Low Temperature Physics/Fizika Nizkikh Temperatur, 2021, vol. 47, No. 7, pp. 633–636

Effect of magnetic field on the modulated spin structure of terbium manganite film

I. E. Chupis

B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, Kharkiv 61103, Ukraine
E-mail: chupis@ilt.kharkov.ua

Received February 1, 2021, published online May 26, 2021

The first-harmonic approximation of the Ginzburg–Landay theory was used to analyze the influence of magnetic field H along the y axis (modulation direction of manganese spins) in incommensurate AFM phases in the orthorhombic $TbMnO_3$ film. It was shown that an increase in magnetic field and a decrease in the film thickness lead to the decrease in the Néel temperature. The dependence of the Néel temperature on magnetic field in the $TbMnO_3$ film was obtained. The boundary lines between modulated AFM phases in magnetic field are changed weakly besides some increase in the temperature $T_c = 28$ K at $H = 0$. It means the conservation of the colossal magnetoelectric effect of the "polarization flop in magnetic field" in the manganite terbium films up to 6 nm thickness. Therefore, such $TbMnO_3$ films (3 periods of the spin cycloid) can become a basis of future nanotechnology of the magnetoelectric devices.

Keywords: antiferromagnetic, incommensurate structure, ferroelectromagnet, film, magnetic field.

Introduction

Ferroelectromagnet (multiferroic) $TbMnO_3$ with an inhomogeneous magnetic structure that generates a state with electric polarization and the significant value of magnetoelectric (ME) effect is of practical interest [1–8]. This ME effect was observed at temperatures 10 K < T < T_N = 42 K, where only manganese spins have antiferromagnetic (AF) ordering. (Terbium spins are not ordered.) At temperatures T_c = 28 K < T < T_N, there is the sine-modulated AFM ordering of A_y-type with the direction of spin modulation along the y axis (**A** is the AFM vector, which represerts the order parameter in the AF transitions) (state 1 in Fig. 1). In the absence of magnetic field at $T < T_c$, there is the orientional transition of manganese spins from state 1 (A_y) into the AFM spiral (cycloidal) state 2 in the (y, z) plane [8], and the electric polarization

$$P_z \sim \left(A_y \frac{\partial A_z}{\partial y} - A_z \frac{\partial A_y}{\partial y} \right)$$

appears (state 2). Magnetic field of the order of few tesla H_y directed along the modulation vector k_y reorients the electric polarization P_z by 90° from z axis to x axis,

$$P_z \to P_x \sim \left(A_y \frac{\partial A_x}{\partial y} - A_x \frac{\partial A_y}{\partial y} \right)$$

(state 3 in Fig. 1). This effect is called the "electric polarization flop" [1] and can be used to control the dielectric properties of the ferroelectromagnets by the magnetic field. A simple model proposed in [9] for the behavior of the spiral structure in magnetic field along the y axis does not explain the experimental observations of the electric polarization

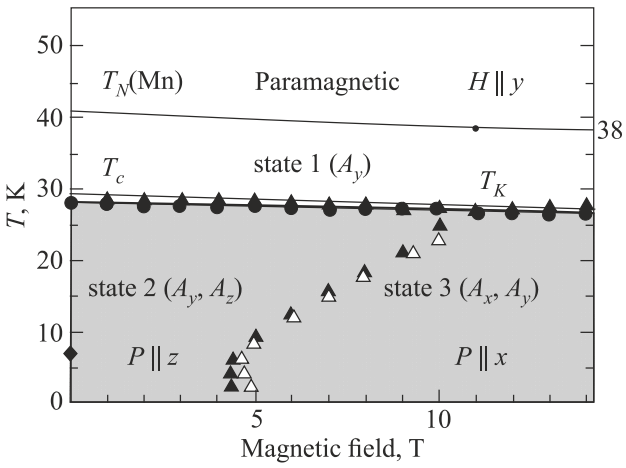

Fig. 1. Magnetic phase diagram of $TbMnO_3$ in a magnetic field along the y axis. Circles and triangles are experimental data [4], solid lines are theoretical calculations [10] for bulk space, thin lines corresponds to theoretical calculations for the film.

flop. It was suggested that anisotropy of a higher order than the second one plays the role in this phenomenon [9].

