

Comparative Study of the Magnetoelectric Effect in $\text{HoAl}_3(\text{BO}_3)_4$ and $\text{HoGa}_3(\text{BO}_3)_4$ Single Crystals

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Abstract—The comparative study of the magnetoelectric properties and magnetostriction of $\text{HoGa}_3(\text{BO}_3)_4$ and $\text{HoAl}_3(\text{BO}_3)_4$ single crystals has been carried out. The investigated compounds exhibit qualitatively similar magnetodielectric and inverse magnetoelectric ME_E effects with the close absolute values, which is indicative of the weak effect of a nonmagnetic metal ion. On the contrary, the magnetostriction of the galloborate has been found to be threefold higher than that of the alumoborate. In addition, the difference between the qualitative behaviors of magnetostriction has been established: the magnetic-field dependence of magnetostriction for the alumoborate has the maximum near 70 kOe at $T = 4.2$ K, while the galloborate magnetostriction has no maximum and does not saturate in a field of 140 kOe.

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1. INTRODUCTION

The materials characterized by the magnetoelectric effect are promising for application in electronics and, therefore, have been topical objects of study in physics of condensed matter. However, practical applications require materials that exhibit the magnetoelectric effect at room temperature. By now, the investigations in this field have been fundamental and aimed at establishing general regularities and mechanisms of the magnetoelectric effect, understanding of which will enable a targeted search for new materials.

One of the groups of single-crystal magnetoelectrics attracting much attention is borates with the general formula $\text{RM}_3(\text{BO}_3)_4$, where R is the rare-earth ion or Y and M is Al, Ga, Sc, Fe, or Cr. In the compounds of this group, the maximum magnetoelectric effect was observed in $\text{HoAl}_3(\text{BO}_3)_4$. This crystal does not belong to multiferroics, since it is not magnetically ordered down to the lowest temperatures, but still exhibits a giant magnetoelectric effect. Since $\text{HoAl}_3(\text{BO}_3)_4$ contains the only magnetic ion (Ho^{3+}) and is not magnetically ordered, it can be considered as a model magnetoelectric.

There has been confusion in the literature concerning sample orientation. Symmetry of the investigated crystals is described by the space group $R32$. At the same time, in studies [1–3], the orientational error was made [4]. In all three studies, the orthogonal system of coordinates with the x , y , and z axes or a , b , and c axes was used, where $z(c)$ is the third-order crystallographic axis, $x(a)$ is the second-order crystallographic

axis, and the $y(b)$ axis forms a perpendicular to the x and z axes and is not crystallographic. To correctly interpret the data of these studies, it is necessary to make the replacement $x \leftrightarrow y$ ($a \leftrightarrow b$).

In a magnetic field applied along the x direction, the polarization P_{yx} along the y direction can occur, along with the longitudinal component P_{xx} . Concerning the P_{xx} component, the data on it can be found in study [5]; component P_{yx} is given in [1, 2] however, in view of the error made in the crystal orientation P_{yx} , this is actually the P_{xy} component. Thus, in studies [1, 2, 5], the polarization of the $\text{HoAl}_3(\text{BO}_3)_4$ single crystal was measured in the same (x) direction. In view of the aforesaid, we may conclude that there has been a great spread of available experimental data. The numerical values of electric polarization P_x at different directions of magnetic field H are given in Table 1.

Based on the data from Table 1, we may conclude that in the three above-mentioned studies, the absolutely different situation was observed for both the absolute values of the electric polarization and the ratio between the electric polarizations at different magnetic field directions within one study ($|P_{xx}|/|P_{xy}|/|P_{xz}|$). In our previous work [1], the ratios between the ME_H and ME_E magnetoelectric responses to the magnetic field applied along different directions are also different.

