Доказательство антисимметричного обмена в $TbMn_2O_5$: *дифракция поляризованных нейтронов*

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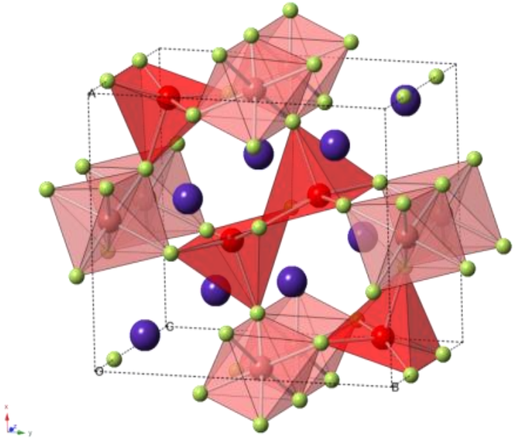
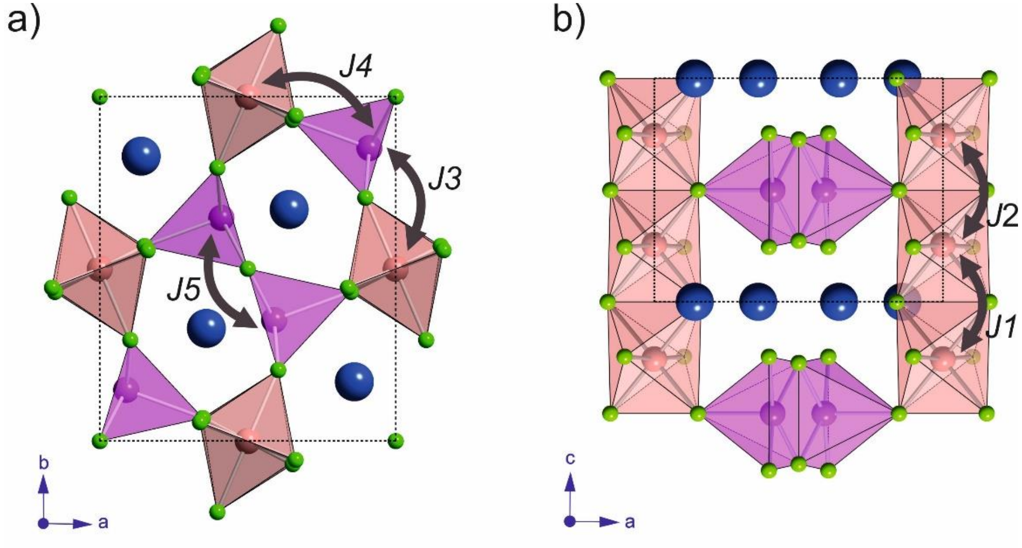
Magnetic multiferroics RMn_2O_5 - R = Tb, Yb, Y, Dy, Er, Eu...

Space group ***Pbam*** (?)





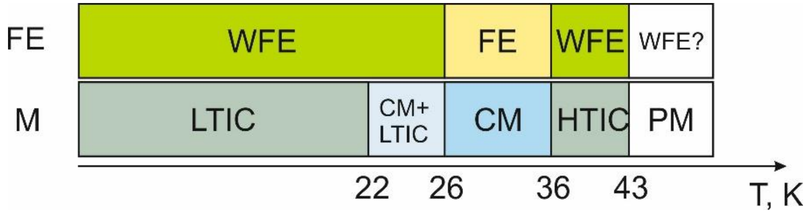
Superexchange
$\mathbf{H_{12} = -J(S_1 \cdot S_2)}$

J3, J4, J5 – in plane ***ab***
J3, J4 – $\mathbf{Mn^{4+}}$ - $\mathbf{Mn^{3+}}$
J5 – $\mathbf{Mn^{3+}}$ - $\mathbf{Mn^{3+}}$

J1 **and** ***J2*** along ***c***
$\mathbf{Mn^{4+}}$ - $\mathbf{Mn^{4+}}$

Exchange frustrated system

$TbMn_2O_5$



$\boldsymbol{k} = (0.5-\delta_x, 0, 0.25+\delta_z)$

Polarization neutron scattering without analysis (PND), DPN PNPI

Helical structure

$\boldsymbol{M}(\boldsymbol{r_n}) = \boldsymbol{u}\mu_u\cos(\boldsymbol{r_n}\cdot\boldsymbol{k}) + \boldsymbol{v}\mu_v\sin(\boldsymbol{r_n}\cdot\boldsymbol{k})$

