Breaking the magnetic symmetry by reorientation transition near 50 K in multiferroic magnetocaloric $HoFeO_3$

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Using the new polarized neutron diffraction (PND) setup at MLZ the spin reorientation transition in the magnetocaloric orthoferrite $HoFeO_3$ was studied at different wavelength. The various experiments provided reproducible results demonstrating high reliability of the used setup. We show that during the phase transition at T_{SR}=53 K in an external magnetic field applied along crystal c-axis, the ordered magnetic moment of the Fe sublattice rotates from the crystallographic direction b to a not just in the ab plane, but through z axis. This means that the applied field breaks the orthorhombic symmetry allowing some magnetization parallel to z within a short temperature region. Interestingly, this is the same temperature region where large magnetocaloric effect for $HoFeO_3$ was previously reported. A general model of the magnetic structure of $HoFeO_3$, unconstrained by the orthorhombic symmetry, would allow the magnitudes and directions of the moments on each of the 8 magnetic sublattices in the unit cell to be independent of one-another, leading to 24 independent magnetic parameters. PND measurements were used to determine the absolute sign of the Dzyaloshinskii-Moriya interaction (DMI) in the ab plane for the Fe magnetic sublattice at 65 K. DMI plays an important role in the energy balance of the system.

Index Terms* – *magnetic structure, spin reorientation transition, polarized neutron diffraction, Dzyaloshinskii-Moriya interaction.

I. INTRODUCTION

Multiferroicity at room temperature has been reported for some representatives of the rare-earth orthoferrites family RFeO3 (e.g. YFeO3, LuFeO3, SmFeO3)[1-4]. It brings these compounds close to being useful for potential applications in switching elements, sensors, memory and other advanced technical devices with low energy consumption. Dzyaloshinskii-Moriya interaction (DMI), which leads to a weak ferromagnetism (WF) in the Fe sublattice is proposed as one of possible reasons for the electric polarization in this materials. A spontaneous electric polarization in HoFeO3 occurs at elevated temperatures ~ 210 K [5]. In addition, a large magnetocaloric effect has been reported for $HoFeO_3$ at low temperatures [6,7], proposing this material as a promising candidate for the efficient magnetic cooling for the cryogenic gases liquefying technology. This further increase the interest on this compound and justifies detailed studies on the complex magnetic ordering processes in the rare-earth orthoferrites generally and in $HoFeO_3$ particularly.

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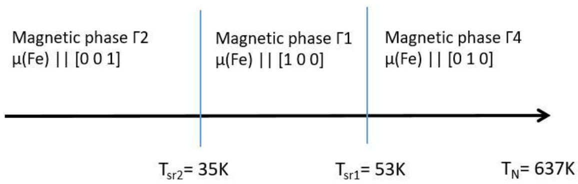

Fig. 1. Scheme of phase transitions in the Fe sublattice in zero magnetic field.

According to recent precise single-crystal neutron diffraction studies on $HoFeO_3$ in zero field its average crystal structure is described well by the orthorhombic space group *Pbnm* [8]. Below T_N= 637 K the Fe sublattice orders antiferromagnetically (AFM) with the strongest component along the a-axis, and a weak ferromagnetic component along the c-axis (magnetic phase Γ4). Two spin reorientation transitions have been reported in zero field (Fig. 1): at T_{sr1}=53 K where the Fe moments rotate in plane from a axis to b axis (magnetic phase Γ1) and at T_{sr2}=35 K where the strongest component of magnetic moments occurs along the c axis (magnetic phase Γ2). Ho orders at a temperatures below T_{NR}=4 K [8].

With applied magnetic field, a strong magnetocaloric effect was found in $HoFeO_3$ at lower temperatures. Three peaks in the entropy-change occur for a field variation of 0-7 T: ΔSM=9 J/Kg K at 53 K, ΔSM=15 J/Kg K at 10 K and ΔSM=18 J/Kg K at 3 K [6]. Apparently the first peak is associated with a spin reorientation in the Fe subsystems solely. The last one should related to the Ho ordering. While the second peak may be related with some processes including both the Ho and Fe magnetic subsystems. However, a recent polarized neutron diffraction study [9] showed an ordered antiferromagnetic moment of about 1.0 μB at the Ho positions with an applied external field of 9 T even above T_{sr1} e.g. at 70 K. Thus, it is important to fully understand the fine interplay between the Fe and Ho magnetic subsystems occurring during the phase transitions in applied external magnetic fields.

