Ural Federal University

Взаимодействие Дзялошинского-Мория и другие обменно-релятивистские взаимодействия в ортоферритах-ортохромитах

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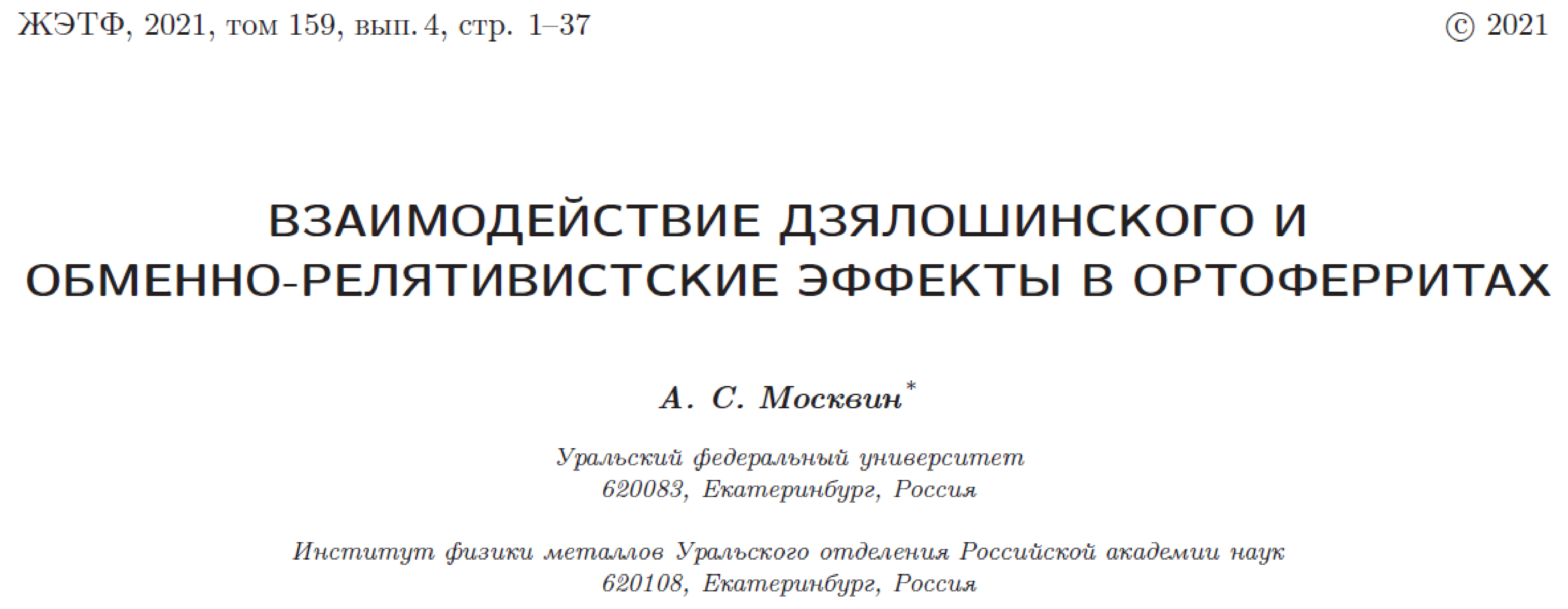

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ВЗАИМОДЕЙСТВИЕ ДЗЯЛОШИНСКОГО И ОБМЕННО-РЕЛЯТИВИСТСКИЕ ЭФФЕКТЫ В ОРТОФЕРРИТАХ

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- Dzyaloshinskii-Moriya (DM) spin coupling in its typical form

$$V_{DM}=\mathbf{D}_{12}\cdot[\mathbf{S}_1\times\mathbf{S}_2],$$

where $\mathbf{D}_{12}$ is the Dzyaloshinskii vector was introduced firstly to explain magnetic properties of weak ferromagnets.

- Weak, or parasitic ferromagnetism of natural hematite α-Fe_2O_3 was observed by Smith [Phys. Rev. **8**, 721 (1916)] almost 100 years ago in 1916 and was assigned to ferromagnetic impurities.

Outline

- Prehistory

- Weak (parasitic?) ferromagnetism
- Canted antiferromagnetism
- Thermodynamic theory by I. Dzialoshinskii
- Microscopic theory by T. Moriya

- “Ferrite epoch”
- “Cuprate epoch”

“Ferrite epoch”

- DM-coupling for S-type 3d ions
- Dzyaloshinskii vector and superexchange geometry
- Sign of the Dzyaloshinskii vector
- Weak ferro-, antiferro-, and ferri-magnetism
- Antisymmetric supertransferred hyperfine coupling
- Antisymmetric spin-other orbit coupling and circular magnetooptics

“Cuprate epoch”

- DM-coupling for Cu^{2+} - O^{2-} - Cu^{2+}
- Anionic contribution to DM coupling
- DM coupling in helimagnetic $CsCuCl_3$
- DM coupling and magnetic anisotropy
- Antiferromagnetism induced by external uniform field
- Antisymmetric exchange and multiferroicity
- “ab-initio” calculations of DM-coupling

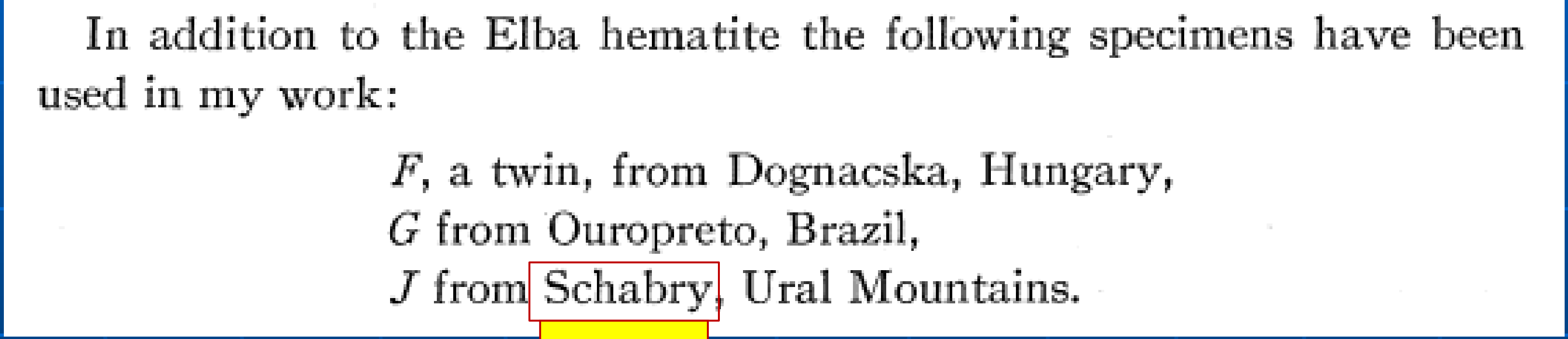
Prehistory:
Weak parasitic ferromagnetism

- T. Smith, Phys. Rev. **8**, 721 (1916) – weak ferromagnetism in natural hematite single crystals α-Fe_2O_3 .
- L. Neel and R. Pauthenet, Compt.rend., **234**, 2171, 1952 – uncompensated moment in hematite α-Fe_2O_3;
- H. Bizette and B. Tsai, Compt.rend., **241**, 369, 1955 – uncompensated moment in $MnCO_3$ oriented perpendicular to trigonal axis;
- R.A. Erickson, Phys. Rev., **90**, 779, 1953 - uncompensated moment in NiF_2;
- W.C. Koehler, O. Wollan, J. Phys. Chem. Solids, **2**, 100, 1957 - uncompensated moment in orthoferrites $RFeO_3$ and orthochromites $RCrO_3$;
- **L.M. Mataresse, J.W. Stout, Phys. Rev., 94, 1792 (1954). – “cocking” of magnetic sublattices in NiF_2**
- L. Neel, Rev. Mod. Phys., 25, 58 (1953).
- P.W. Anderson, F.R. Merritt, J.P. Remeika, W.A. Yager, Phys. Rev., 93, 717 (1954).
- H.M.A. Urquhart, J.E. Goldman, Phys. Rev., 101, 1443 (1956).
- **A.S. Borovik-Romanov and M.P. Orlova, ZhETP, 31, 579, 1956 (Sov.Phys.JETP, 4, 531, 1957) - uncompensated moment in $MnCO_3$ and $CoCO_3$ due to an overt canting of magnetic sublattices;**

T. Smith, Phys. Rev. **8**, 721 (1916)

THE MAGNETIC PROPERTIES OF HEMATITE.[1]

By T. Townsend Smith.

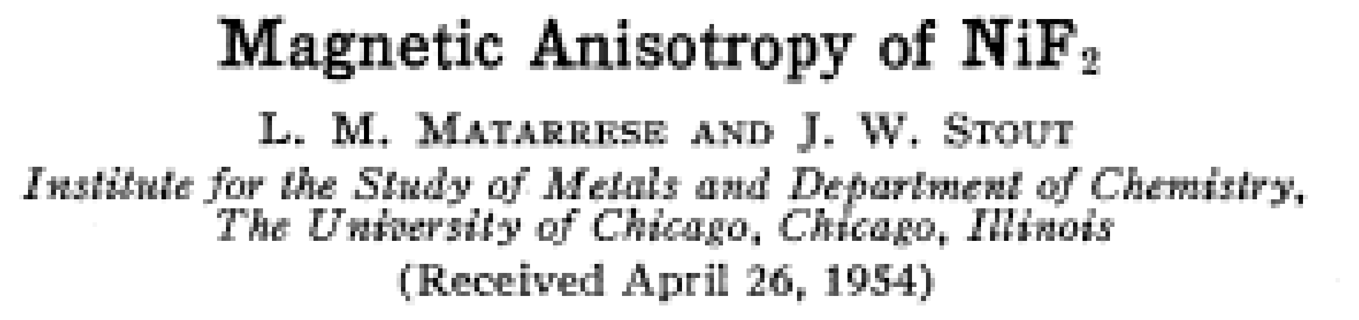


In addition to the Elba hematite the following specimens have been used in my work:

F, a twin, from Dognacska, Hungary,
G from Ouropreto, Brazil,
J from Schabry, Ural Mountains.

Schabry is a small village near Ekaterinburg, my hometown

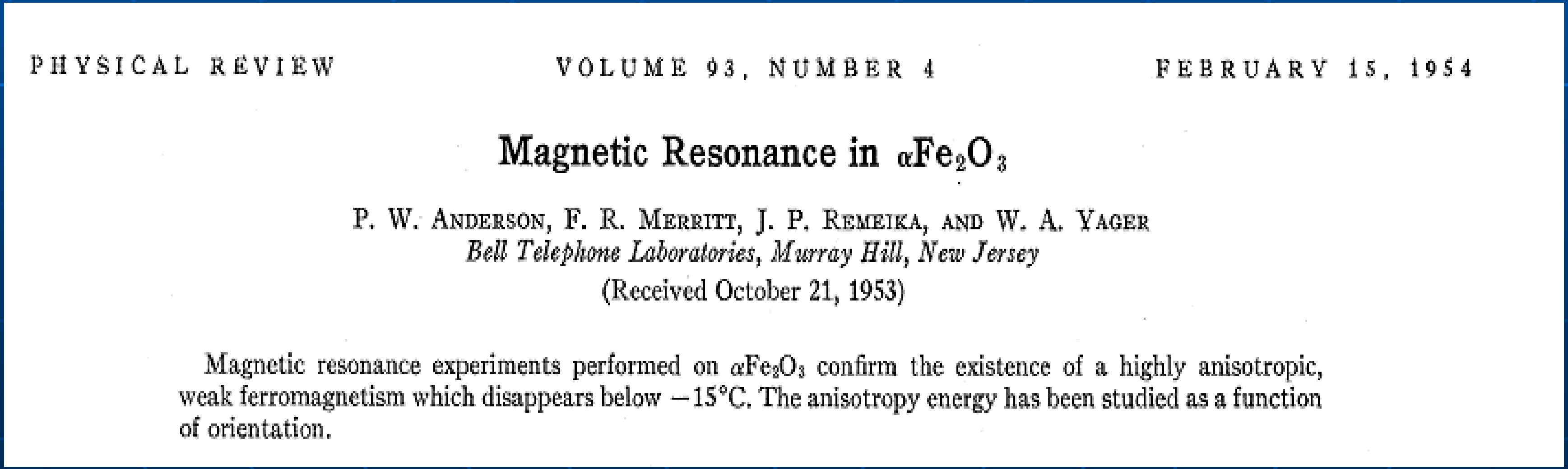
Cocking of magnetic sublattices



Magnetic Anisotropy of NiF_2

L. M. Matarrese and J. W. Stout
Institute for the Study of Metals and Department of Chemistry,
The University of Chicago, Chicago, Illinois

(Received April 26, 1954)



PHYSICAL REVIEW VOLUME 93, NUMBER 4 FEBRUARY 15, 1954

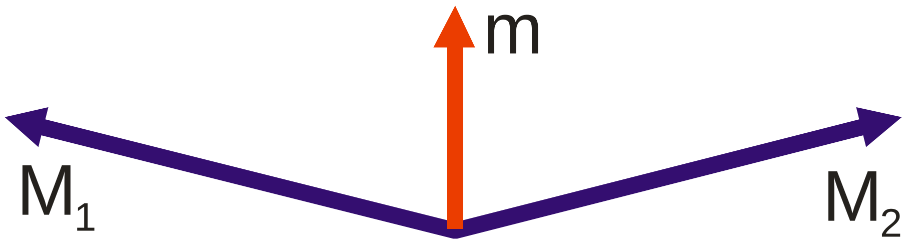
Magnetic Resonance in αFe_2O_3

P. W. Anderson, F. R. Merritt, J. P. Remeika, and W. A. Yager
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received October 21, 1953)

Magnetic resonance experiments performed on αFe_2O_3 confirm the existence of a highly anisotropic, weak ferromagnetism which disappears below −15°C. The anisotropy energy has been studied as a function of orientation.