Nevertheless, in all three works, the qualitative behaviors of polarization $P(H)$ were very similar. Since the identical techniques were used in these studies for

Table 1. Experimental $P_{xi}(H_i)$ data ($i = x, y, z$)

$P_{xx}, \mu\text{C}/\text{m}^2$ ($H_x = 60 \text{ kOe}$)	$P_{xy}, \mu\text{C}/\text{m}^2$ ($H_y = 60 \text{ kOe}$)	$P_{xz}, \mu\text{C}/\text{m}^2$ ($H_z = 60 \text{ kOe}$)	$ P_{xx} / P_{xy} / P_{xz} $	$\beta_{xx}/\beta_{xy}/\beta_{xz}$	T, K
1200 [1]	-800 [1]	—	1.5/1/—	0.45/1/—	4.2
1600 [5]	-3150 [5]	1580 [5]	0.5/0.1/0.5		5
3500 [2]	-3800 [2]	135 [2]	0.9/1/0.03		5

measuring the $P(H)$ dependences, we may conclude that the difference is caused by the measured $\text{HoAl}_3(\text{BO}_3)_4$ single-crystal samples. As was shown in study [6], the $\text{DyFe}_3(\text{BO}_3)_4$ single crystals exhibited twinning, which consists in the difference between the directions of rotation of DyO_6 prism chains in the crystal: there are right- and left-handed domains. This random twinning can occur in the $\text{HoAl}_3(\text{BO}_3)_4$ single crystals, which leads to the difference between the experimental data; however, so far $\text{HoAl}_3(\text{BO}_3)_4$ has been considered to not tend to twinning.

The aim of this study was to clarify the effect of a nonmagnetic metal on the magnetoelectric effect in a $\text{HoM}_3(\text{BO}_3)_4$ compound. To do this, we carried out the comparative study of $\text{HoAl}_3(\text{BO}_3)_4$ and $\text{HoGa}_3(\text{BO}_3)_4$ single crystals.

2. EXPERIMENTAL

Holmium galloborate $\text{HoGa}_3(\text{BO}_3)_4$ single crystals were grown by the flux technique. In this study, we used the orthogonal system of coordinates (x, y, z), where x and z coincide with the a and c crystallographic directions, respectively, and the y direction is perpendicular to the xz plane. Samples for investigations were cut in the form of rectangular plates; the perpendicular to the plate coincides with the x axis.

To measure the permittivity and ME_E effect, the sample faces were coated with a conductive epoxy adhesive. The permittivity was studied by measuring the capacitance with an Agilent E4980A Precision LCR Meter and the ME_E effect was measured using the Astrov's method [7] on an original setup [8].

The $\text{HoGa}_3(\text{BO}_3)_4$ single crystal magnetostriction was measured at the International Laboratory of Strong Magnetic Fields and Low Temperatures (Wrocław, Poland) using a capacitive dilatometer on a facility with an Oxford Cryogenic solenoid on the basis of the well-known scheme [9]. The capacitance was detected with an Andeen Hagerling 2500A device. The $\text{HoAl}_3(\text{BO}_3)_4$ magnetostriction was measured on an original capacitive dilatometer adapted to the PPMS QD measuring system cryostat [10].