Polarized neutron diffraction (PND) is a powerful method to study the magnetic ordering on the microscopic level. It has been applied in $HoFeO_3$ to determine the magnetic structure of Fe in Γ4 phase (70 K) with 9 T and to evidence Fe and Ho ordering in Γ2 phase (< 25 K) at 0.5 T [9]. Recently new PND setup was implemented at Heinz Maier-Leibnitz Zentrum (MLZ) in Garching Germany [10,11]. Here we report on the one of the first studies performed using this new setup. The goals of the present research are both to investigate the detailed temperature-field evolution of the magnetic reorientation phase transition from Γ4 to Γ1 near 50 K in $HoFeO_3$ and to check the reliability of the new PND option at different wavelength.

II. Experiment

PND experiments were performed on the diffractometer POLI at MLZ [12]. Cryogen-free 2.2 T, compact high-T_c superconducting magnet presented in Ref. [11] was employed. Two series of measurements were made to test also the feasibility of the used setup at different wavelengths: the first using a neutron wavelength of 1.15 Å and the second of 0.71 Å. Qualitatively and quantitatively the same results were obtained from both measurements denoting a reliable control over the neutron polarization even using a very short neutron wavelength on POLI. Large high quality single crystal of $HoFeO_3$ used in the previous neutron investigations [8,9] was taken for this study. The studied crystal was aligned with its [001] axis nearly parallel to the ω diffractometer axis (sample rotation axis) which is also the magnetic field axis and neutron polarization direction. Using a lifting detector, a set of in-plane and out-of-plane (hkl) Bragg reflections, with $l = 0, -1$ and -2, could be measured. The evolution with temperature and field was measured using a set of 70 pre-selected Bragg peaks, which obtained the strongest flipping ratios at 70 K. Discrete temperatures points between 47 and 57 K separated by 2 K steps and from 57 to 67 K separated by 5 K steps were used. Between each pair of adjacent temperatures, a zero-field cooling cycle was carried out. In such a cycle, the field was first reduced to zero (remanent field ~350 Oe), then the sample was heated to 70 K and finally cooled to the next higher required temperature before measuring the set of reflections at four field values: 0.15, 0.5, 1.0 and 2.2 T respectively.

III. Results

In the distorted perovskite structure of $HoFeO_3$, the reflections to which the Fe sublattices contribute comprise four sets of Bragg reflections designated as following: F: h + k even, l even; A: h + k even, l odd; C: h + k odd, l even and G: h + k odd, l odd [8,13]. In the magnetic scattering, each of these reflection types is characteristic for a different modulation of the moments on the 4 Fe sublattices (Table 1). In an initial analysis the projection M⊥ P of the

TABLE I
Relative signs of the moments on the Fe sublattices contributing to the structure factors of reflections from HoFeO3.

Sublattice	Position			F	A	C	G
1	0	$\frac{1}{2}$	0	+	+	+	+
2	$\frac{1}{2}$	0	0	+	+	-	-
3	$\frac{1}{2}$	0	$\frac{1}{2}$	+	-	-	+
4	0	$\frac{1}{2}$	$\frac{1}{2}$	+	-	+	-