Model of canted antiferromagnet became the leading model of a weak ferromagnet



$m=M_1+M_2$ - ferromagnetic vector
$l=M_1-M_2$- antiferromagnetic vector

- **A.S. Borovik-Romanov and M.P. Orlova, ZhETP, 31, 579, 1956 (Sov.Phys.JETP, 4, 531, 1957)**

Large variety of weak ferro- and antiferromagnets

- α-Fe_2O_3, $MnCO_3$, $MnCO_3$, $CoCO_3$, NiF_2, $RFeO_3$, $RCrO_3$, FeF_3, $FeBO_3$, CoF_2, β-MnS, MnSi, $CuCl_2\cdot 2H_2O$, La_2CuO_4, $Ba_3Cu_2O_4Cl_2$, $Ba_2CuGe_2O_7$, $NaCu_2O_2$, $CsCuCl_3$, $K_2V_3O_8$, Yb_4As_3, Cu benzoate, magnetic molecules (Mn_{12},…), …….

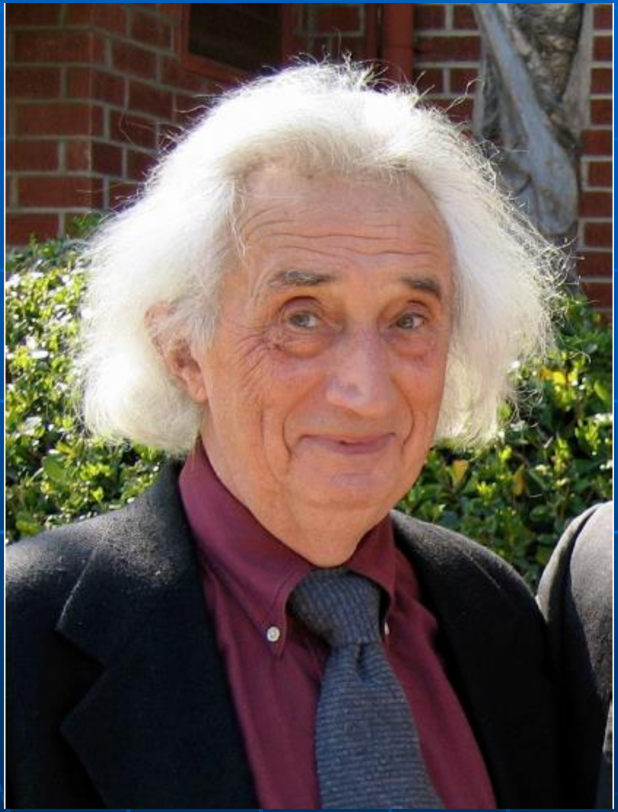
Thermodynamic Theory of “Weak” Ferromagnetism In Antiferromagnetic Substances

I. E. Dzialoshinskii

Soviet Physics JETP, Vol.5, 1259, 1957

- A thermodynamic theory of “weak” ferromagnetism in α-Fe_2O_3, $MnCO_3$, and $CoCO_3$ is developed on the basis of Landau’s theory of phase transitions of the second kind. It is shown that “weak” ferromagnetism is due to relativistic spin-lattice interaction and magnetic dipole interaction. A strong dependence of the properties of such “weak” ferromagnetics upon the magnetic symmetry of the crystal is noted. Their behavior in an external magnetic field is studied.

Игорь Дзялошинский



01.02.1931-14.07.2021

Андрей Боровик-Романов

18.03.1920-31.07.1997

Free energy of the two-sublattice uniaxial weak ferromagnet such as α-Fe_2O_3, $MnCO_3$, $CoCO_3$, $FeBO_3$ was shown to be written as follows

$$\begin{aligned} F &= MH_E(\boldsymbol{m}_1 \cdot \boldsymbol{m}_2) - M\boldsymbol{H}_0(\boldsymbol{m}_1 + \boldsymbol{m}_2) + E_D + E_A \\ &= MH_E(\boldsymbol{m}^2 - \boldsymbol{l}^2) - M\boldsymbol{H}_0\boldsymbol{m} + E_D + E_A \end{aligned}$$

$$E_D = -MH_D[\boldsymbol{m}_1 \times \boldsymbol{m}_2]_z = 2MH_D[\boldsymbol{m} \times \boldsymbol{l}]_z = 2MH_D(m_x l_y - m_y l_x)$$

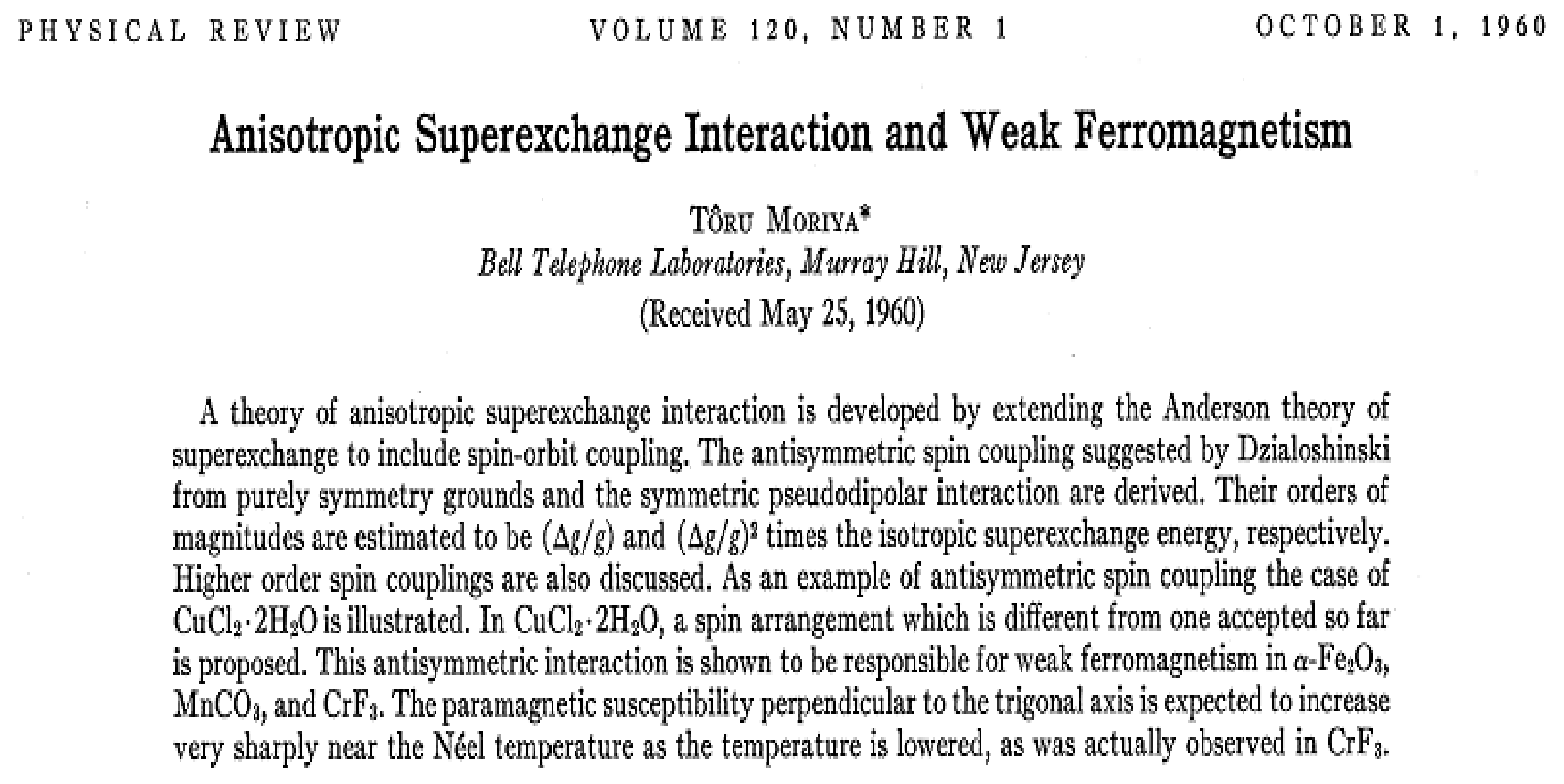
$$E_A = \frac{1}{2M}H_A(m_{1z}^2 + m_{2z}^2) = \frac{1}{M}H_A(m_z^2 + l_z^2)$$

H_E is exchange field; H_D is Dzyaloshinskii field; H_A is anisotropy field

Dzyaloshinskii interaction for orthorhombic orthoferrites $RFeO_3$ and orthochromites $RCrO_3$ includes both antisymmetric and symmetric terms

$$
\begin{aligned}
E_D &= d_1 m_z l_x + d_2 m_x l_z \\
&= \frac{d_1 - d_2}{2}(m_z l_x - m_x l_z) + \frac{d_1 + d_2}{2}(m_z l_x + m_x l_z) \\
&= -2MH_D[\mathbf{m} \times \mathbf{l}]_y + \frac{d_1 + d_2}{2}(m_z l_x + m_x l_z),
\end{aligned}
$$

Moriya theory



PHYSICAL REVIEW VOLUME 120, NUMBER 1 OCTOBER 1, 1960

Anisotropic Superexchange Interaction and Weak Ferromagnetism

TÔRU MORIYA*
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received May 25, 1960)

A theory of anisotropic superexchange interaction is developed by extending the Anderson theory of superexchange to include spin-orbit coupling. The antisymmetric spin coupling suggested by Dzialoshinski from purely symmetry grounds and the symmetric pseudodipolar interaction are derived. Their orders of magnitudes are estimated to be $(\Delta g/g)$ and $(\Delta g/g)^2$ times the isotropic superexchange energy, respectively. Higher order spin couplings are also discussed. As an example of antisymmetric spin coupling the case of $CuCl_2 \cdot 2H_2O$ is illustrated. In $CuCl_2 \cdot 2H_2O$, a spin arrangement which is different from one accepted so far is proposed. This antisymmetric interaction is shown to be responsible for weak ferromagnetism in α-Fe_2O_3, $MnCO_3$, and CrF_3. The paramagnetic susceptibility perpendicular to the trigonal axis is expected to increase very sharply near the Néel temperature as the temperature is lowered, as was actually observed in CrF_3.

Anisotropic Superexchange Interaction and Weak Ferromagnetism

Toru Moriya

Phys. Rev., **120**, 91, 1960

- A theory of anisotropic superexchange interaction is developed by extending the Anderson theory of superexchange to include spin-orbital coupling. The antisymmetric spin coupling suggested by Dzialoshinskii from purely symmetry grounds and the symmetric pseudodipolar interaction are derived. Their orders of magnitudes are estimated to be $(\Delta g/g)$ and $(\Delta g/g)^2$ times the isotropic superexchange energy, respectively. … This antisymmetric interaction is shown to be responsible for weak ferromagnetism in α-Fe_2O_3, $MnCO_3$, and CrF_3 ….

