} (75 and 79 Å, respectively) are smaller in comparison to the Mn-ion radius. This leads to a compressive strain, i.e., to $A_d > A$. In Fig. 2 is demonstrated the Fe-concentration x dependence of the magnetic transition temperature T_N (curve 1), it increases with an increase of x. A similar dependence was obtained also for Co-doping. The increase of T_N is stronger compared to the Fe-doping, because exchange energies for Co^{2+} are typically much larger than for Fe^{2+}. This behavior is experimentally reported by many authors.[14–17] For the ferroelectric transition temperature T_C (curve 2) we obtain a small decrease with an increase of the Fe- and Co-ion doping concentration.

In order to explain the experimentally observed differences in the T_1 behavior by Fe- and Co-ion doping, we must take into account the single-ion anisotropy D.[17,24] The substitution of magnetic transition metal (TM) $Fe^{2+}(S = 2)$ or $Co^{2+}(S = 3/2)$ ions for $Mn^{2+}(S = 5/2)$, which introduces extra Mn-TM ($A^{Mn-Fe}\langle 0, A^{Mn-Co}\rangle 0$) and TM-TM (TM = Fe, Co, $A^{Fe-Fe} > 0$, $A^{Co-Co} > 0$) spin interactions, along with a different local magnetic anisotropy D determined by the TM^{2+} ions, modifies the phase competition. Additively, there is a some competition between the influence of the exchange interaction constant A, which enhances the magnetization, T_N and the spin wave energy, and D, which reduces them.[24]

It is also important that the single-ion anisotropy is of a different sign for Fe and Co and that in Fe is at least one order of magnitude larger than in Co.[25,26] In the case of the Fe-doping (Fig. 2) all this leads to an increase of the transition temperature T_1 (curve 3) which reaches the ferroelectric T_2 curve, i.e., the Fe-doping would stabilize the AF1 order. On the contrary, by the Co-ion doping (Fig. 3) T_1 (curve 3) would decrease with increasing Co-concentration, i.e., it would suppress the AF1 state and stabilize the spin-spiral
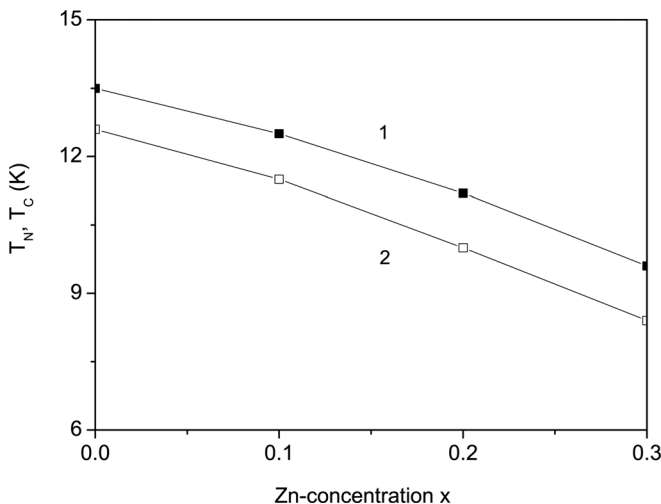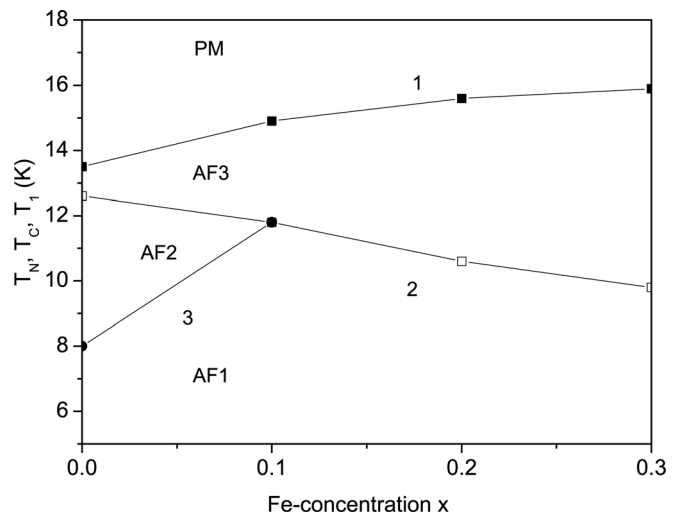
FIG. 1. Zn-concentration dependence x of the (1) magnetic T_N and (2) ferroelectric T_C transition temperatures in $Mn_{1-x}Zn_xWO_4$ with $A^{Mn} = -12.2$ K, $A_d^{Mn} = 0.8A^{Mn}$, $D_d^{Mn} = D^{Mn} = -5$ K, $A^{-Mn} = -6$ K, $J_d = 0.8J = 8$ K.