3. RESULTS AND DISCUSSION

Similar to the case of holmium alumoborate [1], the ME_E magnetoelectric response of the galloborate was found to be linear with respect to the electric field; i.e., the crystal magnetization changes proportionally to the applied electric field: the amplitude of sample magnetic moment variation along direction i is $\Delta M_{ij} = \beta_{ij} E_j$ in electric field E_j applied along the j direction. The second harmonic of the magnetoelectric effect quadratic in the electric field $\Delta M_{ij} = \gamma_{ij} E_j^2$ observed in samarium ferrobaborate [11] was not found. Figure 1 shows the dependences of the susceptibility of the ME_E magnetoelectric effect for (a) the $\text{HoAl}_3(\text{BO}_3)_4$ and (b) $\text{HoGa}_3(\text{BO}_3)_4$ single crystals. It can be seen from the plots that the qualitative behavior of the ME_E magnetoelectric effect in both compounds is almost identical; however, the ME_E magnetoelectric susceptibility value β_{xx} was found to be larger in the alumoborate than in the galloborate. The difference, however, was not large ($\sim 15\%$). At the same time, the published data on the ME_H effect in these compounds showed the larger polarization difference $\Delta P(H)$. In study [3] devoted to the $\text{HoGa}_3(\text{BO}_3)_4$ single crystal, the $\Delta P_{yx}(H)$ polarization values were reported, but, because of the orientational error made, the reported ΔP_{ba} values (in designations of study [3]), they correspond to $\Delta P_{xy}(H)$ and in a field of 90 kOe the magnetoelectric polarization is $-1000 \mu\text{C}/\text{m}^2$ at a temperature of 5 K, while the polarization in the alumoborate attains $-5000 \mu\text{C}/\text{m}^2$ under the same conditions [2]; i.e., it differs by a factor of five. Such a large difference in the behaviors of the ME_E and ME_H effects upon substitution of Ga^{3+} ions for Al^{3+} ions can speak about different effects of the domain structure on the direct and inverse magnetoelectric effects.

Thus, our measurements showed that the ME_E magnetoelectric effect remains nearly invariable upon substitution of Ga for Al in the paramagnetic holmium oxiborate, which is indicative of the weak effect of the nonmagnetic metal ion on the magnetoelectric effect.

Figure 2 shows the dependences of the magnetodielectric effect on applied magnetic field H and temperature T . The magnetic field was applied along the x direction of the crystal; the electric capacitance was measured between two sample faces, the normal to which coincided also with the x axis. It can be seen

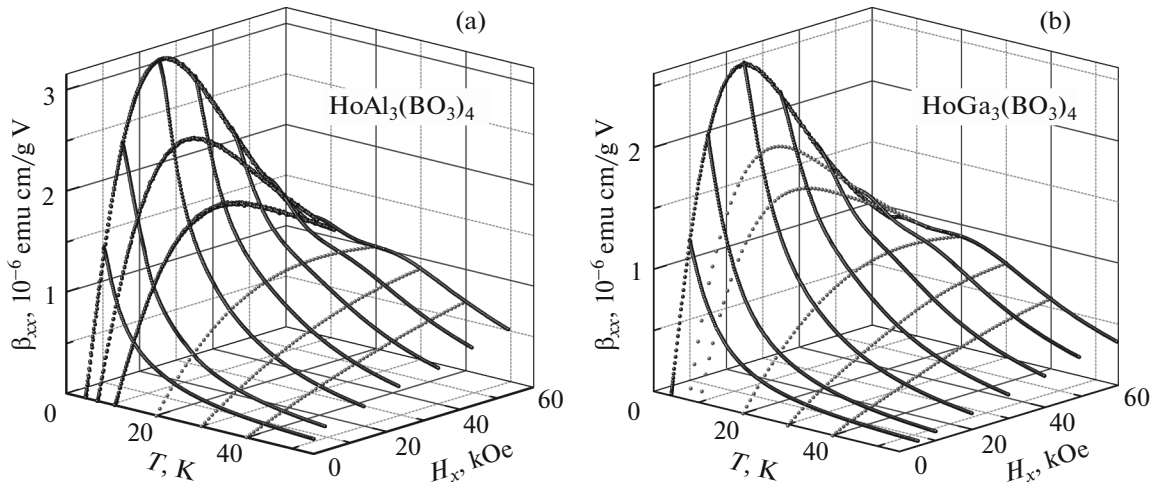


Fig. 1. ME_F magnetolectric susceptibility of (a) holmium alumoborate $\text{HoAl}_3(\text{BO}_3)_4$ [1] and (b) galloborate $\text{HoGa}_3(\text{BO}_3)_4$ single crystals as a function of magnetic field H_x and temperature. The experimental data are colored with black and the spline approximation data, with gray.