$\boldsymbol{m} = [\boldsymbol{u}\times\boldsymbol{v}]$ – helix vector

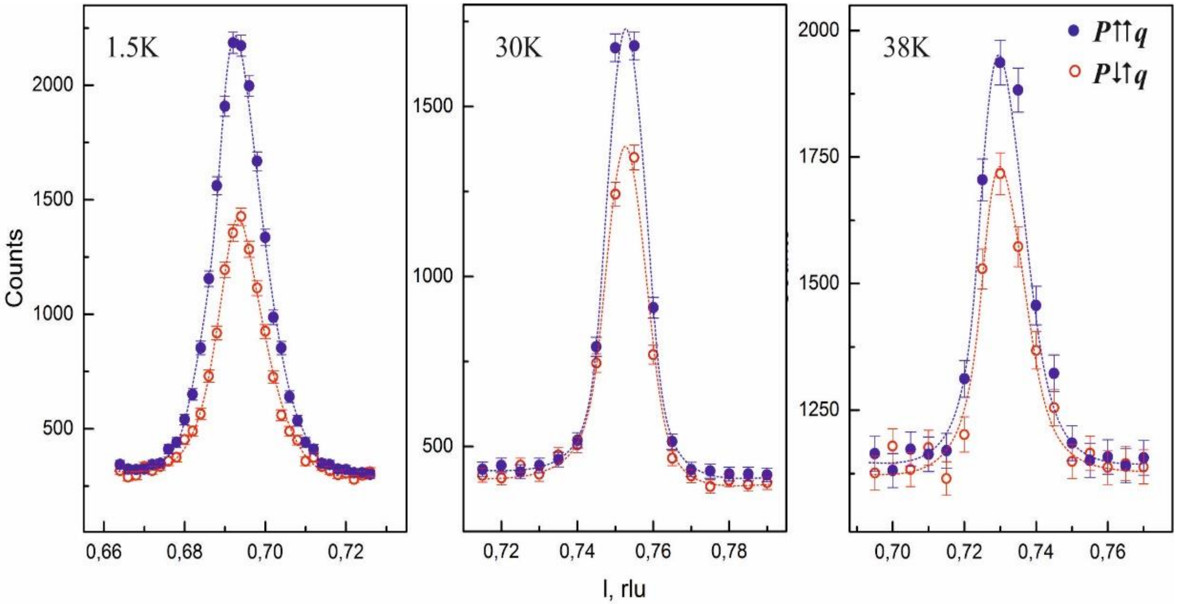
$$I(\boldsymbol{k}) \sim F^2(\boldsymbol{q})\frac{1}{4}[1+(\boldsymbol{em})^2 \pm 2(\boldsymbol{em})(\boldsymbol{eP})(n_r - n_l)]\boldsymbol{\delta}(\boldsymbol{q}-\boldsymbol{\tau}\pm\boldsymbol{k})$$

n_r - portion of “right” domains, n_l - portion of “right” domains

Measurement of satellites with $\boldsymbol{k}_1 = (k_x\ 0\ k_z)$ and $\boldsymbol{k}_2 = (k_x\ 0\ \text{-}k_z)$

$\lambda = 2.08$Å

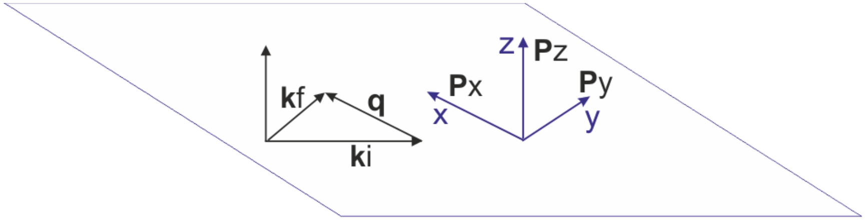
(1 0 1)-$\boldsymbol{k}_1$



$n_r \approx 0.75(5)$
$n_l \approx 0.25\ (5)$

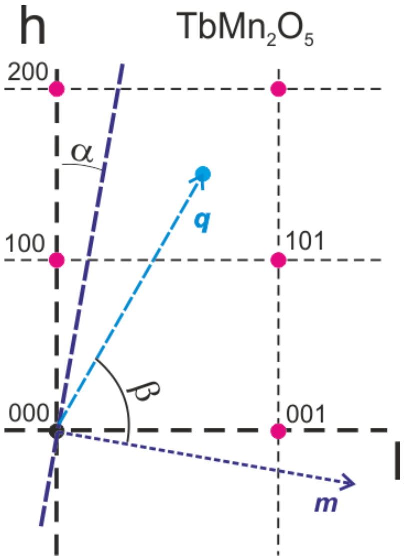
Ratio between domains with “right” and “left” helices remains approximately the same for all temperatures of measurements.