Dzyaloshinskii-Moriya antisymmetric exchange interaction:

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

$$\alpha\text{-}Fe_2O_3\text{: } \mathbf{D} \parallel C_3 \text{ and } V_{DM} \rightarrow D(m_x l_y - m_y l_x)$$

Elements of Moriya’s theory

- Moriya starts with a single electron Hamiltonian

$$\hat{H} = \sum_{\vec{R}m\sigma} \varepsilon_m(\vec{R}) a^{\dagger}_{m\sigma}(\vec{R}) a_{m\sigma}(\vec{R}) + \sum_{\vec{R}\neq\vec{R}^{'},mn\sigma} t_{mn}(\vec{R}-\vec{R}^{'}) a^{\dagger}_{m\sigma}(\vec{R}) a_{n\sigma}(\vec{R}^{'})$$

$$+ \sum_{\vec{R}\neq\vec{R}^{'},\sigma\sigma^{'}} a^{\dagger}_{m\sigma}(\vec{R})[\vec{C}_{mn}(\vec{R}-\vec{R}^{'})\cdot\vec{\sigma}]a_{n\sigma^{'}}(\vec{R}^{'})$$

- where

$$\vec{C}_{mn}(\vec{R}-\vec{R}^{'}) = -\frac{\lambda}{2}\sum_{k}\frac{\vec{L}_{mk}}{\varepsilon_k} t_{kn}(\vec{R}-\vec{R}^{'})$$

is a spin-orbital correction to transfer integral, then calculates kinetic exchange

Crystal symmetry and Dzyaloshinskii vector (Moriya rules)

- Let two ions 1 and 2 are located at the points A and B, respectively, with C point bisecting the AB line:

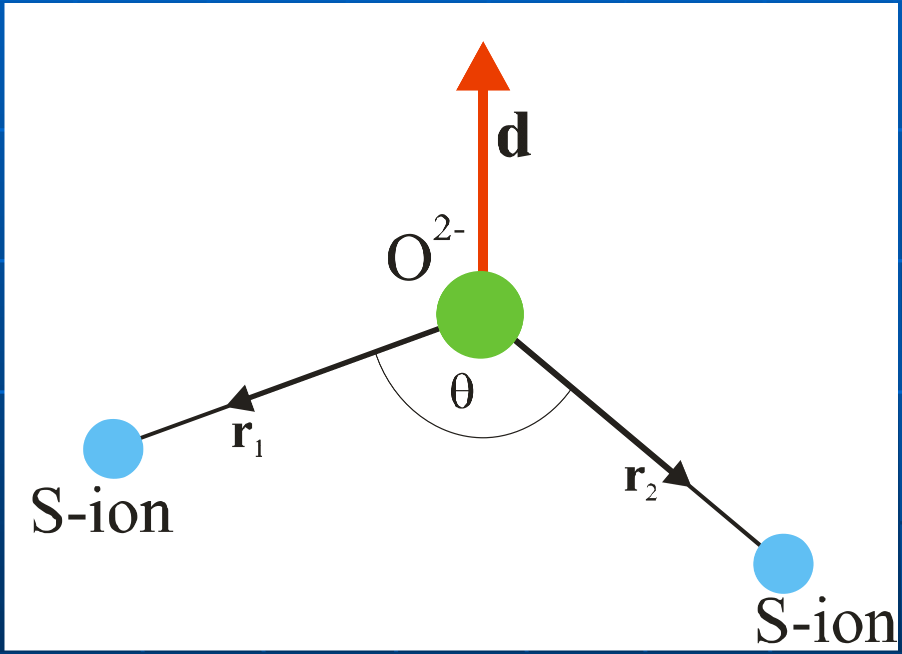
1. When C is a center of inversion: **D**=0.
2. When a mirror plane ⊥ AB passes through C,
   D || mirror plane or **D** ⊥ AB.
3. When there is a mirror plane including A and B,
   D ⊥ mirror plane.
4. When a twofold rotation axis ⊥ AB passes through C,
   D ⊥ twofold axis.
5. When there is an *n*-fold axis (*n*≥2) along AB, **D** ||AB.

Antisymmetric exchange = exchange-relativistic interaction

$$\hat{V}_{DM} = \sum_{ES} \frac{\langle GS | V_{SO} V_{ex} + V_{ex} V_{SO} | GS \rangle}{\Delta E}$$

$$\vec{S}_1 \left(\vec{S}_1 \cdot \vec{S}_2 \right) + \left(\vec{S}_1 \cdot \vec{S}_2 \right) \vec{S}_2 = -i \left[\vec{S}_1 \times \vec{S}_2 \right]$$

Dzyaloshinskii vector and superexchange geometry

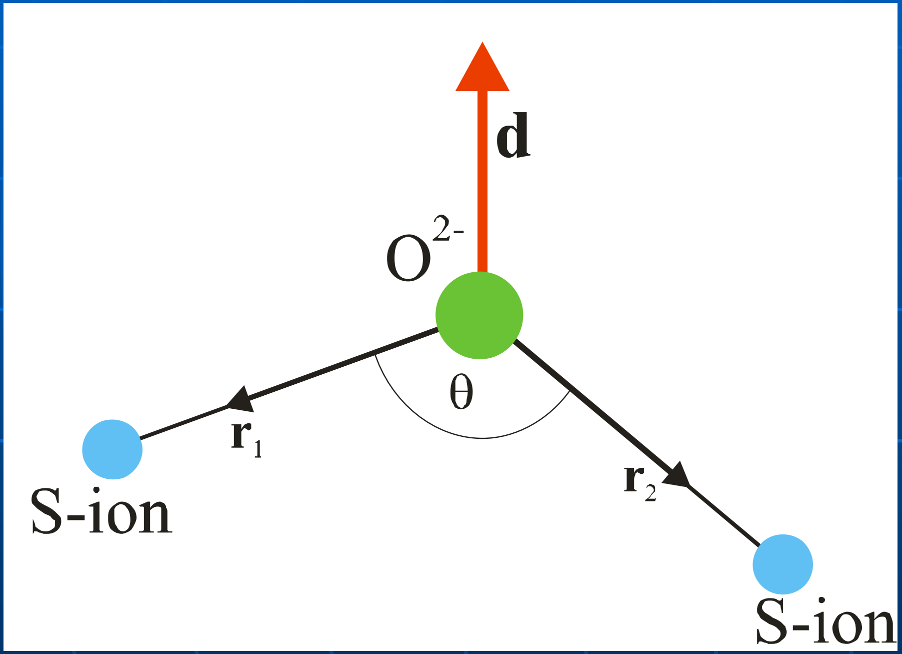


Moriya’s symmetry rules provide a phenomenological relation:

$$\mathbf{d} \propto [\mathbf{r}_1 \times \mathbf{r}_2]$$

proposed by F. Keffer
(Phys. Rev. **126**, 896 (1962))

Dzyaloshinskii vector and superexchange geometry

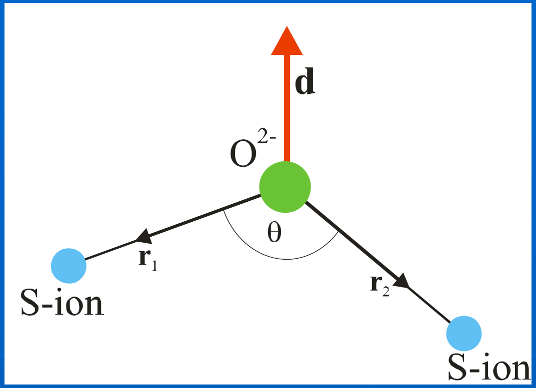


Microscopic theory:

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

only for S-type ions!

A.S. Moskvin, Soviet Phys. Solid State, 12, 2593 (1971)



For S-type 3d-ions

($3d^{3,5,8}$ – Cr^{3+}, Mn^{4+}, Mn^{2+}, Fe^{3+}, Ni^{2+})

- **Antisymmetric DM coupling**

$$V_{DM} = \vec{d}_{12}(\theta) \cdot \left[\vec{S}_1 \times \vec{S}_2 \right]$$

Isotropic Heisenberg exchange

$$H_{iso} = -2J_{12}\left(\vec{S}_1 \cdot \vec{S}_2 \right)$$

$$J_{12} = \alpha + \beta \cdot \cos\theta + \gamma \cdot \cos^2\theta$$

- **Dzyaloshinskii vector**

$$\vec{d}_{12}(\theta) = d_{12}(\theta) \cdot \left[\vec{r}_1 \times \vec{r}_2 \right]$$

- **Dzyaloshinskii factor**

$$d_{12}(\theta) = d'_{12} + d''_{12} \cos\theta$$

A.S. Moskvin, Soviet Phys. Solid State, 1971; A.S. Moskvin & E.V. Sinitsyn, Soviet Phys. Solid State, 1972; A.S. Moskvin & I.G. Bostrem, Soviet Phys. Solid State, 1977.

Superexchange geometry and isotropic Heisenberg exchange

$$H_{iso} = -2J_{12}\left(\vec{S}_1 \cdot \vec{S}_2\right)$$

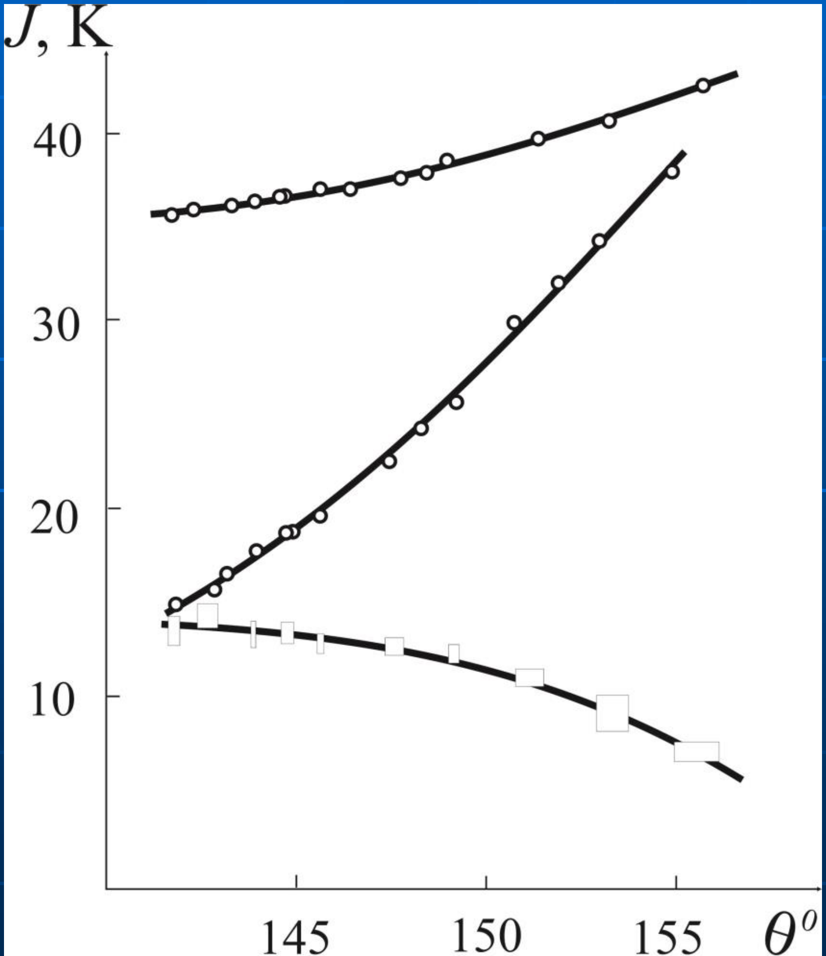
- For S-type 3d-ions

$$J_{12} = \alpha + \beta \cdot \cos\theta + \gamma \cdot \cos^2\theta$$

- For $3d^5$-$3d^5$ pair (Fe^{3+}-Fe^{3+}, Mn^{2+}-Mn^{2+})

$$J_{12} = -\frac{1}{25}\left[\frac{\left(t_{ss} + t_{\sigma\sigma}\cos\theta\right)^2}{U} + \frac{2t_{\sigma\pi}^2 \sin^2\theta}{U} + \frac{t_{\pi\pi}^2\left(2 - \sin^2\theta\right)}{U}\right]$$

Angular dependence of Fe-Fe, Cr-Cr, and Fe-Cr superexchange



A. S. Moskvin, N. S. Ovanesyan, and V. A. Trukhtanov, Angular dependence of the superexchange interaction Fe^{3+}-O^{2-}-Cr^{3+}, Hyperfine Interactions, 1, 265, 1975

$$V_{DM} = \vec{d}_{12}(\theta) \cdot \left[\vec{S}_1 \times \vec{S}_2\right]$$

$$\vec{d}_{12}(\theta) = d_{12}(\theta) \cdot \left[\vec{r}_1 \times \vec{r}_2\right]$$

$$d_{12}(\theta) = d'_{12} + d''_{12} \cos\theta$$

Dzyaloshinskii factor does not depend on the choice of 1-2 ion numeration and has a certain sign!