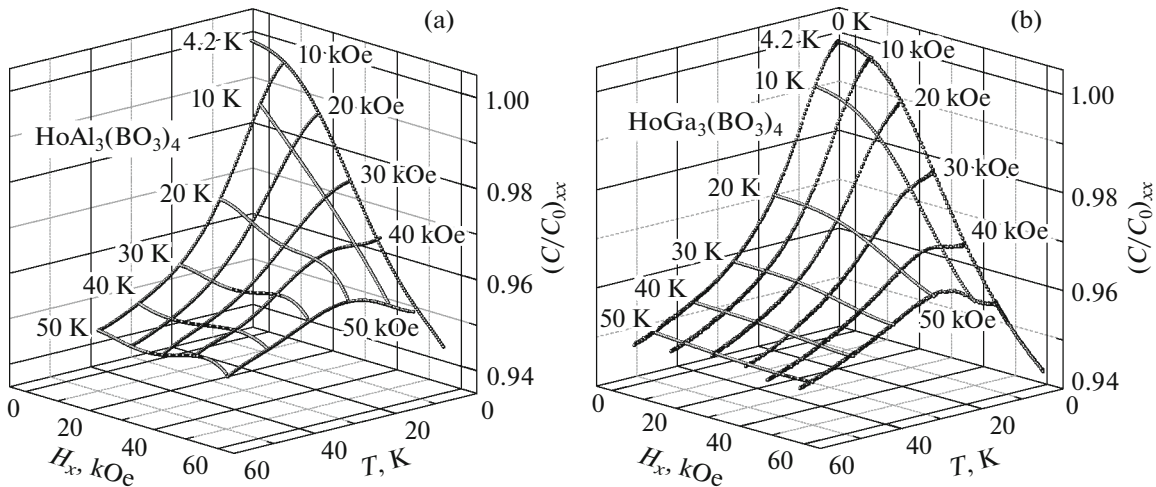


Fig. 2. Dependences of the longitudinal magnetodielectric effect in (a) holmium alumoborate $\text{HoAl}_3(\text{BO}_3)_4$ [1] and (b) galloborate $\text{HoGa}_3(\text{BO}_3)_4$ single crystals on temperature T and magnetic field H_x . The experimental data are colored with black and the spline approximation data, with gray.

that substitution of Ga^{3+} ions for Al^{3+} ones does not lead to significant differences in the behavior of the permittivity in the applied magnetic field, which also indicates the weak effect of the nonmagnetic ion metal on the correlation between the magnetic and electric properties in the $\text{HoM}_3(\text{BO}_3)_4$ compound.

In addition, we performed the magnetostriction measurements (Fig. 3). The magnetostriction found in $\text{HoGa}_3(\text{BO}_3)_4$ exceeds that in $\text{HoAl}_3(\text{BO}_3)_4$ [5] by a factor of more than three, which, however, does not lead to an increase in the magnetolectric polarization [3]. The magnetostriction of the $\text{HoGa}_3(\text{BO}_3)_4$ and $\text{HoAl}_3(\text{BO}_3)_4$ compounds was measured on different equipment: in the first case, we used the experimental

setup described in [9] and, in the second case, the dilatometer recently developed by us [10]. It can be seen from the plots that the results obtained are drastically different, despite the similarity of investigated compounds. The measured magnetostriction of $\text{HoAl}_3(\text{BO}_3)_4$ is consistent with the results reported in [5], but, due to the wider range of available magnetic fields, the behavior of magnetostriction λ_{aa} after 70 kOe was established, where the magnetostriction decreases with an increase in the magnetic field. Similar behavior was observed in this compound at the different orientation of the measured magnetostriction λ_{xz} , when the magnetic field was applied along the third-order axis z and the crystal strain was measured along the x direction [5].