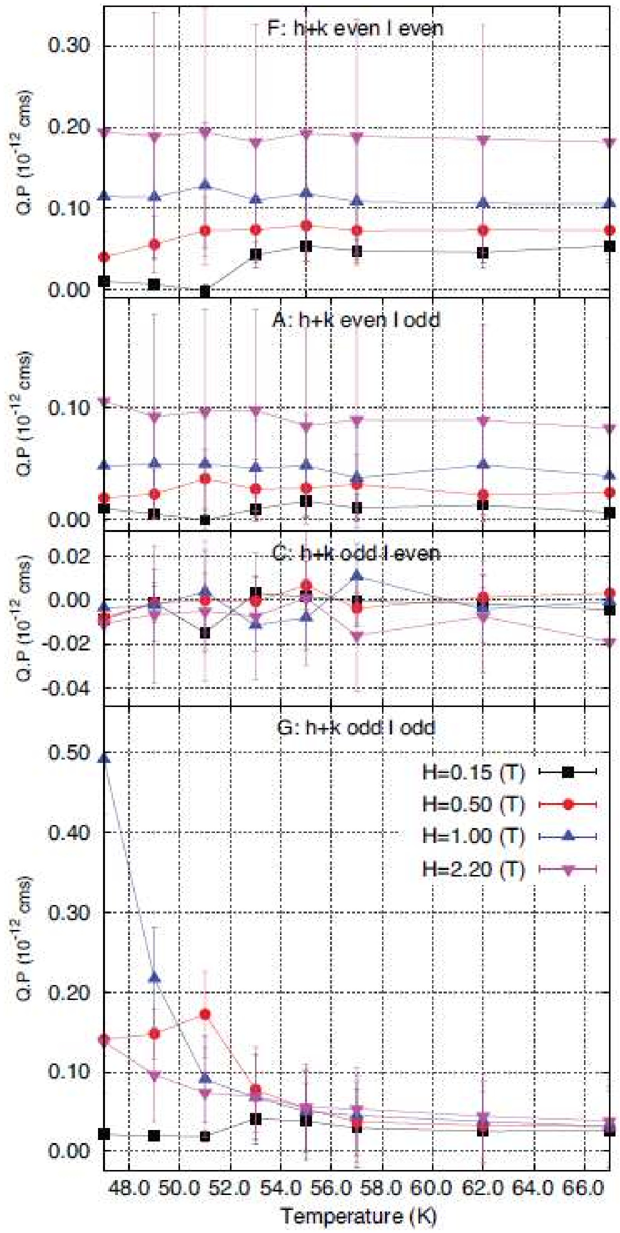

Fig. 2. Mean values of M⊥ P for the F, A, C and G reflections in $HoFeO_3$ measured in magnetizing fields of 0.15, 0.5,1.0 and 2.2 T respectively. The plotted error bars indicate the spread of the measured values in each reflection type.

magnetic interaction vector M⊥ on the polarization direction P was calculated from the measured asymmetry A = (I+- I-)/(I++ I-) of each reflection. Here, I± denotes the measured intensity for the two antiparallel spin orientations of the incoming neutron beam in regard to the quantization axis of the field. The analysis results, illustrated in Fig. 2, are divided according to the reflection type. This analysis shows that the asymmetries in the F, C and A reflections have essentially the same behavior: they vary only weakly with temperature and the F and A reflections increase with increasing field. The asymmetries of the C reflections are hardly significant. The largest asymmetries are observed in the G reflections which depend strongly on both temperature and field (Fig.2). A significant asymmetry in the intensity of polarized neutron diffraction from an antiferromagnet with zero propagation vector can only arise if the two 180° domains are unequally populated. In the weak ferromagnetic Γ4 phase of $HoFeO_3$, stable between 56 and 700 K, the weak [001] axis ferromagnetism ensures that the domain with its ferromagnetic moment in the field direction will dominate. The sense of the DMI leading to weak ferromagnetism is given by the sum of the cross products of nearly antiparallel spins on interacting atoms. Therefore, antiferromagnetic components of the magnetic moments are always perpendicular to the ferromagnetic axis.

The asymmetry values for 275 Bragg reflections were measured at 65 K. Using these values, we could refine the precise orientation of the AFM moments of the Fe sublattice in $HoFeO_3$ in the Γ4 phase. Our results are in good agreement with the previously published magnetic structure at 70 K [8]. To follow the magnetic phase transition explicitly, the asymmetries of 70 selected peaks (mostly of G-type) were measured in 2 K steps between 67-47 K, and the resulting magnetic moment components for the Fe atoms calculated (Fig. 3). The experimentally measured asymmetry map for the exemplary G-type reflection (30-1) is shown in Fig. 4. As predominantly G-type reflections were measured, a precise calculation of the Ho magnetic moments was barely possible. Below 53 K in the lowest field (0.15 T), the magnitude of the x-component of the Fe moment decreases abruptly whilst that of the y-component increases. This behavior is consistent with the reorientation transition to the Γ1 structure observed in zero field. Further increasing the applied field lowers the temperature of the transition, until it does not occur within the scanned temperature range for 2.2 T. However, an attempt to fit the intermediate phase as a linear combination of different volume fractions of Γ1 and Γ4 phases did not lead to a converging solution.