FIG. 2. Fe-concentration dependence x of the transition temperatures (1) T_N, (2) T_C, and (3) T_1 in $Mn_{1-x}Fe_xWO_4$ with $A^{Mn} = -12.2$ K, $A_d^{Mn} = 1.2A^{Mn}$, $D_d^{Mn} = 0.8D^{Mn}$, $A^{Fe} = 30$ K, $D^{Fe} = -24$ K, $A^{-Mn} = -21$ K.
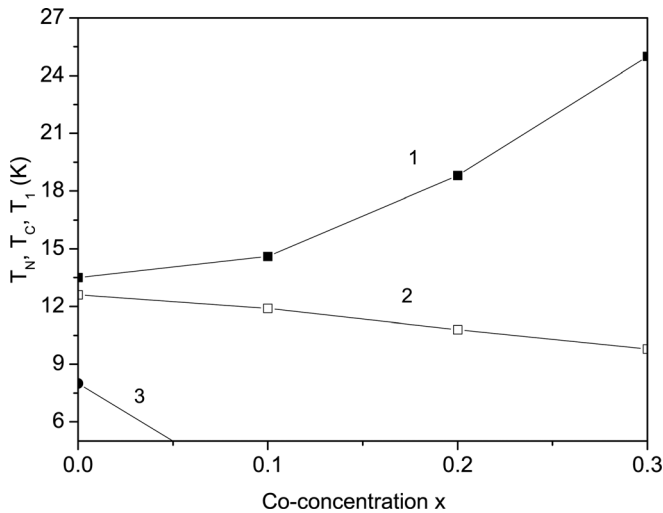
FIG. 3. Co-concentration dependence x of the transition temperatures (1) T_N, (2) T_C, and (3) T_1 in $Mn_{1-x}Co_xWO_4$ with $A^{Mn} = -12.2$ K, $A_d^{Mn} = 1.5A^{Mn}$, $D_d^{Mn} = 1.4D^{Mn}$, $A^{Co} = 49.5$ K, $D^{Co} = 12$ K, $A^{-Mn} = 30$ K.

AF2 magnetic structure. This behavior is in agreement with that reported in Refs. 14 and 17. It must be mentioned that in $MnWO_4$, as in many other multiferroics, the spin-phonon interaction is strong and plays an important role.[27,28] Therefore, it must be taken into account in order to obtain correct results. It would contribute also to clearing if the origin of the polarization is electronic or ionic. This will be considered in the next paper.

In conclusion, in this paper we report an initial study of the doping effects of nonmagnetic and magnetic substitution at the Mn site on the phase transition temperatures of $MnWO_4$. Using a microscopic model proposed for $MnWO_4$ we show that depending on the ionic radius of the doping ions, i.e., on the exchange interaction constants in the defect sites, the magnetic phase transition temperature can be smaller (for non-magnetic Zn or Mg ions) or larger (for transition metal Fe or Co ions) compared to the case without defects. The differences in the Fe- and Co-doping concentration dependence of T_1 could be explained by the different sign of the single-ion anisotropy.