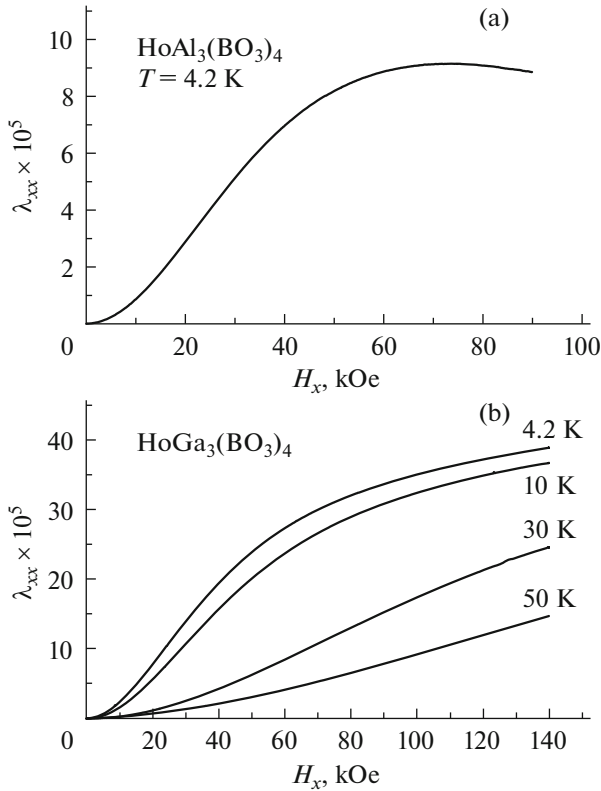


Fig. 3. Longitudinal magnetostriction λ_{xx} of (a) $\text{HoAl}_3(\text{BO}_3)_4$ and (b) $\text{HoGa}_3(\text{BO}_3)_4$ single crystals.

Our measurements showed that the $\text{HoAl}_3(\text{BO}_3)_4$ and $\text{HoGa}_3(\text{BO}_3)_4$ compounds have similar magneto-electric properties; the same concerns the ME_E magneto-electric and magnetodielectric effects, which contradicts, to a certain extent, the ME_H -effect data reported in [2, 3], according to which the magneto-electric polarization in the $\text{HoAl}_3(\text{BO}_3)_4$ compound exceeds the polarization in $\text{HoGa}_3(\text{BO}_3)_4$ by a factor of five. The discrepancy between the experimental data can be attributed to the use of different single-crystal samples in the investigations. In addition, the situation is complicated by the twinning found in study [6] in the $\text{DyFe}_3(\text{BO}_3)_4$ single crystal, which can occur also in the investigated paramagnetic aluminoborates. This is indicated by the discrepancy between the experimental data reported in the published works (see Table 1).

One more intriguing feature is the different behavior of magnetostriction. The longitudinal relative strain λ_{xx} in $\text{HoAl}_3(\text{BO}_3)_4$ attains its maximum in a field of ~ 70 kOe, while the magnetostriction in $\text{HoGa}_3(\text{BO}_3)_4$ does not saturate and continues growing with an increase in the field of up to 140 kOe, which is valid to a temperature of, at least, 4.2 K. The absolute value of the galloborate magnetostriction in a field of ~ 70 kOe appeared larger by a factor of ~ 3 than in the aluminoborate. Nevertheless, such a high magne-

tostriction does not increase the magneto-electric effect.

In addition, note the confusion in the crystallographic directions, which concerned also our previous study on $\text{HoAl}_3(\text{BO}_3)_4$ [1]. In view of the error made, the considerations concerning the microscopic mechanism of the formation of magneto-electric effect should be corrected. We believe, however, that the general idea about the mechanism of magneto-electric effect in this compound is true. It consists in the fact that the magneto-electric effect is caused by the non-spherical electron $4f$ shell of a rare-earth Ho^{3+} ion. In view of the strong spin-orbit coupling, the sample is magnetized not only due to the variation in the spin moment distribution over its directions, but also due to the change in the distribution of the orbital moment. The latter indicates that the electron density distribution in the $4f$ subshell also changes. Thus, the overlap between the rare-earth ion $4f$ orbital and oxygen orbitals changes during sample magnetization. This induces additional Coulomb forces and leads to the magnetostriction and shifts of ions, which is accompanied by the occurrence of polarization.