The sequential analysis of the modulated spin states of orthorhombic $TbMnO_3$ in a magnetic field H_y with the magnetic anisotropy of the fourth order within the Ginzburg–Landau (GL) theory was provided in [10]. It was first shown that the magnetic anisotropic energy of the fourth order plays the key rule in the polarization flop and in existence of the three-critical point T_k in the $TbMnO_3$ phase diagram (Fig. 1). The competition of the anisotropic energy terms of the fourth order $A_y^2A_z^2$ and $A_y^2A_x^2$ leads to the reorientation of spin cycloid from the (y, z) plane to the (x, y) plane and to the "polarization flop" in magnetic field of several tesla.

The "polarization flop" effect has a colossal ME effect and leads to a renaissance of interest in ferroelectromagnets due to use of their ME properties in field converters, memory devices, storage devices, etc. [5, 6]. Currently, the use in electronics requires the miniaturization of devices, and various nanotechnologies are under development. The production of $TbMnO_3$ films with the conservation of a modulated AFM structure is of the practical interest.

In Ref. 11, single-domain epitaxial $TbMnO_3$ films without twins grown on a $YAlO_3$ substrate demonstrated the existence of the spiral spin structure and electric polarization, up to a 6 nm thickness, corresponding to 3 periods of the spin cycloid.

The experimental results from [11] were analyzed in [12] by the GL method in the first-harmonic approximation. A qualitative agreement was obtained for the experimentally observed decrease in the film modulation vector with a decreasing temperature, as well as an increase in the vector as the film thickness decreases at a constant temperature [12]. There was no magnetic field in the works [11, 12].

Phase states in $TbMnO_3$ films in magnetic field along the y axis

In this article, the first-harmonic approximation of GL theory for modulated AFM structures of epitaxial $TbMnO_3$ films is used to explain the changes of film spin structure in magnetic field H_y directed along the modulation vector k_y. For the bulk $TbMnO_3$ modulation vector $k_y = k_0 \approx 0.28b^*$ (b^* is the reciprocal lattice vector), $k_0^2 = -\gamma/2\alpha$.

The GL functional for magnetic energy of the $TbMnO_3$ film in the (x, z) plane with the thickness along the y axis equal to l, can be written as

$$F = \frac{1}{l}\int_0^l dy\{a\mathbf{A}^2 + wA_z^2 + w'A_x^2 + r\mathbf{A}^4 + \lambda_1 A_x^2A_y^2 + \lambda_2 A_y^2A_z^2 +$$

$$+\gamma(\partial_y\mathbf{A})^2 + \alpha(\partial_y^2\mathbf{A})^2 + BM^2 + D(\mathbf{AM})^2 - \mathbf{MH}\}. \quad (1)$$

The coefficients a, r, B, D represent the constants of homogeneous exchange interaction; $\gamma < 0$, $\alpha > 0$ correspond to inhomogeneous exchange constants, w, w', λ_1, λ_2 are constants of anisotropy and $w' > w > 0$. The constants r, B, D are positive, M is the magnetization in a magnetic field H_y. The constant a depends on temperature: $a = \xi(T - T_0)$, where T_0 is the temperature of the transition into a commensurate state.

The equilibrium states 1, 2 and 3 in $TbMnO_3$ film in a magnetic field H_y are found in the single-harmonic approximation of GL theory after integration in (1) and minimization of the functional (1) by the coefficients of expansion and the wave vector k of the modulated structure. It was taken into account the changes associated with the film thickness, which are about $1/(kl)$.

State 1. AFM state $A_y = a_y \cos ky$, $P = 0$. This state at $H = 0$ was analyzed earlier in [12]:

$$a_y^2 = -L_y/rR, \quad L_y = a + y + \gamma k^2 + \alpha k^4 +$$

$$+(a + y - yk^2 + \alpha k^4)\frac{\sin 2kl}{2kl}, \quad R = \frac{3}{2} + \frac{\sin 2kl}{kl},$$

$$y = DM^2, \quad M \approx H/2B, \quad (a - a_c) = \xi(T - T_N), \quad a_c = \alpha k^4,$$

$$F_1^l = -\frac{L_y^2}{4rR} - \frac{H^2}{4B}, \quad T_N^l = T_N - (y + 2a_c/kl)\xi^{-1},$$

$$k = k_0 - \sqrt{\frac{\xi(T_N^l - T)}{4\alpha k_0^2}}. \quad (2)$$

The upper index l corresponds to the case of the film with the thickness l.