Dzyaloshinskii factor for S-type ions

$$\hat{V}_{DM} = \sum_{ES} \frac{\langle GS | V_{SO} V_{ex} + V_{ex} V_{SO} | GS \rangle}{\Delta E}$$

$$d_{12}(\theta) = X_1 Y_2 + X_2 Y_1$$

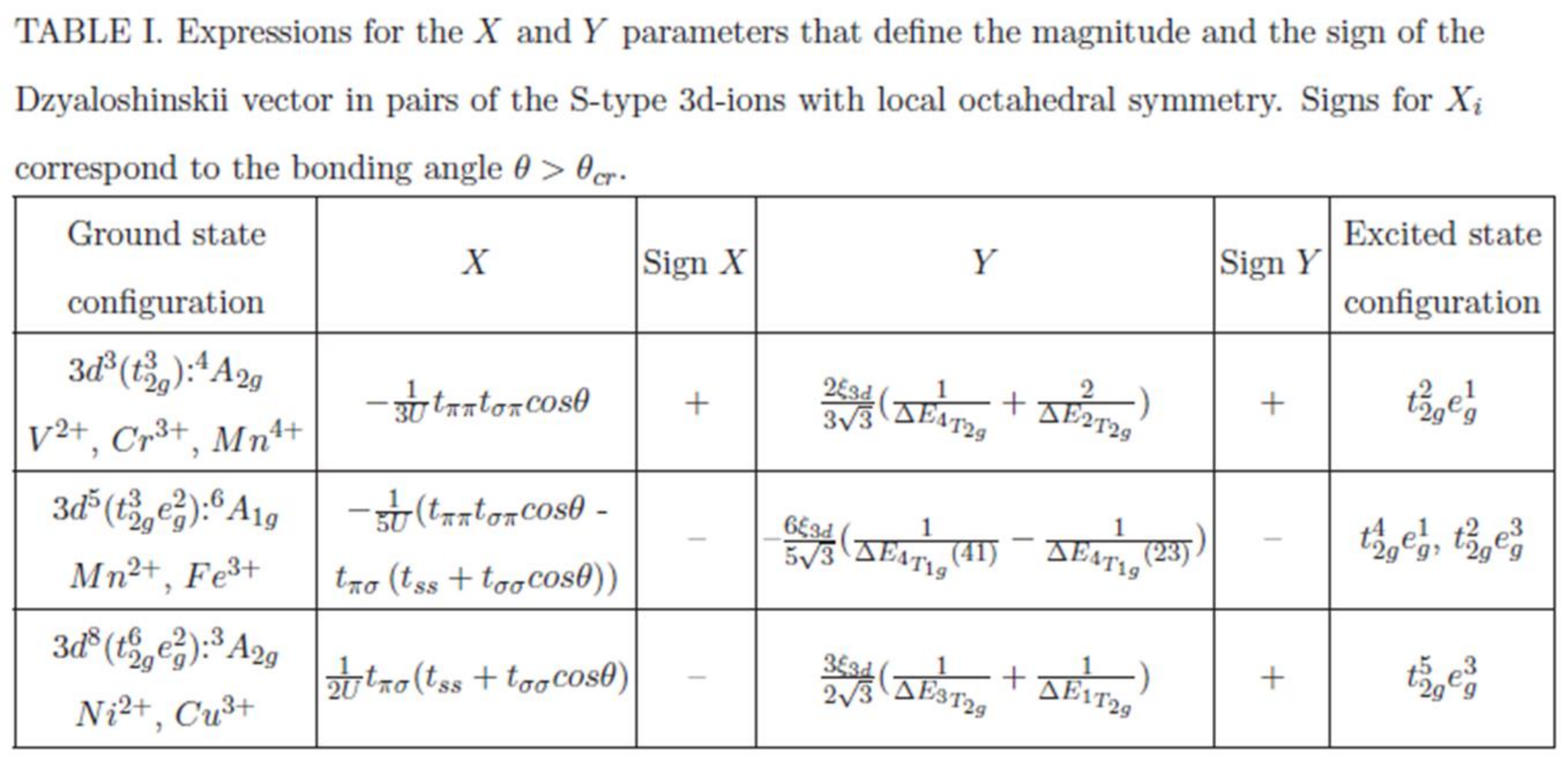


TABLE I. Expressions for the X and Y parameters that define the magnitude and the sign of the Dzyaloshinskii vector in pairs of the S-type 3d-ions with local octahedral symmetry. Signs for X_i correspond to the bonding angle $\theta > \theta_{cr}$.

Ground state configuration	X	Sign X	Y	Sign Y	Excited state configuration
$3d^3(t_{2g}^3)$:$^4A_{2g}$ V^{2+}, Cr^{3+}, Mn^{4+}	$-\frac{1}{3U} t_{\pi\pi} t_{\sigma\pi} cos\theta$	+	$\frac{2\xi_{3d}}{3\sqrt{3}}(\frac{1}{\Delta E_{^4T_{2g}}} + \frac{2}{\Delta E_{^2T_{2g}}})$	+	$t_{2g}^2 e_g^1$
$3d^5(t_{2g}^3 e_g^2)$:$^6A_{1g}$ Mn^{2+}, Fe^{3+}	$-\frac{1}{5U}(t_{\pi\pi} t_{\sigma\pi} cos\theta$ - $t_{\pi\sigma}(t_{ss} + t_{\sigma\sigma} cos\theta))$	–	$-\frac{6\xi_{3d}}{5\sqrt{3}}(\frac{1}{\Delta E_{^4T_{1g}}(41)} - \frac{1}{\Delta E_{^4T_{1g}}(23)})$	–	$t_{2g}^4 e_g^1$, $t_{2g}^2 e_g^3$
$3d^8(t_{2g}^6 e_g^2)$:$^3A_{2g}$ Ni^{2+}, Cu^{3+}	$\frac{1}{2U} t_{\pi\sigma}(t_{ss} + t_{\sigma\sigma} cos\theta)$	–	$\frac{3\xi_{3d}}{2\sqrt{3}}(\frac{1}{\Delta E_{^3T_{2g}}} + \frac{1}{\Delta E_{^1T_{2g}}})$	+	$t_{2g}^5 e_g^3$

The formulas provide a basis for reliable estimates of the value and sign for the Dzyaloshinskii vector. We argue that the Moriya's estimation for the Dzyaloshinskii vector:

$$d \approx (\Delta g/g)J$$

seems to be an oversimplification

The sign of the Dzyaloshinskii factor/vector in the pair of S-type 3d-ions (A.S. Moskvin, 1977)

$$d_{12}(\theta) = d'_{12}(R) + d''_{12}(R)\cos\theta$$

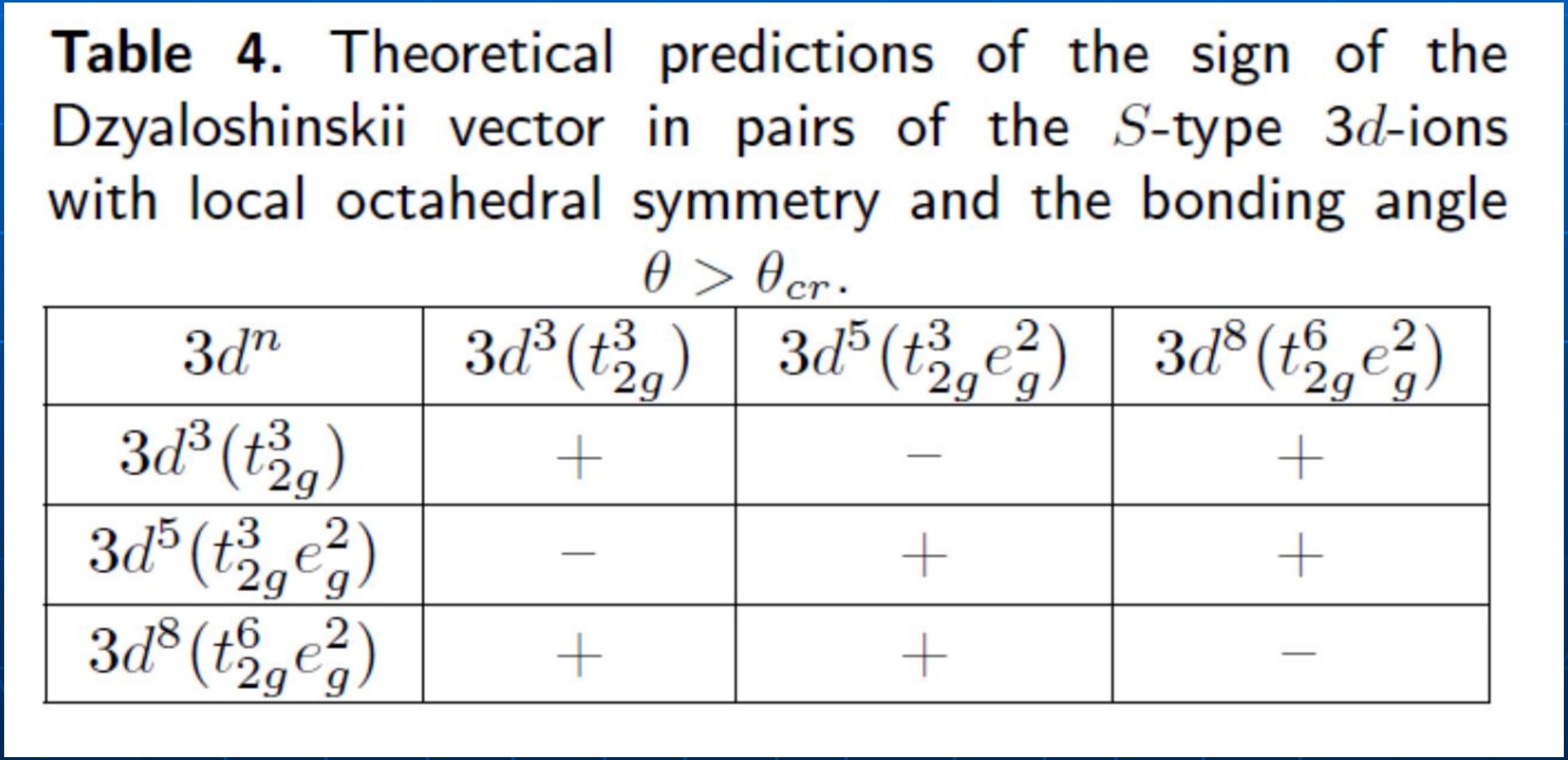


Table 4. Theoretical predictions of the sign of the Dzyaloshinskii vector in pairs of the S-type $3d$-ions with local octahedral symmetry and the bonding angle $\theta > \theta_{cr}$.

$3d^n$	$3d^3(t_{2g}^3)$	$3d^5(t_{2g}^3e_g^2)$	$3d^8(t_{2g}^6e_g^2)$
$3d^3(t_{2g}^3)$	$+$	$-$	$+$
$3d^5(t_{2g}^3e_g^2)$	$-$	$+$	$+$
$3d^8(t_{2g}^6e_g^2)$	$+$	$+$	$-$

This table allowed us to predict a new class of mixed 3d systems with competing signs of the Dzyaloshinskii vector, so called weak ferrimagnets!

Let turn to determination of the sign of the Dzyaloshinskii vector...

V.I. Ozhogin et al. in 1968 were the first who raised the issue of the sign of the Dzyaloshinskii vector

V.I. Ozhogin, S.S. Yakimov, R.A. Voskanyan, and V.Ya. Gamlitskii,

Pisma Zh. Eksp. Teor. Fiz. 8, 256 (1968) [JETP Lett. 8, 157 (1968)].

Валерий Ожогин первым поставил вопрос об экспериментальном определении знака вектора Дзялошинского

05.03.1937 – 27.09.2016

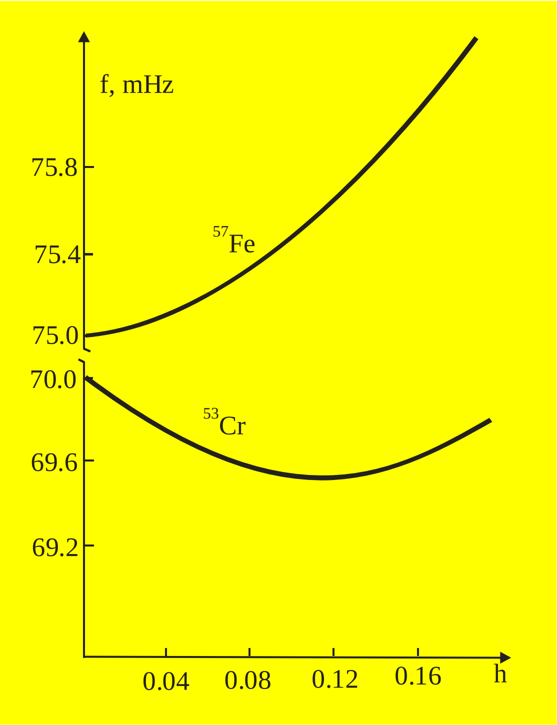
Positive muons in orthoferrites as a tool to examine the sign of Dzyaloshinskii vector

(E. Holzschuh, A. B. Denison, W. Kundig, P. F. Meier, and B. D. Patterson, Phys. Rev. B 27, 5294 (1983)).

$$\mathbf{H}(\mathbf{r}_\mu) = \sum_j \left(\frac{3\mathbf{r}_{\mu j}(\mathbf{M}_j \cdot \mathbf{r}_{\mu j})}{r_{\mu j}^5} - \frac{\mathbf{M}_j}{r_{\mu j}^3} \right),$$

$$H(\mathbf{r}_\mu) = \frac{8\pi}{3} \mu_B \rho_s(\mathbf{r}_\mu)$$

Field dependence of the NMR frequencies in ferrites-chromites $RFe_{1-x}Cr_xO_3$ ($x<<1$) as a way to compare relative signs of DM coupling Fe-Fe and Cr-Fe



$$^{57}f(h) = {}^{57}f(0)\left[1+F_z h+\frac{1}{2}h^2\right];$$

$$^{53}f(h) = {}^{53}f(0)\left[1+(2\delta-1)F_z h+\frac{1}{2}h^2\right];$$

$$^{53}f_{\min} = {}^{53}f(0)\left[1-\frac{(2\delta-1)^2}{2}F_z^{\,2}\right];\ h_{\min}=(1-2\delta)F_z\,;$$

$$h = H/H_{loc}; \quad \delta = \frac{d_{CrFe}/I_{CrFe}}{d_{FeFe}/I_{FeFe}} \quad .$$