XYZ polarization analysis, DPN PNPI



$\boldsymbol{v} \parallel \boldsymbol{b} \parallel \boldsymbol{z}$

$\boldsymbol{u}$ – in horizontal plane



$I_x^{SF} \sim M_{ch\perp} \cdot n_r + \mu_u^2 cos^2\beta + \mu_v^2$ $\quad I_y^{SF} \sim \mu_v^2$ $\quad I_z^{SF} \sim \mu_u^2 cos^2\beta$

$I_x^{NSF} \sim M_{ch\perp} \cdot (1 - n_r)$ $\quad I_y^{NSF} \sim \mu_u^2 cos^2\beta$ $\quad I_z^{NSF} \sim \mu_v^2$

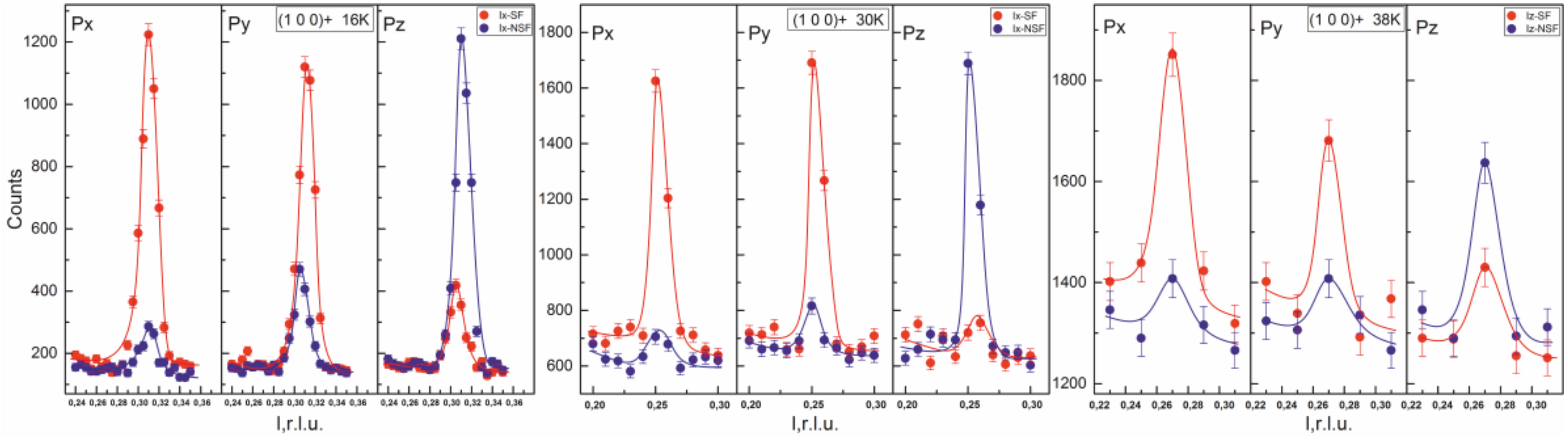
$M_{ch\perp} = \mu_u \mu_v [\boldsymbol{u} \times \boldsymbol{v}]_x$

β – angle between helix vector $\boldsymbol{m}$ and scattering vector $\boldsymbol{q}$

α – angle between helix plane and *ab* crystal plane

Measurement of satellites with k $_1$ = (k_x 0 k_z) and $\boldsymbol{k}_2$ = (k_x 0 -k_z)