Between 66 and 47 K, the magnetic scattering is dominated by the contributions from the ordered Fe moments, which have magnetic structure factors of the form:

$$M = \pm f(k)(m_1 - m_2 + m_3 - m_4) \qquad (1)$$

where $f(k)$ is the Fe magnetic form factor for the corresponding reflection and m_1, m_2, m_3 and m_4 are the magnetic moments of the Fe atoms. The leading + sign applies for h even and the − for h odd. If the Ho ordering is neglected, the x, y, and z components of the Fe magnetic moments, which

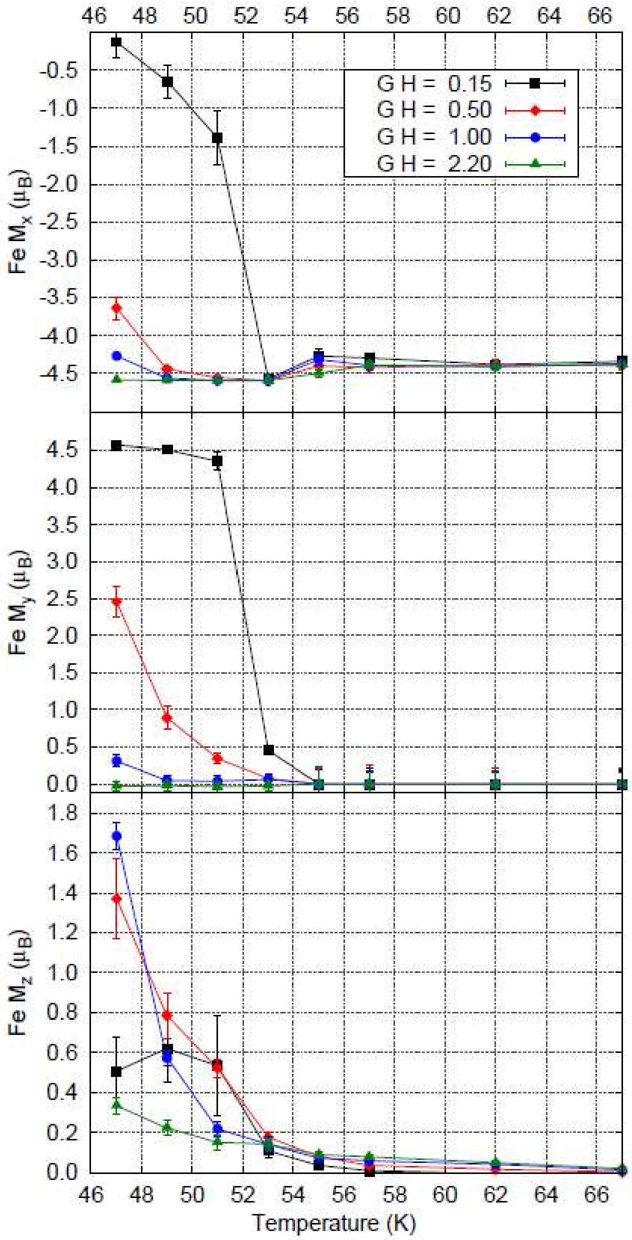

Fig. 3. Components of the G modulation of ordered magnetic moment in HoFeO3 calculated from sums and differences between the asymmetries of equivalent reflections

contribute to each of the F, A, C and G modulations, can be determined from the differences between the asymmetries (A) of equivalent reflections of the corresponding type. The values of the x,y,z components of the G modulation of the Fe moments calculated from the least squares fits to both series of measurements are shown in Figure 3. At the highest temperature and only the x component of the magnetic moment contributes to the asymmetries in the G reflections independent of the applied field value, as it is expected for the Γ4 structure. With decreasing temperature, no significant changes occur until between 55 and 54 K the absolute values of the x components start to fall and the y and z components rise. Below this temperature, the effect of an increasing field becomes important. Increasing the field lowers the temperature at which