The ligand NMR in weak ferromagnets as an effective tool to study the DM coupling and to find the absolute sign of the Dzyaloshinskii vector

Local field on the ligand nucleus is a sum of ferro- and antiferromagnetic terms

$$\vec{H}_n = A_F \vec{F} + \overleftrightarrow{A}_G \vec{G}$$

A_F – isotropic hyperfine coupling constant

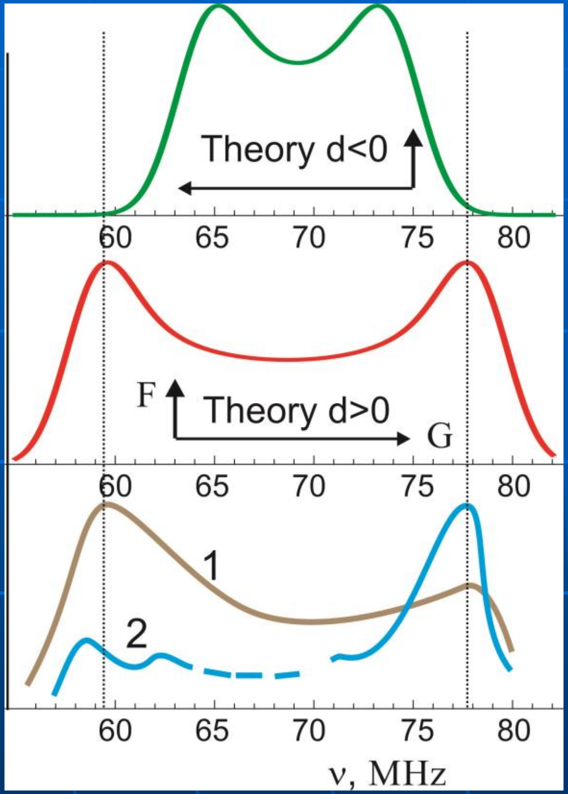
A_G – anisotropic hyperfine coupling tensor

NMR frequency depends on the sign of the Dzyaloshinskii vector

$$\nu_{NMR} = \left[A_F{}^2 \vec{F}^2 + \left(\overleftrightarrow{A}_G \vec{G}\right)^2 + 2A_F \vec{F}\overleftrightarrow{A}_G \vec{G}\right]^{\frac{1}{2}}$$

because of $\vec{F}\overleftrightarrow{A}_G \vec{G}$ depends on the mutual orientation of the F and G vectors. It should be noted that $\overleftrightarrow{A}_G \vec{G}$ does not change sign after the sublattice renumeration

First time determination of the sign of the Dzyaloshinskii vector



^{19}F NMR spectrum in FeF_3:

1. A.V. Zalesskii V.V. Vanchikov, V.G. Krivenko, A.N. Ivashchenko, Phys. St. Sol. (a) 54, 471-476 (1979)
2. M.P. Petrov, P.A. Paugurt, G.A. Smolenskii , Pisma ZHETPH, 15, 305-307 (1972)

- A.S. Moskvin, Sov. Phys. Solid State **32**, 959 (1990)

- **Analysis of ^{19}F NMR data in weak ferromagnet FeF_3 points to $d(\theta)>0$ for Fe^{3+}- F^- - Fe^{3+} superexchange.**
- **Theoretical calculations are performed at A_p=21 MHz, A_s=70 MHz**

Recent papers on the sign of the Dzyaloshinskii vector

1. V.E. Dmitrienko, E.N. Ovchinnikova, J. Kokubun, K. Ishida, JETP Lett. 92, 383 (2010).
2. V.E. Dmitrienko, E.N. Ovchinnikova, S.P. Collins, G. Nisbet, G. Beutier, Y.O. Kvashnin, V.V. Mazurenko, A.I. Lichtenstein, and M.I. Katsnelson, Nature Physics 10, 202 (2014).

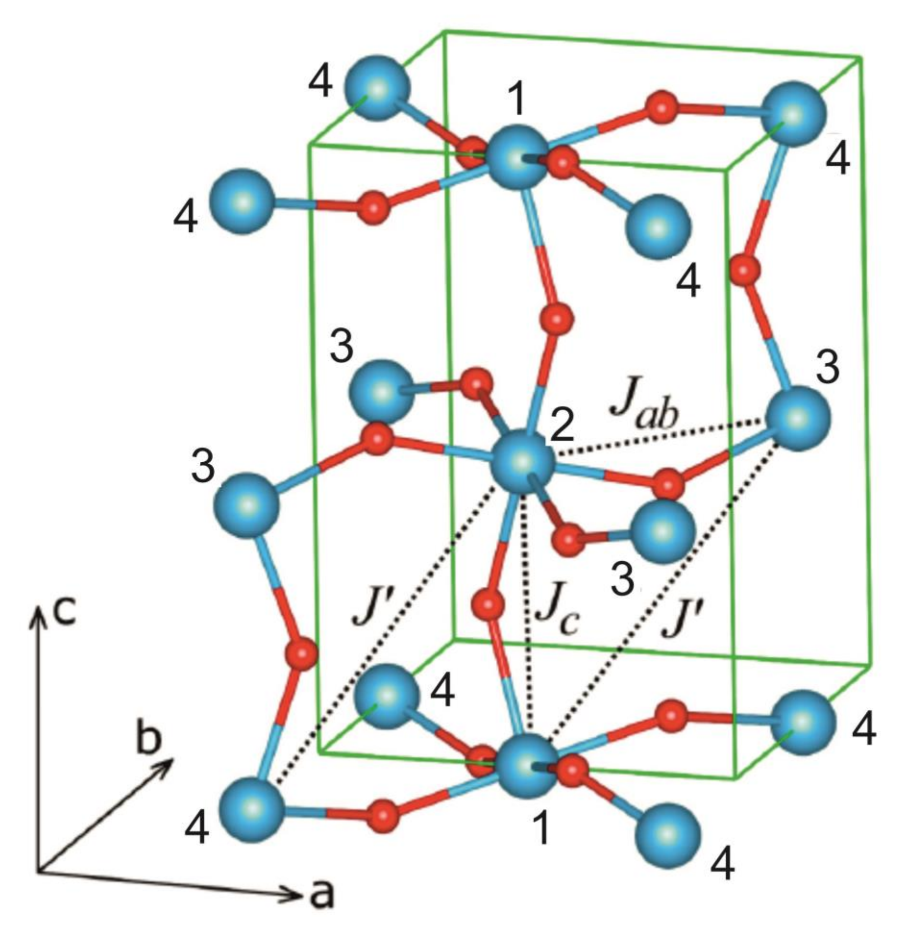
See, also oral presentation at ICM 2015:

Determination of the sign of the Dzyaloshinskii-Moriya interaction in crystals, Andrei Rogalev, V. E. Dmitrienko, F. de Bergevin, E. N. Ovchinnikova, F. Wilhelm, J. Kokubun

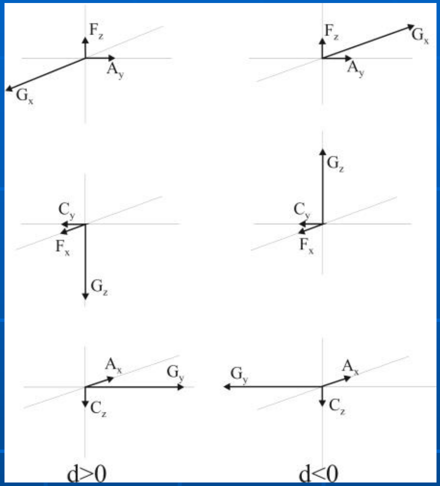
DM Coupling in orthoferrites, orthochromites, …

“Ferrite” epoch

Structure of the Fe^{3+}–O^{2-}–Fe^{3+} superexchange bonding in orthoferrites $RFeO_3$



Antisymmetric exchange and four-sublattice model of orthoferrites $RFeO_3$

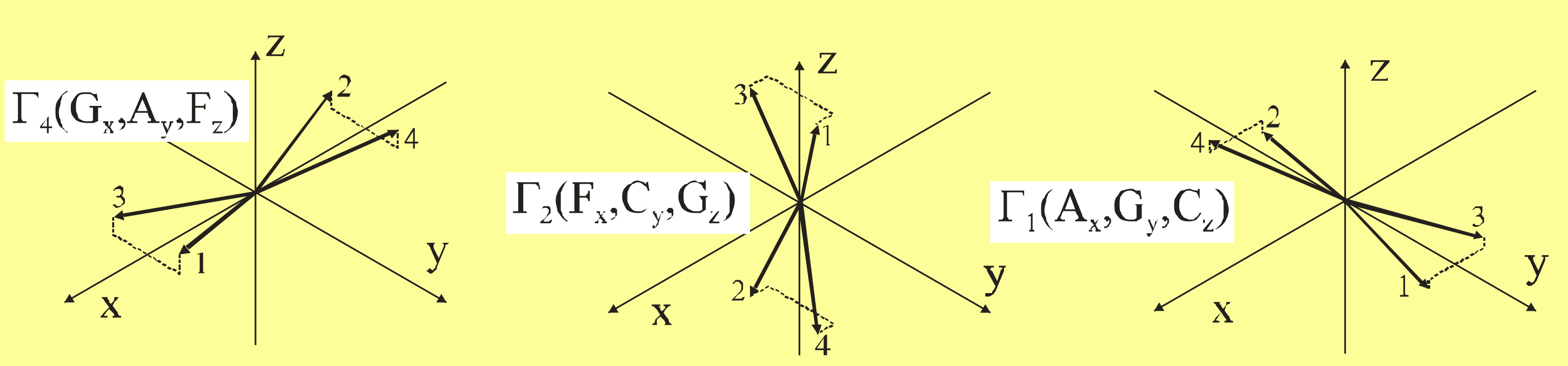


$F=S_1+S_2+S_3+S_4$; $G=S_1-S_2+S_3-S_4$;

$C=S_1+S_2-S_3-S_4$; $A=S_1-S_2-S_3-S_4$

$F \ll G$ – weak ferromagnetic moment (overt canting)

A, $C \ll G$ – weak antiferromagnetic moments (hidden canting)



Orthoferrite $YFeO_3$ as compared with other weak ferromagnets

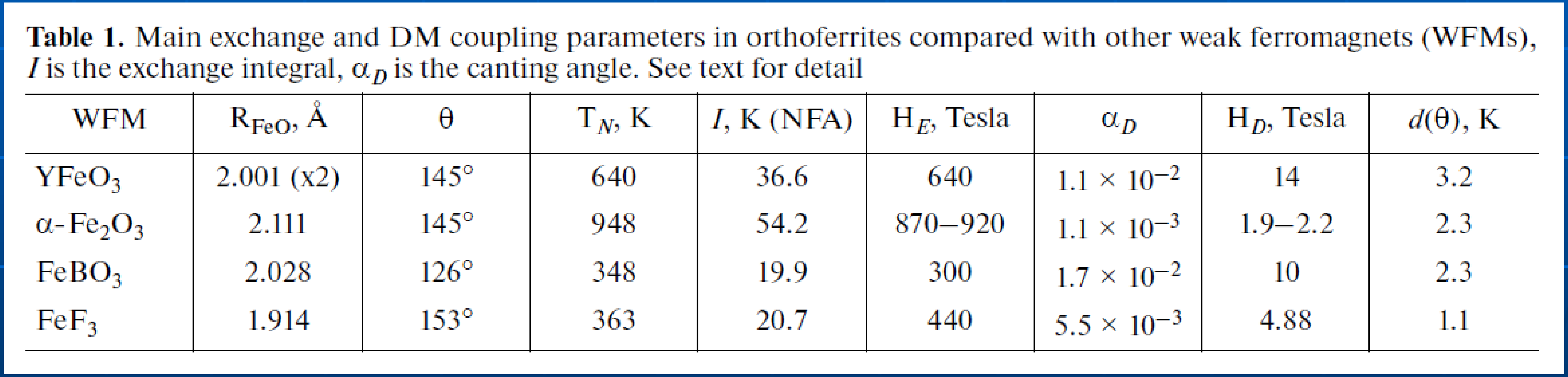


Table 1. Main exchange and DM coupling parameters in orthoferrites compared with other weak ferromagnets (WFMs), I is the exchange integral, α_D is the canting angle. See text for detail