λ = 2.08Å



XYZ polarization analysis

I^{SF}/I^{NSF} for magnetic satellites (1 0 0)+$\boldsymbol{k}_1$ and (-1 0 1)-$\boldsymbol{k}_1$			
(1 0 0)+$\boldsymbol{k}_1$	16 K (LTIC)	30 K (CM)	38 K (HTIC)
$I_x^{SF}:I_x^{NSF}$	0.91(2):0.09(1)	0.93(3):0.07(3)	0.90(10):0.10(10)
$I_y^{SF}:I_y^{NSF}$	0.82(1):0.18(1)	0.84(3):0.16(2)	0.76(11):0.24(11)
$I_z^{SF}:I_z^{NSF}$	0.15(1):0.85(1)	0.11(3):0.89(4)	0.33(10):0.67(10)
(-1 0 1)-$\boldsymbol{k}_1$	16 K (LTIC)	30 K (CM)	38 K (HTIC)
$I_x^{SF}:I_x^{NSF}$	0.95(5):0.05(3)	0.94(3):0.06(2)	0.94(5):0.06(4)
$I_y^{SF}:I_y^{NSF}$	0.37(4):0.63(5)	0.22(2):0.78(3)	0.29(5):0.71(5)
$I_z^{SF}:I_z^{NSF}$	0.62(4):0.38(4)	0.79(3):0.21(2)	0.84(5):0.16(5)

In LTIC phase (T<22K) $\alpha \sim 7(1)°$**;**
tilt angle of some “average” magnetic moment *γ ~18(2)° with a-axis*

In CM (22K<T<36K), and in HTIC (36K<T<43) $\alpha \sim 4(1)°$**;**
*γ ~13(2)°, cf. G. R. Blake et al. Phys.Rev. B **71**, 214402, 2005*

In all phases

$\boldsymbol{n_r} \approx \mathbf{0.70\ (5)}$

$\boldsymbol{n_l} \approx \mathbf{0.30\ (5)}$

Spherical neutron polarimetry (SNP), POLI - MLZ

Elements of polarizing matrix, E = 0, LTIC , CM, HTIC									
5К (LTIC)	(0.49, 0, 2.31)			(0.51, 0, -2.31)			(1.49, 0, 0.31)		
	x	y	z	x	y	z	x	y	z
x	-1.04(3)			-0.81(7)			-0.87(9)		
y	-0.17(1)	0.84(2)		0.10(1)	0.78(2)		0.08(3)	-0.44(6)	
z	-0.13(1)		-0.82(2)	0.12(1)		-0.84(3)	0.09(2)		0.36(6)
30К (CM)	(0.50, 0, 2.25)			(0.50, 0, -2.25)			(1.50, 0, 0.25)		
	x	y	z	x	y	z	x	y	z
x	-1.00(4)			-1.02(5)			-1.03(2)		
y	0.04(4)	0.97(4)		0.03(4)	1.05(6)		0.09(4)	-0.75(4)	
z	-0.03(4)		-0.90(5)	0.04(4)		-1.00(6)	0.09(4)		0.70(4)
37К (HTIC)	(0.49, 0, 2.27)								
	x	y	z						
x	-0.93(5)								
y	-0.11(6)	0.96(7)							
z	0.04(2)		-0.92(2)						

$\lambda = 0.7\text{Å}, 1.14\text{Å}$

$R = \mu_u / \mu_v$ - ec

Elliptical parameter

$$\mathcal{P}_{yy} = -\mathcal{P}_{zz} \sim \frac{\mu_u{}^2 - \mu_v{}^2}{\mu_u{}^2 + \mu_v{}^2} = \frac{R^2 cos^2\beta - 1}{R^2 cos^2\beta + 1}$$

Chiral parameter

$$\mathcal{P}_{yx} = \mathcal{P}_{zx} \sim \frac{2(1 - 2n_r)\mu_u\mu_v}{\mu_u{}^2 + \mu_v{}^2} = \frac{2(1 - 2n_r)R cos\beta}{R^2 cos^2\beta + 1}$$

In LTIC phase (T<22K) $\alpha \sim 3(1)°$;
γ ~19(2)° with a-axis

In CM (22K<T<36K), and in HTIC (36K<T<43) $\alpha \sim 5(1)°$;
γ ~ 7(2)°

In all phases
$\boldsymbol{n_r} \approx \mathbf{0.62\ (3)}$
$\boldsymbol{n_l} \approx \mathbf{0.38\ (3)}$

SNP results are in good agreement with XYZ !