State 2. Spin cycloid in the (y, z) plane, $P = P_z$:

$$A_y = a_y \cos ky, \quad A_z = a_z \sin ky, \quad P_z = c_1 k a_y a_z,$$

$$F_2{}^l = \frac{a_y^2}{2}L_y + \frac{a_z^2}{2}L_z + \frac{vR}{6}a_y^4 + \frac{v\bar{R}}{6}a_z^4 + \frac{u_2}{2}a_y^2a_z^2 - \frac{H^2}{4B}, \quad (3)$$

$$L_z = a + y + \gamma k^2 + \alpha k^4 + w - (a + y - \gamma k^2 + \alpha k^4 + w)\frac{\sin 2kl}{2kl},$$

$$\bar{R} = \frac{3}{2} - \frac{\sin 2kl}{kl}, \quad a_y^2 = (u_2L_z - \frac{3v}{2R}L_y)(v^2 - u_2^2)^{-1},$$

$$a_z^2 = (u_2L_y - \frac{3v}{2\bar{R}}L_z)(v^2 - u_2^2)^{-1}, \; 4u_2 = \lambda_2 + 2r, \; 2v = 3r,$$

$$k_0^2 = -\gamma/2\alpha, \quad v^2 > u_2^2, \quad a_c = \alpha k_0^4 = \xi(T_N - T_0).$$

The modulation vector k is found by minimizing the energy in the film (3) with respect to $\mathbf{k}$ and transition to the case of a bulk sample ($l \to \infty$) (see [12]). After this we get

$$\frac{\partial F_2{}^l}{\partial k} = (v^2 - u_2^2)^{-1}\left\{\frac{\cos 2kl}{k}(y - w)[6u_2\gamma k^2 - \right.$$

$$-v(2a + y + w - 4\gamma k^2 + 2\alpha k^4)] -$$

$$\left. -3v(2\gamma k + 4\alpha k^3)(2a + y + w + 2\gamma k^2 + 2\alpha k^4)\right\} = 0. \quad (4)$$

For the bulk sample $k^2 = k_0^2 = -\gamma / 2\alpha$, and so in Eq. (4) $2\gamma k + 4\alpha k^3 = 0$, $\cos 2kl = 0$, and $\sin 2kl = 1$.

State 3. Spin cycloid in the (y, x) plane, $P = P_x$:

$$A_y = a_y \cos ky, \quad A_x = a_x \sin ky, \quad P_x = c_2 k a_y a_x,$$

$$F_3^{\,l} = \frac{a_y^2}{2} L_{\,y} + \frac{a_x^2}{2} L_x + \frac{vR}{6} a_y^4 + \frac{v\overline{R}}{6} a_x^4 + \frac{u_1}{2} a_y^2 a_x^2 - \frac{H^2}{4B}, \quad (5)$$

$$L_x = a + y + \gamma k^2 + \alpha k^4 + w' - \\ - (a + y - \gamma k^2 + \alpha k^4 + w') \frac{\sin 2kl}{2kl},$$

$$4u_1 = \lambda_1 + 2r, \nu^2 > u_1^2, \quad a_y^2 = (u_1 L_x - \frac{3v}{2R} L_y)(v^2 - u_1^2)^{-1},$$

$$a_x^2 = (u_1 L_y - \frac{3v}{2\overline{R}} L_x)(v^2 - u_1^2)^{-1}, \quad \cos 2kl = 0, \quad \sin 2kl = 1.$$

The lines of second-order phase transitions in $TbMnO_3$ film between the states 1 and 2 $T_{12}^l(H)$ and between the states 1 and 3 $T_{13}^l(H)$ are determined by the equations $a_z = 0$, $a_x = 0$, from (3) and (5).