WFM	R_{FeO}, Å	θ	T_N, K	I, K (NFA)	H_E, Tesla	α_D	H_D, Tesla	$d(\theta)$, K
$YFeO_3$	2.001 (x2)	145°	640	36.6	640	1.1×10^{-2}	14	3.2
α-Fe_2O_3	2.111	145°	948	54.2	870–920	1.1×10^{-3}	1.9–2.2	2.3
$FeBO_3$	2.028	126°	348	19.9	300	1.7×10^{-2}	10	2.3
FeF_3	1.914	153°	363	20.7	440	5.5×10^{-3}	4.88	1.1

Making use of simple formula for Dzyaloshinskii vector:

$$\vec{d}_{12}(\theta) = d_{12}(\theta) \cdot \left[\vec{r}_1 \times \vec{r}_2\right]$$

we calculated all “weak” F,C,A moments (overt and hidden canting) in all the orthoferrites $RFeO_3$

A.S. Moskvin and E.V. Sinitsyn, Sov. Phys. Solid State, **17**, 1664 (1975)

$RFeO_3$:Relation between crystal and magnetic structures

$$\Gamma_4\!:\ F_z = \frac{(x_1 + 2z_2)ac}{12l^2}\frac{d}{I}G_x\,; \quad A_y = \frac{(\frac{1}{2} + y_2 - x_2)ab}{4l^2}\frac{d}{I}G_x\,;$$

$$\Gamma_2\!:\ F_x = -\frac{(x_1 + 2z_2)ac}{12l^2}\frac{d}{I}G_z\,; \quad C_y = \frac{(\frac{1}{2} - y_1)bc}{4l^2}\frac{d}{I}G_z\,;$$

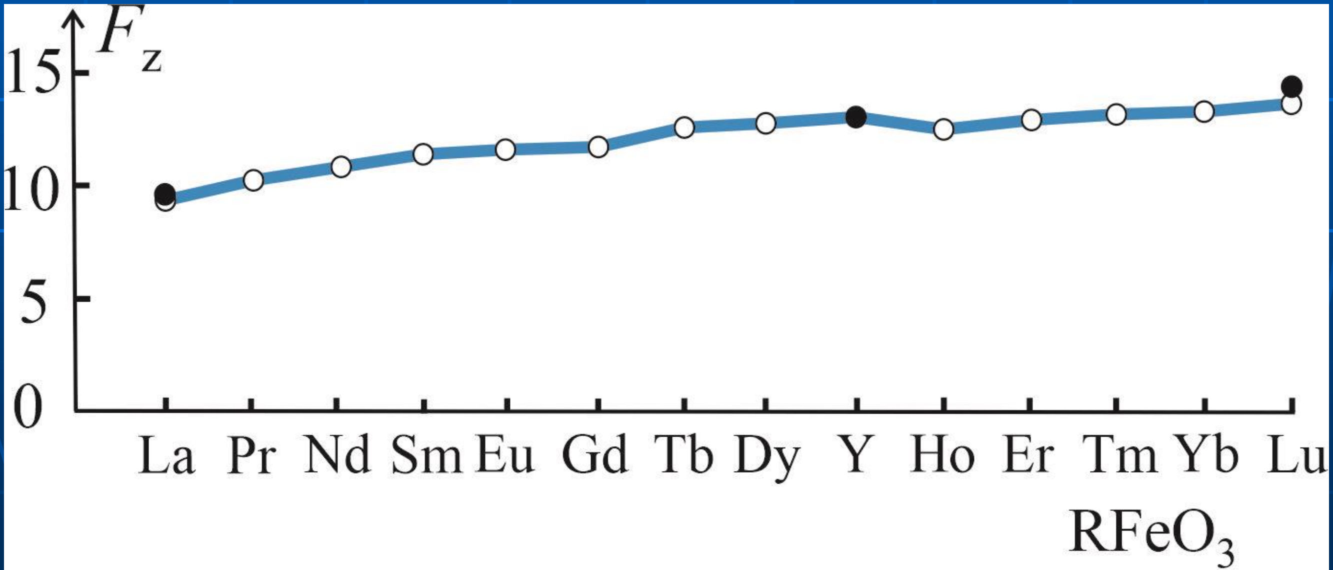
$$\Gamma_1\!:\ A_x = -\frac{(\frac{1}{2} + y_2 - x_2)ab}{4l^2}\frac{d}{I}G_y\,; \quad C_z = -\frac{(\frac{1}{2} - y_1)bc}{4l^2}\frac{d}{I}G_y\,;$$

$RFeO_3$: Experimental verification of the theoretically predicted direct relation between crystalline and magnetic structures

- H. Luetgemeier, H.G. Bohn and M. Brajczewska, JMMM, 21, 289 (1980) – ^{57}Fe NMR in $YFeO_3$ and $TmFeO_3$
- V.P. Plakhtii, Yu.P. Chernenkov, J. Schweizer, and M.N. Bedrizova, JETP, 53, 1291 (1981) – neutron diffraction in $YFeO_3$
- V.P. Plakhtii, Yu.P. Chernenkov, M.N. Bedrizova, and J. Schweizer, AIP Conference Proceedings, 89 330-332 (1982)
- V.P. Plakhtii, Yu.P. Chernenkov, M.N. Bedrizova, Solid State Commun. 47, 309-312(1983) – neutron diffraction in $YbFeO_3$
- D.G. Georgieva, K.A. Krezhov, and V.V. Nietza, Solid State Commun. 96, 535 (1995) – neutron diffraction in $YFeO_3$ and $HoFeO_3$

Theoretical predictions for the overt canting (×10^{-3}) in orthoferrites (hollow circles) normalized on experimental data for $YFeO_3$. Solid circles are latest experimental data for orthoferrites with nonmagnetic R-ion

(J.-S. Zhou, L. G. Marshall, Z.-Y. Li, X. Li, and J.-M. He, Phys. Rev. B 102, 104420 (2020)).



Weak antiferromagnetism in RFeO$_3$

A.S. Moskvin and E.V. Sinitsyn, Sov. Phys. Solid State, **17**, 1664 (1975)

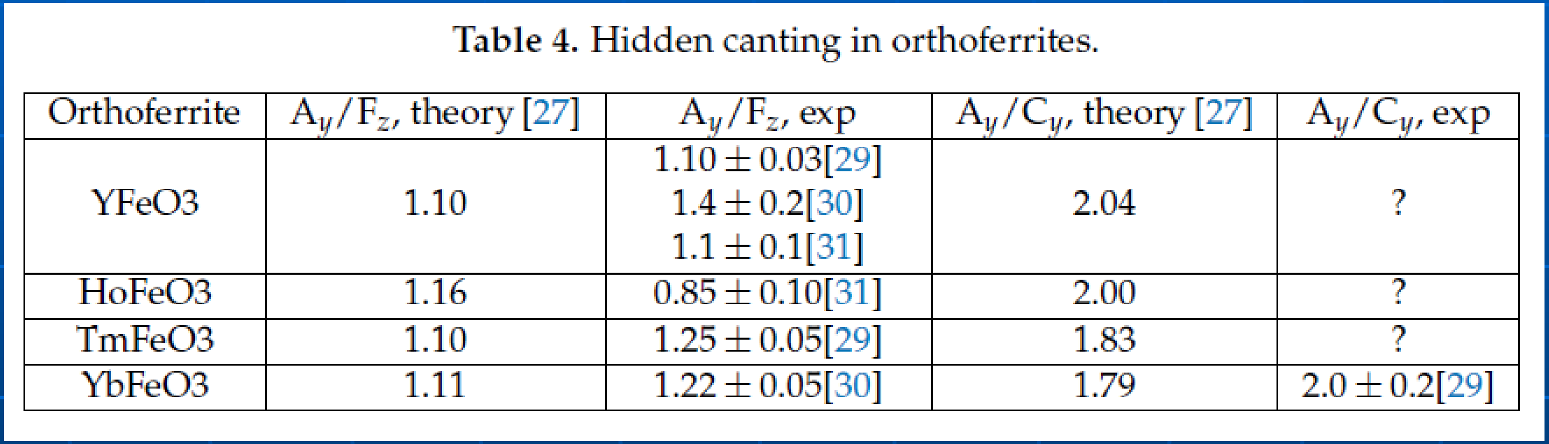
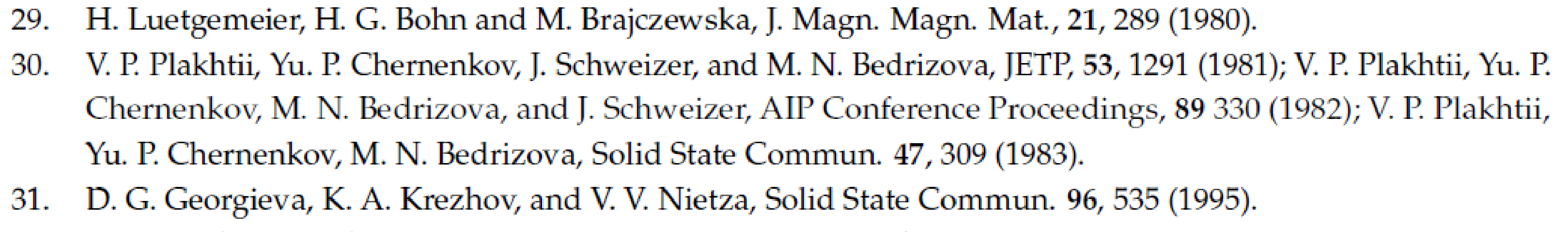
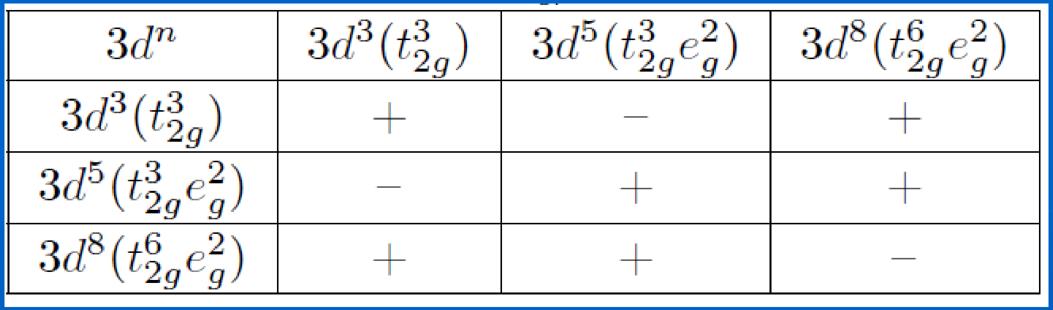


Table 4. Hidden canting in orthoferrites.

Orthoferrite	A_y/F_z, theory [27]	A_y/F_z, exp	A_y/C_y, theory [27]	A_y/C_y, exp
YFeO3	1.10	1.10 ± 0.03[29] 1.4 ± 0.2[30] 1.1 ± 0.1[31]	2.04	?
HoFeO3	1.16	0.85 ± 0.10[31]	2.00	?
TmFeO3	1.10	1.25 ± 0.05[29]	1.83	?
YbFeO3	1.11	1.22 ± 0.05[30]	1.79	2.0 ± 0.2[29]



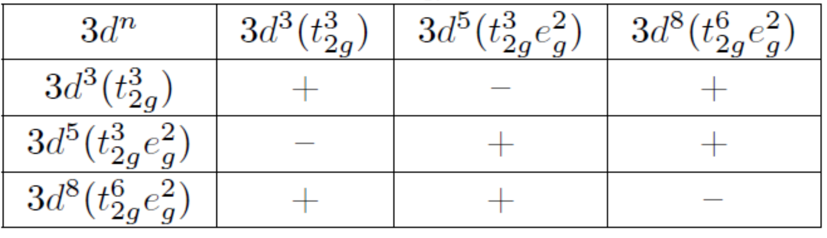
29. H. Luetgemeier, H. G. Bohn and M. Brajczewska, J. Magn. Magn. Mat., **21**, 289 (1980).
30. V. P. Plakhtii, Yu. P. Chernenkov, J. Schweizer, and M. N. Bedrizova, JETP, **53**, 1291 (1981); V. P. Plakhtii, Yu. P. Chernenkov, M. N. Bedrizova, and J. Schweizer, AIP Conference Proceedings, **89** 330 (1982); V. P. Plakhtii, Yu. P. Chernenkov, M. N. Bedrizova, Solid State Commun. **47**, 309 (1983).
31. D. G. Georgieva, K. A. Krezhov, and V. V. Nietza, Solid State Commun. **96**, 535 (1995).