We suggest that the ion polarization in the family of borates plays a key role and exceeds by far the electron polarization, since there are no permittivity anomalies in the frequency range of 200–400 GHz at the Neel point and the magnetodielectric effect is only observed at low frequencies [12], which is valid for, at least, the $\text{SmFe}_3(\text{BO}_3)_4$ single crystal.

Concerning the inverse ME_E magneto-electric effect, in an applied electric field oxygen ions shift relative to the holmium ion due to the piezoelectric effect, which leads to the changes in the Stark structure and in the distribution of populations of different energy levels; i.e., the resulting magnetic moment of the sample changes in the external magnetic field. This effect only manifests itself in the external magnetic and electric field in this compound, since it does not belong to piezomagnets, such as Cr_2O_3 , where the magnetic moment can occur without external magnetic field.

Zhang et al. [13] attempted to find the shift of Ho^{3+} ions relative to the oxygen environment using element-oriented X-ray analysis, but failed. To explain this fact, we estimate the Ho^{3+} ion shift relative to the oxygen environment, which is sufficient to obtain the polarization observed in the experiment. We assume the polarization to be caused by the shift of only the Ho^{3+} ion without distortion of the oxygen prism.

To estimate the Ho^{3+} ion shift, we should consider the shift that meets the resulting polarization $P = \sqrt{P_{xx}^2 + P_{yx}^2 + P_{zx}^2}$ or $P = \sqrt{P_{xy}^2 + P_{yy}^2 + P_{zy}^2}$. However, since the P_{yy} and P_{zy} data are lacking, we consider the ion shift only along the x direction in the magnetic

field applied along the y axis, since the polarization P_{xy} is maximum within the reported experimental data.

The electric polarization is a dipolar moment of the unit substance volume. To determine the Ho^{3+} ion shift, we investigate the unit cell. Since the dipole moment of the cell in the equilibrium position without magnetic field is zero (the crystal is not ferroelectric), the polarization will be only determined by the Ho^{3+} ion shift in the applied magnetic field. Then, the electric polarization is

$$P_x = \frac{1}{V} \sum q_i \Delta x_i, \quad (1)$$

where summation is only made over Ho^{3+} ions, V is the unit cell volume, q is the rare-earth ion charge, and x is the rare-earth ion shift. Due to the presence of the third-order symmetry axis, the contributions of all the three holmium ions located in the equivalent symmetry positions in the unit cell will be the same. Each of them has a charge equal to three elementary charges e . Therefore, using Eq. (1), we find the Ho^{3+} ion shift

$$\Delta x = \frac{P_x V}{9e}. \quad (2)$$

At the electric polarization $P_{xy} = -5240 \mu\text{C}/\text{m}^2$ obtained in a field of $H_y = 90 \text{ kOe}$ in [2], the estimation yields a rare-earth ion shift of $\Delta x \approx 0.02 \text{ \AA}$. In this case, the maximum change in the distance between the oxygen atom of the triangular prism and holmium ion is $\Delta R = R_0 - \sqrt{(X_O - \Delta x)^2 + Y_O^2 + Z_O^2} \approx 0.016 \text{ \AA}$, where R_0 is the distance between oxygen and holmium ions in the nonshifted position and X_O , Y_O , and Z_O are the coordinates of the oxygen atom with the reference point coinciding with the position of the nonshifted Ho^{3+} ion. Thus, assuming the electric polarization to be exclusively caused by the shift of holmium ions, the maximum change in the Ho–O distance will only be 0.7%. In study [13], where the authors attempted to fix the variation in this distance by the XAFS technique, it was shown that the holmium ion is not shifted relative to the nearest oxygen neighborhood, possibly due to the limited accuracy of the technique, since a distance variation of 0.7% is difficult to detect.