Correspondingly,

$$T_{12}^l = T_{12} + \frac{1}{2kl\xi(v-u_2)}[u_2(y+a+3a_c) + \frac{v}{3}(a+w+11a_c],$$

$$T_{12} = T_c + \frac{u_2 y}{\xi(v-u_2)},$$

$$T_{13}^l = T_{13} + \frac{1}{2kl\xi(v-u_1)}[u_1(y+a+3a_c) + \frac{v}{3}(a+w'+11a_c], \quad (6)$$

$$T_{13} = T_N - \frac{w'v - u_1 y}{\xi(v-u_1)},$$

$$T_c^l = T_c + \frac{1}{2\xi kl(v-u_2)}[u_2(a+3a_c) + \frac{v}{3}(a+w+11a_c)].$$

$$T_c = T_N - \frac{vw}{\xi(v-u_2)} = 28 \text{ K}.$$

The changes in the lines of second-order phase transitions (6), which are connected with the finite film thickness l, are about $1/(kl)$. For a bulk sample (very high film thickness l), the upper index l will be omitted below. The temperatures of the second-order phase transitions T_{12} and T_{13} slightly decrease with increasing field (i.e., $u_1 < 0$ and $u_2 < 0$, $u_2 > u_1$) and intersect at the critical point (T_k, y_k). In bulk space [10]

$$T_k = 26.7 \text{ K}, \quad H_k = 11 \text{ T}, \quad y_k = 0.142w \cong 0.14w. \quad (7)$$

For the critical point in the film we find

$$T_k^l = T_k + 2v(u_2 - u_{1)})(y_k + a + 5a_c)[3kl\xi(v-u_1)(v-u_2)]^{-1},$$

$$y_k^l = y_k - 2(y_k + a + 5a_c)/3kl. \quad (8)$$

The line of first-order phase transition in film $y_{23}^l(T)$ between the states 2 and 3 is found from the equality of their energies $F_2 = F_3$:

$$y_{23}(T) = \frac{\xi}{(\delta_1^2 - \delta_2^2)} \times \\ \times \Big\{ (T - T_N)(\delta_1 - \delta_2)(1 - \delta_1)(1 - \delta_2) + \\ + 14\delta_1(1 - \delta_2)(1 - \delta_2^2)w'/w - 14\delta_2(1 - \delta_2)(1 - \delta_1^2) + \\ + (\delta_2 - \delta_1)(T - T_k)\sqrt{(1 - \delta_1^2)(1 - \delta_2^2)} \Big\}. \quad (9)$$

Using expressions (6)–(9) and values of parameters for $TbMnO_3$ from [7, 10]

$$a = \xi(T - T_0), \quad a_k = \xi(T_k - T_N), \\ a_c = \xi(T_N - T_0) = 0.276w, \quad \delta_1 = u_1/v = -0.7, \\ \delta_2 = u_2/v = -0.63, \quad \xi = 0.0438w, \\ w'/w = 1.038, \quad T_0 = 35.7 \text{ K}, \quad (10)$$

for the film with $l = 6$ nm we can find the following values: $T_c^l = (28 + 0.39)$ K, $T_k^l = (26,7 + 0.03)$ K, $y_{23}^l(T_k) = (0,142 - 0.002)w \cong 0.14w$, $y_k^l \cong 0.09w$.

In a bulk sample $(l \to \infty)$

$$y_{23}(T_k) \cong 0.14w. \quad (11)$$

It can be seen from (11) that the boundary temperatures between the modulated states 1 and 2 (T_c^l) and states 1 and 3 (T_k^l) increase in film, and this increase is considerable more at $H = 0$, at $T = T_c^l$. The values of the critical magnetic fields at the boundary between states 2 and 3 are almost equal in bulk and film samples, $y_{23}(T_k) \cong y_{23}^l(T_k) = 0.14w$. However, the value of the critical magnetic field at the second-order phase transition between states 1 and 2 and states 1 and 3 $(T_{12} = T_{13})$ in the film is somewhat smaller than in bulk space: $y_k^l - y_k = 0.09w - 0.14w = -0.05w$.

The Néel temperature T_N depends on magnetic field and the film thickness according to the formula (2). It is possible using some values from (7) and (10) for the film with thickness l = 6 nm to receive the quantities $T_N^l(H = 0) \cong 41.2$ K, $T_N^l(H_k) \cong 38$ K. The dependence $T_N^l(H)$ is approximately represented in Fig. 1.