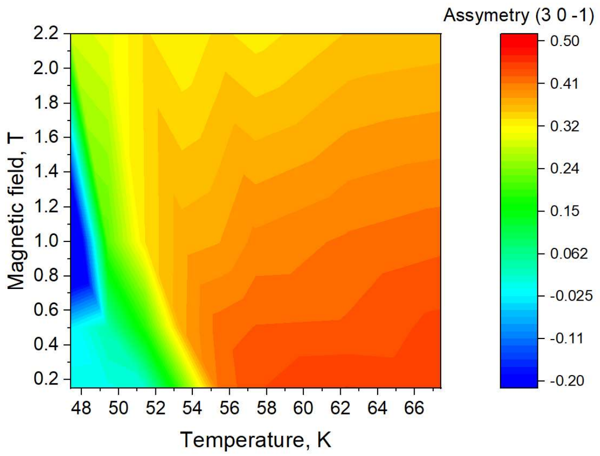

Fig. 4. Temperature/field map for the measured asymmetry of G-type peak (3 0 -1). The reddish area corresponds to the magnetic phase Γ4, blue to Γ1, celestial-greenish to the intermediate monoclinic magnetic phase.

the changes start to occur and it reduces the overall redistribution between the magnetic moment components. At 53 K a reorientation transition takes place in zero field as the magnetic symmetry changes from Γ4 to Γ1 and the Fe moments with G modulation reorient from x to y. The results suggest that the reorientation transition temperature falls with increasing field and in 2.2 T applied along the z direction, it is reduced to below 47 K and thus, not visible in Fig. 3.

The Γ1 symmetry of the AF1 phase does not allow an intrinsic ferromagnetic component in any direction and so applying a magnetic field should not favor one of the 180° domains over the other. However, the finite asymmetries observed in the data collected for the three lower fields in the temperature range 54-47 K and their relative reproducibility over several temperature cycles suggests, that the applied field still favors one of the 180◦ domains even below the reorientation transition. The persistence of a polarization dependent cross-section may indicate a field induced phase with a lower symmetry. The existence of a z component of the asymmetry in the G reflections suggests that the applied field breaks the magnetic symmetry of the Γ4 and Γ1 phase which do not allow some G-type magnetization parallel to z (Fig. 5). A general, unconstrained model of the magnetic structure of $HoFeO_3$

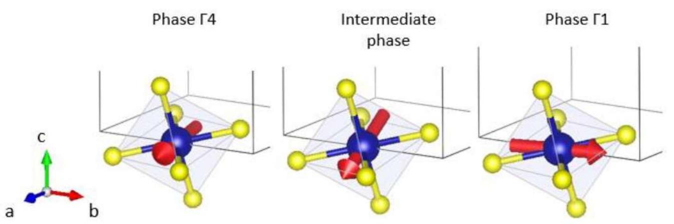

Fig. 5. Fe magnetic moment rotation by the reorientation phase transition in $HoFeO_3$ near 50 K with magnetic field B=0.5T along [001]. An intermediate phase braking orthorombic simmetry occurs between the magnetic phases Γ4 and Γ1. Here: blue balls - Fe ions, yellow - O, red arrows denote ordered magnetic moments.

would allow the magnitudes and directions of the moments on each of the 8 magnetic sublattices (Fe and Ho) in the unit cell to be independent of one-another, leading to 24 independent magnetic parameters. Thus, the external magnetic field changes the energy balance of the exchange interactions near the phase transition. It leads to the appearance of a new magnetic phase.

IV. Absolute sign of the DMI

In the Γ4 phase, the magnetic field aligns the WF moment along its direction. This lifts the degeneracy between 180° AFM domains since the orientation of the AFM structure to the weak ferromagnetic moment is fixed by the DMI. Conversely, the sign of the DMI can be determined by refining the precise orientations of the AFM moments in the Γ4 phase from PND data. In the general case, the asymmetric DMI D_{ij} for each spin pair s_i, s_j contributes to the energy as:

$$\Delta E = \sum_{i \neq j} D_{ij} \cdot (s_i \times s_j) \quad (2)$$

A general symmetry restrictions for the DMI vector has been developed by Thoma et al. in Ref. [14]. As the DMI is antisymmetric D_{21}=-D_{21}, it is important to precisely define (fix) the bond directions. Here we adopt atom position notation as used in Ref. [9]. By performing a proper averaging over the four Fe sublattices of the Γ4 structure, we could reduce the DMI interaction in HoFeO3 as follows. Starting with Fe1, it is connected to Fe2 within the ab-plane by D_{12}^{Fe} and to Fe4 along the c-axis by D_{14}^{Fe}. D_{12}^{Fe} and D_{14}^{Fe} are not related by symmetry and thus might have different values. D_{34}^{Fe} is connected by a two-fold inversion screw axis with D_{12}^{Fe}, leading to D_{34}^{Fe} =(0, D_{12y}^{Fe} , -D_{12z}^{Fe}). The averaged DMI vector between Fe2 and Fe3 is given by D_{23}^{Fe} =(D_{14x}^{Fe} , - D_{14y}^{Fe} , 0). Thus, equation (2) applied for the magnetic structure Γ4 can be written by two independent parameters D_{12}^{Fe} and D_{14}^{Fe} as:

$$\Delta E_{\Gamma 4}^{Fe} = 4D_{12}^{Fe} \cdot (m^{Fe1} \times m^{Fe2}) + 2D_{14}^{Fe} \cdot (m^{Fe1} \times m^{Fe4})$$
$$+4D_{34}^{Fe} \cdot (m^{Fe3} \times m^{Fe4}) + 2D_{23}^{Fe} \cdot (m^{Fe2} \times m^{Fe3})$$
$$= -8m_x m_z (D_{14y}^{Fe-Fe} + 2D_{12y}^{Fe-Fe})$$

where m is the magnetic moment of Fe1. The refinement results at 65 K show a positive m_x and m_z, and a negligible small m_y. Thus, the sum of the DMI vector components D_{14y}^{Fe} and D_{12y}^{Fe} must be positive as well in order to minimize the DMI energy. These results on the DMI sign complements the findings of our previous work where numerical values for the DMI and exchange interactions were determined by inelastic neutron scattering [15].This previous study revealed DMI magnitudes of D_a^{Fe}=0.12 meV and D_c^{Fe}=0.08 meV for Fe subsystem and an exchange interaction strength of $J_{Fe\text{-}Ho}$= -0.026 meV between the Fe and Ho.

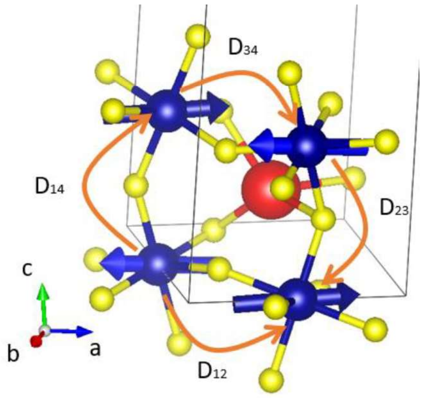

Fig. 6. Scheme of the DMI inside the Fe sublattice. Blue balls - Fe ions, red - Ho, yellow – O. Orange arrows show the paths with the same sing of the D_y^{Fe}.

V. CONCLUDING REMARKS

PND at the instrument POLI at MLZ could be successfully applied to study the temperature evolution of the spin reorientation transition in $HoFeO_3$ near 50 K under applied magnetic fields up to 2.2 T along the c-axis. One observed that the transition from the Γ4 to the Γ1 phase, which takes place in zero field at 53 K, gets shifted to lower temperatures by increasing the field and is unreachable above 47 K under applied field of 2.2. T. Moreover it was observed that the spin reorientation from the b axis in the Γ4 phase to the a-axis in the Γ1 phase is not restricted just to the ab plane but accompanied with the occurrence of a significant component along the external field (c direction). This intermediate phase breaking the magnetic symmetry could not be explained as a linear combination of the Γ4 and Γ1 phases and should be considered as a new low-symmetry magnetic phase. Using PND, a mapping of the new phase in the experimentally available temperature/field region could be done. Also using PND, the absolute positive sign of the DMI for the Fe-Fe interaction in the Γ4 phase could be determined. One may conclude that the competition between the external magnetic field, the asymmetric DMI and the isotropic exchange interactions between the Fe and Ho sublattice and inside the Fe sublattice leads to a complex picture of phase transitions in the rare-earth orthoferrites. In $HoFeO_3$, the exchange interactions inside the Fe sublattice and the DMI order the system into the magnetic phase Γ4 at room temperature. With decreasing temperature, the iron polarizes the holmium. It leads to a phase transition into the magnetic phase Γ1. External magnetic fields change this energy balance and break the magnetic symmetry such that a new intermediate phase appears. This complex behavior might cause the useful functionality observed in the rare-earth orthoferrites.

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