Spherical neutron polarimetry, electric field dependence, POLI - MLZ

Electric field dependence of chiral parameter $\mathcal{P}_{yx}$ for reflection (1 0 -2)-$\boldsymbol{k}_1$ at 7K (LTIC) and chiral population

	ZFC	FC -5kV/cm	FC +5kV/cm
$\mathcal{P}_{yx}$	0.14(1)	0.03(2)	0.09(2)
n_r	0.62(2)	0.52(3)	0.58(3)

We couldn’t change noticeably chirality parameters under reversal of the electrical field from -3kV/cm to +3kv/cm at permanent temperature 14K after cooling in zero field - chiral domains are strongly pinned.

Electric field - 3 kV (-5 kV/cm) change chiral domain population in FC mode from non-equilibrium to equal portions.

Cooling in field +5 kV/cm restores non-equality in chiral domain population.

Chirality in helical structures

Chiral sense is defined by Dzyaloshinsky-Moria interaction.

S. Maleyev, Phys. Usp. ***45****, 569, 2002*
S. Maleyev, Physica B ***350****, 26, 2004*

Regarding magnetic spiral structure as Dzyaloshinsky-Moriya helix, one could assume that direction of helix vector $\boldsymbol{m}$ coincides in direction with DM vector $\boldsymbol{D}$.

Chiral population by different methods

SNP

$n_r \approx 0.62\ (3)$
$n_l \approx 0.38\ (3)$

XYZ

$n_r \approx 0.70\ (5)$
$n_l \approx 0.30\ (5)$

PND

$n_r \approx 0.75\ (5)$
$n_l \approx 0.25\ (5)$

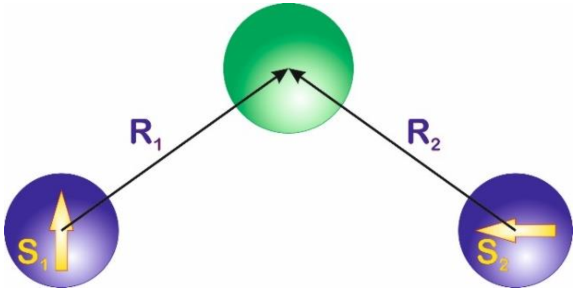
Antisymmetric exchange – Dzyaloshinsky-Moria interaction, DMI

$$V_{DM} = \mathbf{D}[\mathbf{S}_1\times\mathbf{S}_2]$$

I. Dzayloshinsky, J.Phys.Chem.Solids ***4****, 241, 1958*
T. Morya, Phys.Rev. ***120****, 91, 1960*

Antisymmetric superexchange through anion

F. Keffer, Phys.Rev. ***126****, 896, 1962*
A. S. Moskvin, I. G. Bostrem, Sov. Phys. Solid State ***19*** *1532, 1977*



$$V_{DM}=\underbrace{d(\theta)[\mathbf{R}_1\times\mathbf{R}_2]}_{}[\mathbf{S}_1\times\mathbf{S}_2];\quad d(\theta) = d_1+d_2 cos\theta$$

$$\mathbf{D} = d(\theta)[\mathbf{R}_1\times\mathbf{R}_2]$$

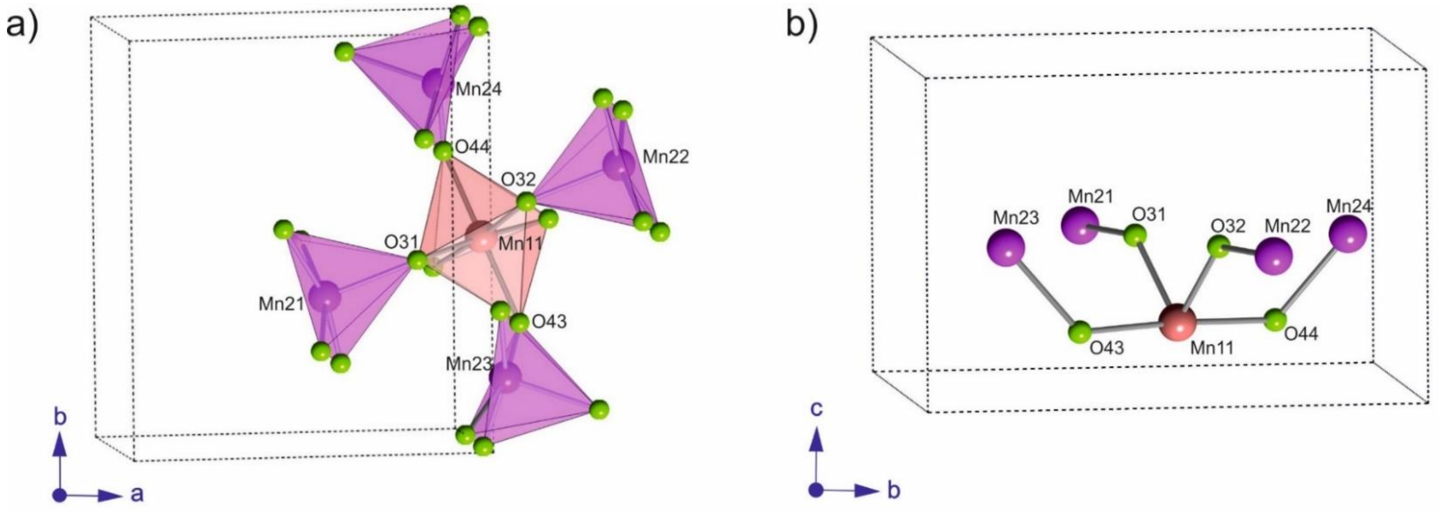
$[\mathbf{R}_1\times\mathbf{R}_2]$ - determines ***the sense*** of Dzyaloshinsky vector.