Conclusions

The first-harmonic approximation of the GL theory was used to analyze the influence of magnetic field directed along the vector of spin modulation on the AFM structure in the $TbMnO_3$ film. It was predicted some decrease in the Néel temperature with increasing of magnetic field and decreasing film thickness. The vector modulation k increases under the increasing magnetic field at a constant temperature in the state 1 [see (2)]. The magnetic field slightly increases the temperatures of lines for the second-order transitions between states 1 and 2, 1 and 3 (6). But this change is greater at H = 0 [see Fig. 3(b) in [11]].

The line of the first-order phase transition between states 2 and 3 in a magnetic field in film practically does not change: $y_{23}^{l}(T_k) \cong y_{23}(T_k) \cong 0.14w$.

A more noticeable effect of the magnetic field H_y in the $TbMnO_3$ film can be expected near the critical magnetic field of the second-order phase transitions, when the critical field in the film decreases: $y_k = 0.14w$, $y_k^l = 0.09w$. The dependence of T_N on the magnetic field in film was predicted in Fig. 1. The weak changes in the AFM-modulated states in the $TbMnO_3$ film in the magnetic field H_y mean the conservation of the colossal ME effect of the "polarization flop" in the $TbMnO_3$ nanofilms with thickness $l = 6$ nm.

1. T. Kimura, T. Goto, H. Shintanl, K. Ishizaka, T. Arima, and Y. Tokura, *Nature (London)* **426**, 55 (2003).
2. G. A. Smolenskii and I. E. Chupis, *Usp. Fiz. Nauk* **137**, 415 (1982); *Problems in Solid-State Physics,* Mir Publishers, Moscow (1984), p. 81.
3. M. Fiebig, *J. Phys. D: Appl. Phys*. **38**, R123 (2005).
4. T. Kimura, G. Lawes, T. Goto, Y. Tokura, and A. P. Ramirez, *Phys. Rev. B* **71**, 224425 (2005).
5. D. Rubi, C. de Graaf, C. J. M. Daumont, D. Mannix, R. Broer, and B. Noheda, *Phys. Rev. B* **79**, 014416 (2009).
6. I. E. Chupis, *Fiz. Nizk. Temp*. **36**, 597 (2010) [*Low Temp. Phys*. **36**, 477 (2010)].
7. G. Lawes and G. Srinivasan, *J. Phys. D: Appl. Phys*. **44**, 243001 (2011) .
8. A. P. Pyatakov and A. K. Zvezdin, *Phys. Usp*. **55**, 557 (2012).
9. M. Mostovoy, *Phys. Rev. Lett.* **96**, 067601 (2006).
10. I. E. Chupis and H. A. Kovtun, *J. Appl. Phys*. **103,** 182901 (2013).
11. A. Glavic, C. Becher, I. Voight, F. Schierle, E. Weschke, M. Fiebig, and T. Bruckel, *Phys. Rev. B* **88**, 054401 (2013).
12. I. E. Chupis, *Fiz. Nizk. Temp*. **46**, 720 (2020) [*Low Temp. Phys*. **46**, 602 (2020)].

Вплив магнітного поля на модульовану спінову структуру плівки манганіту тербію

I. E. Chupis

У одногармонічному наближенні теорії Гінзбурга–Ландау проаналізовано вплив магнітного поля вздовж осі y (напрямок модуляції спінів марганцю) на нерозмірні антиферомагнітні (АФ) стани у плівках орторомбічного $TbMnO_3$. Доведено, що температура Нееля зменшується як при зменшенні товщини плівки, так і при збільшенні магнітного поля. Запропоновано залежність температури Нееля від магнітного поля у плівці $TbMnO_3$. Межові лінії модульованих АФ станів змінюються слабо, окрім деякого збільшення температури T_c = 28 K при H = 0. Це означає збереження колосального магнітоелектричного ефекту «поляризаційного флопу» у магнітному полі у плівках манганіту тербію товщиною 6 нм. Такі плівки $TbMnO_3$ можуть бути використані у технології магнітоелектричних приладів.

Ключові слова: антиферомагнетик, нерозмірні структури, фероелектромагнетик, плівка, магнітне поле.