$3d^n$	$3d^3(t_{2g}^3)$	$3d^5(t_{2g}^3e_g^2)$	$3d^8(t_{2g}^6e_g^2)$
$3d^3(t_{2g}^3)$	+	−	+
$3d^5(t_{2g}^3e_g^2)$	−	+	+
$3d^8(t_{2g}^6e_g^2)$	+	+	−

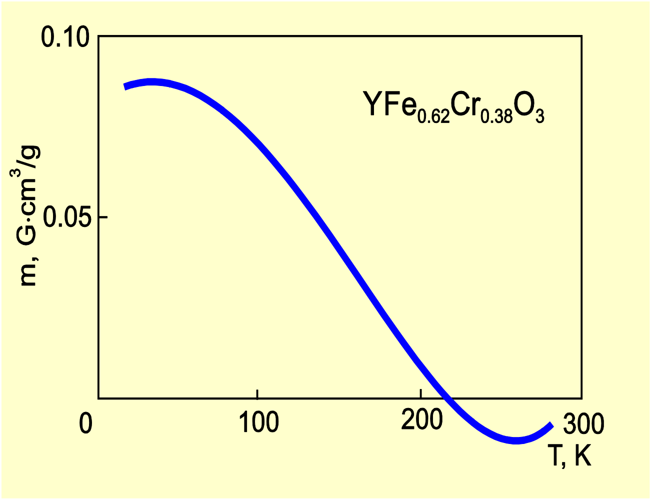
Weak ferrimagnetism in mixed 3d systems with DM coupling and competing signs of the Dzyaloshinskii vector

Competition of d^3-d^3, d^5-d^5, and d^3-d^5 DM coupling and weak FERRIMAGNETISM in mixed ferrites-chromites $RFe_{1-x}Cr_xO_3$



$3d^n$	$3d^3(t_{2g}^3)$	$3d^5(t_{2g}^3e_g^2)$	$3d^8(t_{2g}^6e_g^2)$
$3d^3(t_{2g}^3)$	+	−	+
$3d^5(t_{2g}^3e_g^2)$	−	+	+
$3d^8(t_{2g}^6e_g^2)$	+	+	−

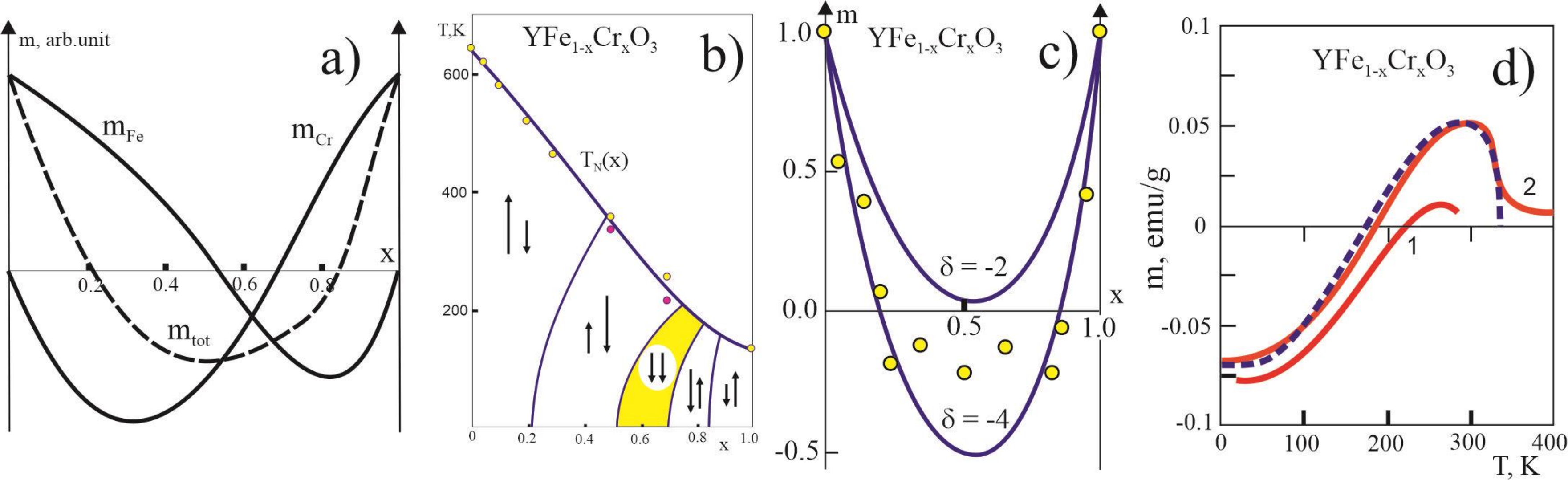
First experimental observation of weak ferrimagnetism in $YFe_{1-x}Cr_xO_3$



A.M. Kadomtseva, A.S. Moskvin, I.G. Bostrem, B. M. Wanklyn, and N.A. Khafizova, Sov. Phys. JETP **45**, 1202 (1977)

A.M. Kadomtseva, V.N. Milov, A.S. Moskvin, and M. Pardavi-Khorvat, Compensation of a weakly ferrimagnetic moment in yttrium ferrites–chromites, Sov. Phys. Solid State 20, 474 (1978)

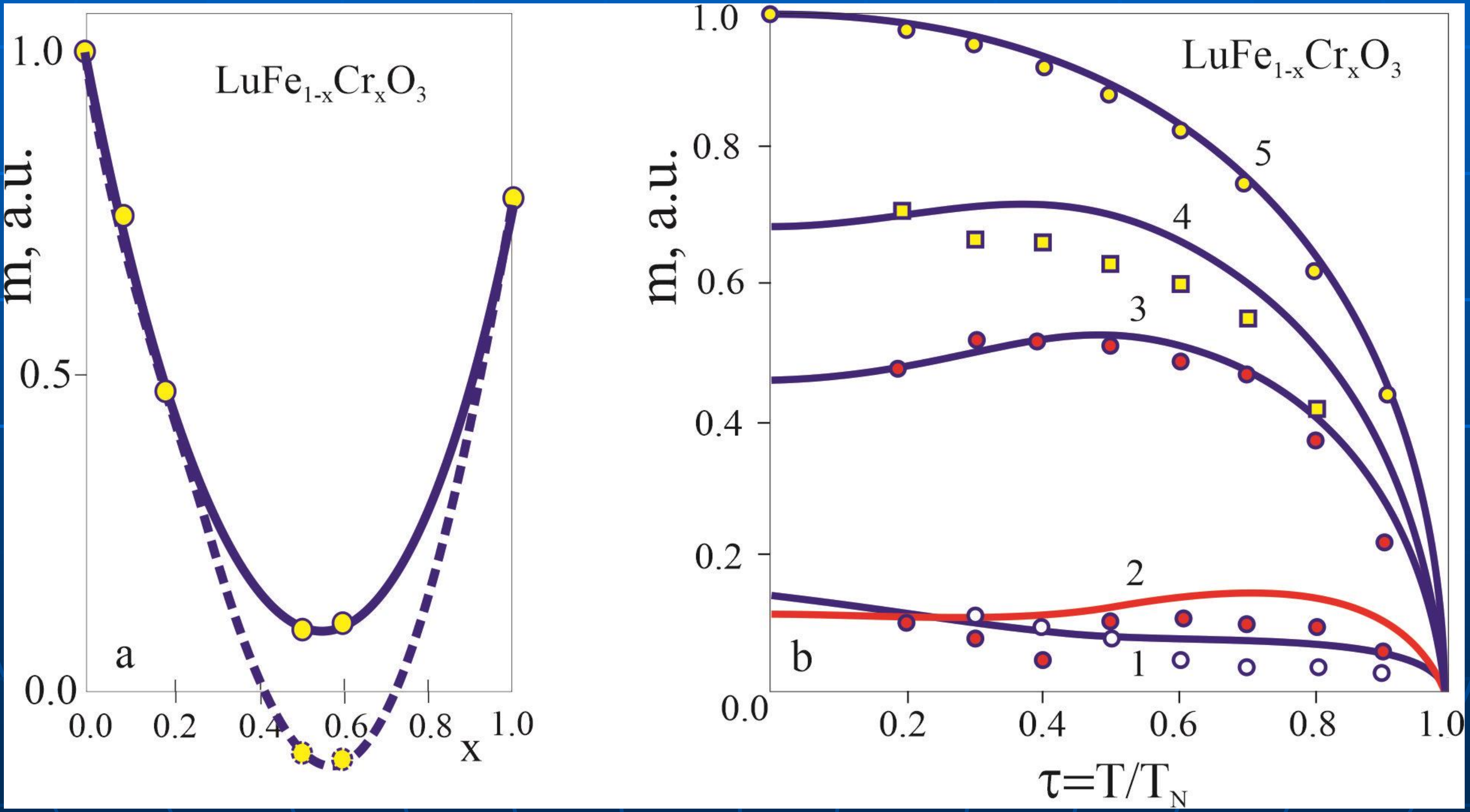
$YFe_{1-x}Cr_xO_3$: Phase diagram and magnetization of weak ferrimagnet (MFA)



First observation of the compensation point in weak ferrimagnet $YFe_{1-x}Cr_xO_3$

- A.M. Kadomtseva, V.N. Milov, A.S. Moskvin, and M. Pardavi-Khorvat, Compensation of a weakly ferrimagnetic moment in yttrium ferrites–chromites, Sov. Phys. Solid State 20, 474 (1978)

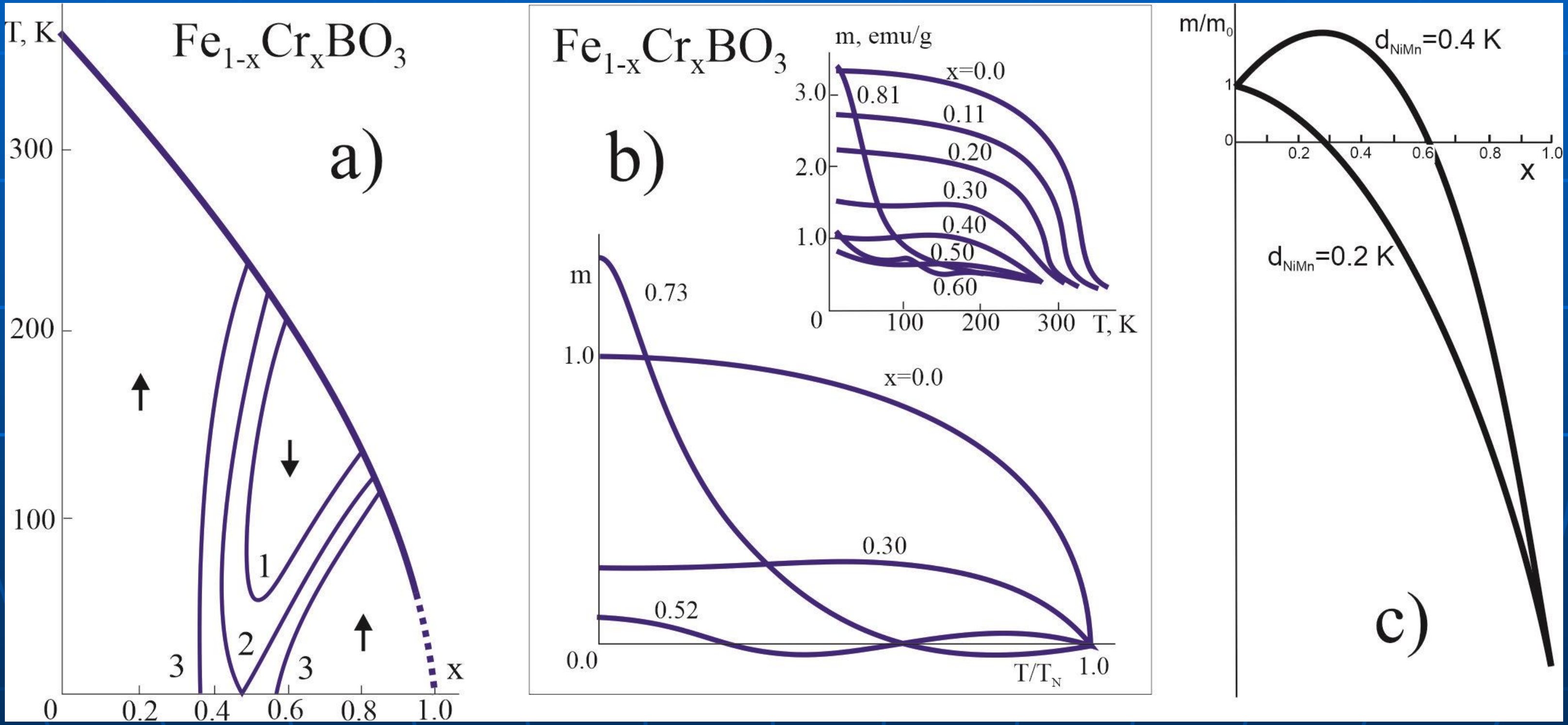
Weak ferrimagnet $LuFe_{1-x}Cr_xO_3$: magnetization