d(θ) =d1+d2(θ) determines ***the sign*** of Dzyaloshinsky vector, does not depend on the choice of ion numeration

The sign of antisymmetric exchange parameter *d(θ)* is very sensitive to the bond angle in the vicinity of some critical angle value θ_k:

$$cos\theta_k = - d_1/d_2$$

DMI in $TbMn_2O_5$



Four pairs (two sets):

$$\left.\begin{array}{l}\mathrm{Mn1\text{-}Mn21} \rightarrow \mathrm{Mn1 - O31 - Mn21}\\ \mathrm{Mn1\text{-}Mn22} \rightarrow \mathrm{Mn1 - O32 - Mn22}\end{array}\right\} d(\mathrm{s1})$$

$\Theta \sim 132^o$

$$\left.\begin{array}{l}\mathrm{Mn1\text{-}Mn23} \rightarrow \mathrm{Mn1 - O43 - Mn23}\\ \mathrm{Mn1\text{-}Mn24} \rightarrow \mathrm{Mn1 - O44 - Mn24}\end{array}\right\} d(\mathrm{s2})$$

$\Theta \sim 123^o$

$$d(\mathrm{s1}) \approx \pm\, d(\mathrm{s2})$$

for Pbam **D = 0**

$$Pbam \longrightarrow Pm,\ \gamma = 90°$$

O31, O32, O43, O44 displacements

V. Baledent et al, Phys.Rev.Lett. 114, 117601, 2015

$$\mathbf{D}/|\mathbf{D}| = \begin{array}{l}\{[\mathbf{R}_{1\text{-}31} \times \mathbf{R}_{21\text{-}31}] + \\ [\mathbf{R}_{1\text{-}32} \times \mathbf{R}_{22\text{-}32}]\} \pm \\ \{[\mathbf{R}_{1\text{-}43} \times \mathbf{R}_{23\text{-}43}] + \\ [\mathbf{R}_{1\text{-}44} \times \mathbf{R}_{24\text{-}44}]\}\end{array}$$

$\alpha(+) = 5°$
$\alpha(-) = 15°$

angle between Dzyaloshinsky vector ***D*** *and c-axis*

ВЫВОДЫ

Антисимметричное DMI-взаимодействие эффективно во всех магнитоупорядоченных фазах (HTIC, CM, LTIC) в обменно-фрустрированном $TbMn_2O_5$.
Возможность существования DMI в $TbMn_2O_5$ подтверждается анализом модели антисимметричного суперобмена для нецентросимметричной структуры *Pm*.

Приложение электрического поля приводит к изменению углов связей Mn-O, близких к критической величине θ_k, характерной для $TbMn_2O_5$. Эти изменения достаточны, чтобы изменить знак параметра антисимметричного обмена $d(\theta)$ в некоторых доменах.

Поскольку DMI-взаимодействие приводит к неравновесной заселенности киральных доменов, его можно рассматривать как причину возникновения ферроэлектричества в $TbMn_2O_5$.
Усиление электрической поляризации в соразмерной CM фазе происходит включением Гейзенберговского обменного взаимодействия.

Спасибо за внимание!