ACKNOWLEDGMENTS

[1]M. Fiebig, J. Phys. D: Appl. Phys. **38**, R123 (2005).
[2]S.-W. Cheong and M. Mostovoy, Nature Mater. **6**, 13 (2007).
[3]N. A. Hill, J. Phys. Chem. B **104**, 6694 (2000).
[4]D. I. Khomskii, J. Magn. Magn. Mater. **306**, 1 (2006).
[5]P. A. Sharma, J. S. Ahn, N. Hur, S. Park, S. B. Kim, S. Lee, J.-G. Park, S. Guha, and S.-W. Cheong, Phys. Rev. Lett. **93**, 177202 (2004).
[6]C. dela Cruz, F. Yen. B. Loremz, Y. Q. Wang, Y. Y. Sun, M. M. Gospodinov, and C. W. Chu, Phys. Rev. B **71**, 060407R– (2005).
[7]M. Fiebig, Th. Lottermoser, D. Froehlich, A. V. Goltsev, and R. V. Pisarev, Nature **419**, 818 (2002).
[8]Th. Lottermoser, Th. Lonkal, U. Amann, D. Hohlwein, J. Ihringer, and M. Fiebig, Nature **430**, 541 (2004).
[9]I. Apostolova and J. M. Wesselinowa, J. Magn. Magn. Mater. **321**, 2477 (2009).
[10]G. Lautenschlaeger, H. Weitzel, T. Vogt, R. Hock, A. Boehm, M. Bonnet, and H. Fuess, Phys. Rev. B **48**, 6087 (1993).
[11]K. Taniguchi, N. Abe, H. Sagayama, S. Otani, T. Takenobu, Y. Iwasa, and T. Arima, Phys. Rev. B **77**, 064408 (2008).
[12]R. P. Chaudhury, F. Ye, J. A. Fernandez-Baca, B. Lorenz, Y. Q. Wang, Y. Y. Sun, H. A. Mook, and C. W. Chu, Phys. Rev. B **83**, 014401 (2011).
[13]L. Meddar, M. Josse, P. Deniard, C. La, G. Andre, F. Damay, V. Petricek, S. Jobic, M.-H. Whangbo, M. Maglione, and C. Payen, Chem. Mater. **12**, 1501 (2000); L. Meddar, M. Josse, P. Deniard, C. La, G. Andre, F. Damay, V. Petricek, S. Jobic, M.-H. Whangbo, M. Maglione, and C. Payen, Chem. Mater. **21**, 5203 (2009).
[14]K.-C. Liang, R. P. Chaudhury, B. Lorenz, Y. Q. Wang, Y. Y. Sun, and C. W. Chu, Integr. Ferroelectr. **131**, 47 (2011).
[15]R. P. Chaudhury, B. Lorenz, Y. Q. Wang, Y. Y. Sun, and C. W. Chu, Phys. Rev. B **77**, 104406 (2008).
[16]R. P. Chaudhury, F. Ye, J. A. Fernandez-Baca, Y.-Q. Wang, Y. Y. Sun, B. Lorenz, H. A. Mook, and C. W. Chu, Phys. Rev. B **82**, 184422 (2010).
[17]Y.-S. Song, J.-H. Chung, J. M. S. Park, and Y.-N. Choi, Phys. Rev. B **79**, 224415 (2009).
[18]J. M. Wesselinowa and I. Georgiev, Phys. Status Solidi B **245**, 1653 (2008).
[19]R. Blinc and B. Zeks, *Soft Modes in Ferroelectric and Antiferroelectrics* (North-Holland, Amsterdam, 1974).
[20]R. Pirc and R. Blinc, Phys. Rev. B **70**, 134107 (2004).
[21]H. X. Cao and Z. Y. Li, J. Phys.: Condens. Matter **15**, 6301 (2003).
[22]M. Mostovoy, Phys. Rev. Lett. **96**, 067601 (2006).
[23]N. A. Benedek and C. J. Fennie, Phys. Rev. Lett. **106**, 107204 (2011).
[24]J. M. Wesselinowa and I. Apostolova, J. Phys.: Condens. Matter **19**, 216208 (2007).
[25]N. P. Thuy and J. J. M. Franse, J. Magn. Magn. Mater. **54–57**, 915 (1986).
[26]I. S. Tereshina, A. P. Tulyakov, S. A. Nikitin, G. A. Politova, and K. P. Skokov, Phys. Solid State **49**, 315 (2007).
[27]M. Maczka, M. Ptak, K. Hermanowicz, A. Majchrowski, A. Pikul, and J. Hanuza, Phys. Rev. B **83**, 174439 (2011).
[28]M. Ptak, M. Maczka, K. Hermanowicz, A. Pikul, and J. Hanuza, Spectrochim. Acta A **86**, 85 (2012).