4. CONCLUSIONS

Thus, we investigated first the inverse magnetoelectric effect in the $\text{HoGa}_3(\text{BO}_3)_4$ compound and measured the magnetodielectric effect. The measurements revealed properties very similar to those of the $\text{HoAl}_3(\text{BO}_3)_4$ crystal. This statement contradicts the results of measurements of the direct magnetoelectric effect, which showed the growth of magnetoelectric polarization of the $\text{HoAl}_3(\text{BO}_3)_4$ compound over the $\text{HoGa}_3(\text{BO}_3)_4$ compound. This can be attributed to the difference between single-crystal samples used in the measurements.

We measured the longitudinal magnetostriction of $\text{HoAl}_3(\text{BO}_3)_4$ and $\text{HoGa}_3(\text{BO}_3)_4$. In contrast to the magnetoelectric polarization, the magnetostriction of the $\text{HoGa}_3(\text{BO}_3)_4$ compound appeared higher by a factor of ~ 3 . In addition, the magnetostrictions of these compounds are qualitatively different. In particular, in the holmium alumoborate the longitudinal magnetostriction λ_{xx} increases with a magnetic field and attains its maximum at $\sim 70 \text{ kOe}$, but then starts decreasing with an increase in the magnetic field, whereas in the holmium galloborate the magnetostriction maximum is not observed and the magnetostriction does not saturate in a field of 140 kOe.

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REFERENCES

1. A. L. Freidman, A. D. Balaev, A. A. Dubrovskiy, E. V. Eremin, V. L. Temerov, and I. A. Gudim, *J. Appl. Phys.* **115**, 174103 (2014).
2. A. I. Begunov, A. A. Demidov, I. A. Gudim, and E. V. Eremin, *JETP Lett.* **97**, 528 (2013).
3. N. V. Volkov, I. A. Gudim, E. V. Eremin, A. I. Begunov, A. A. Demidov, and K. N. Boldyrev, *JETP Lett.* **99**, 67 (2014).
4. V. L. Temerov, private communication.
5. K.-C. Liang, R. P. Chaudhury, B. Lorenz, Y. Y. Sun, L. N. Bezmaternykh, V. L. Temerov, and C. W. Chu, *Phys. Rev. B* **83**, 180417(R) (2011).
6. T. Usui, Y. Tanaka, H. Nakajima, M. Taguchi, A. Chainani, M. Oura, S. Shin, N. Katayama, H. Sawa, Y. Wakabayashi, and T. Kimura, *Nat. Mater.* **13**, 611 (2014).
7. D. N. Astrov, *Sov. Phys. JETP* **11**, 708 (1960).
8. A. D. Balaev and A. L. Freidman, *J. Surf. Invest.: X-ray, Synchrotron Neutron Tech.* **8**, 17 (2014).
9. V. I. Nizhankovskii, *Eur. Phys. J. B* **71**, 55 (2009).
10. A. L. Freidman, S. I. Popkov, S. V. Semenov, and P. P. Turchin, *Tech. Phys. Lett.* **44** (2018), in press.
11. A. L. Freidman, A. D. Balaev, A. A. Dubrovskii, E. V. Eremin, K. A. Shaikhutdinov, V. L. Temerov, and I. A. Gudim, *Phys. Solid State* **57**, 1357 (2015).
12. A. A. Mukhin, G. P. Vorob'ev, V. Yu. Ivanov, A. M. Kadamtseva, A. S. Narizhnaya, A. M. Kuz'menko, Yu. F. Popov, L. N. Bezmaternykh, and I. A. Gudim, *JETP Lett.* **93**, 275 (2011).
13. H. Zhang, T. Yu, Z. Chen, C. S. Nelson, L. N. Bezmaternykh, A. M. M. Abeykoon, and T. A. Tyson, *Phys. Rev. B* **92**, 104108 (2015).

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