Weak ferrimagnets: Phase diagram and magnetization

$Fe_{1-x}Cr_xBO_3$

$Mn_{1-x}Ni_xCO_3$



A. S. Moskvin and M. A. Vigura, Sov. Phys. Solid State **28**, 1268 (1986).

A. S. Moskvin, M. A. Vigura, and A. P. Agafonov, Sov. Phys. Solid State **28**, 1631 (1986).

DM coupling and magnetic anisotropy in $RFeO_3$

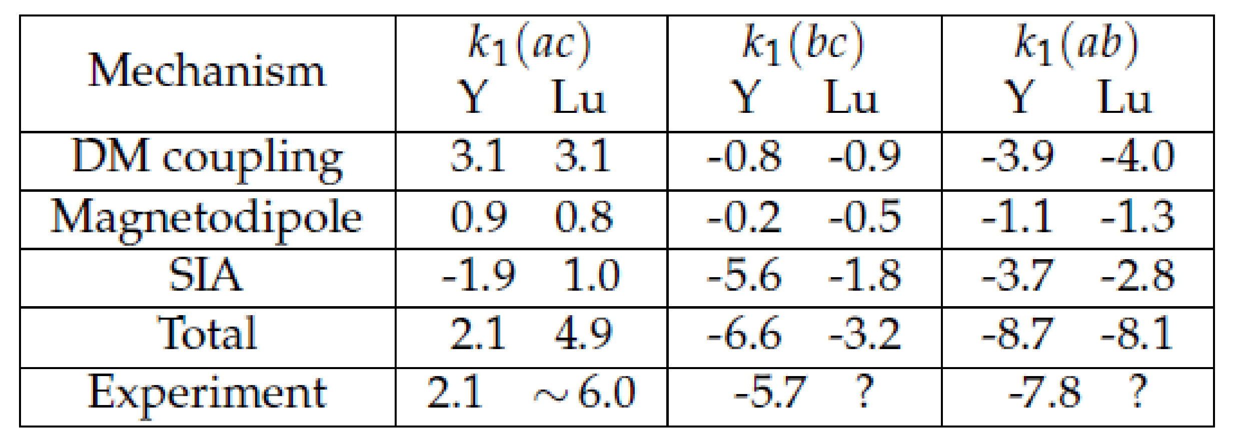
$$E_{\Gamma_1} = I_G - 48IS^2F^2\left[\frac{1}{3}\left(\frac{C}{F}\right)^2 + \frac{2}{3}\left(\frac{A}{F}\right)^2\right]$$

$$E_{\Gamma_2} = I_G - 48IS^2F^2\left[1 + \frac{1}{3}\left(\frac{C}{F}\right)^2\right]$$

$$E_{\Gamma_4} = I_G - 48IS^2F^2\left[1 + \frac{2}{3}\left(\frac{A}{F}\right)^2\right]$$

Classical energies of the three spin configurations $\Gamma_1(G_y)$, $\Gamma_2(G_z)$, $\Gamma_3(G_x)$ in orthoferrites

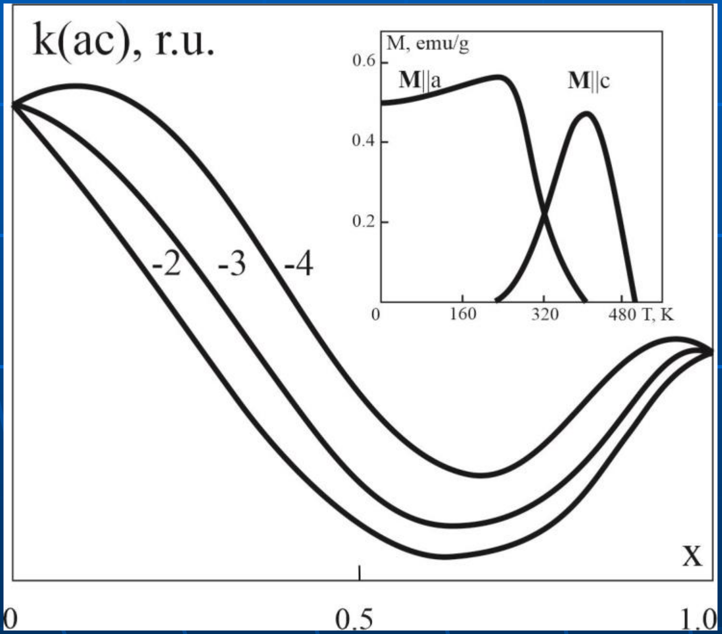
$$E_{\Gamma_4} < E_{\Gamma_1} \leq E_{\Gamma_2}$$



Mechanism	$k_1(ac)$ Y	$k_1(ac)$ Lu	$k_1(bc)$ Y	$k_1(bc)$ Lu	$k_1(ab)$ Y	$k_1(ab)$ Lu
DM coupling	3.1	3.1	-0.8	-0.9	-3.9	-4.0
Magnetodipole	0.9	0.8	-0.2	-0.5	-1.1	-1.3
SIA	-1.9	1.0	-5.6	-1.8	-3.7	-2.8
Total	2.1	4.9	-6.6	-3.2	-8.7	-8.1
Experiment	2.1	~ 6.0	-5.7	?	-7.8	?

Contributions of the main mechanisms to the first constants of the magnetic anisotropy of orthoferrites $YFeO_3$ and $LuFeO_3$ (10^5 erg/cm^3)

DM coupling and magnetic anisotropy in weak ferrimagnets: unconventional spin-reorientation in weak ferrimagnets without magnetic rare earth ions



$$\delta = \frac{d_{\mathrm{CrFr}}}{d_{\mathrm{FeFe}}}\frac{I_{\mathrm{FeFe}}}{I_{\mathrm{CrFe}}}$$

Concentration dependence of the DM coupling contribution to the first anisotropy constant in *ac*-plane given different values of the parameter δ. Inset: Temperature dependence of the magnetization in the weak ferrimagnet

$YFe_{0.85}Cr_{0.15}O_3$ demonstrating the Γ_4–Γ_2 spin-reorientation transition in the temperature range 240–400 K.

(A. M. Kadomtseva and A. S. Moskvin, Acta Phys. Polon. A 68, 303 (1985))

Some papers on weak ferrimagnets

(Ural State University+Moscow State University, 1977-1997)

1. A. M. Kadomtseva, A. S. Moskvin, I. G. Bostrem, B. M. Wanklyn, and N. A. Khafizova, Sov. Phys. JETP 45, 1202 (1977)

2. A. S. Moskvin and I. G. Bostrem, Sov. Phys. Solid State 19, 1532 (1977).

3. A. M. Kadomtseva, V. N. Milov, A. S. Moskvin, and M. Pardavi-Khorvat, Sov. Phys. Solid State 20, 474 (1978)

4. A. M. Kadomtseva, M. M. Lukina, A. S. Moskvin, and N. A. Khafizova, Sov. Phys. Solid State 20, 1235 (1978)

5. D. V. Belov, A. K. Zvezdin, A. M. Kadomtseva et al., Sov. Phys. Solid State 23, 1654 (1981)

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9. A. M. Kadomtseva et al., JETP, 57, 833-837, 1983.

10. A. M. Kadomtseva, A. S. Moskvin, Acta Physica Polonica, Vol. A68 (1985) 303-316.

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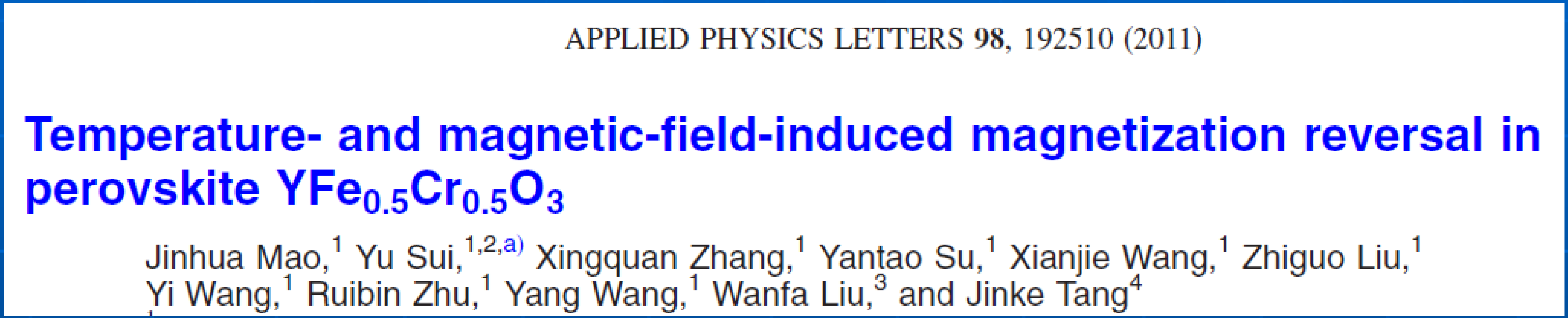
Weak ferrimagnetism in $RFe_{1-x}Cr_xO_3$

A revival of interest a few decades after the discovery and intensive studies in Russia….

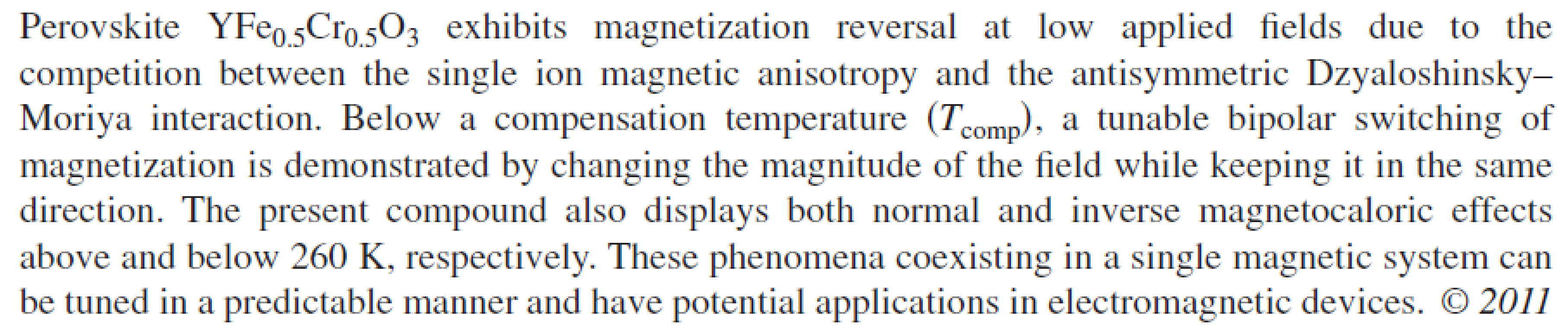
Recent studies of weak ferrimagnets



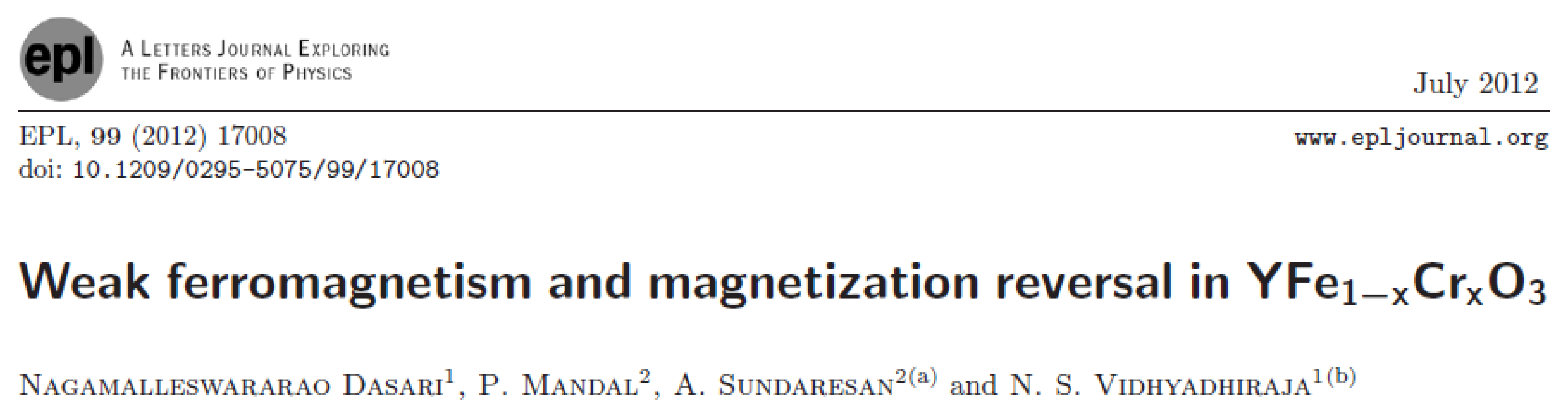
APPLIED PHYSICS LETTERS **98**, 192510 (2011)

Temperature- and magnetic-field-induced magnetization reversal in perovskite $YFe_{0.5}Cr_{0.5}O_3$

Jinhua Mao,[1] Yu Sui,[1,2,a)] Xingquan Zhang,[1] Yantao Su,[1] Xianjie Wang,[1] Zhiguo Liu,[1]
Yi Wang,[1] Ruibin Zhu,[1] Yang Wang,[1] Wanfa Liu,[3] and Jinke Tang[4]



Perovskite $YFe_{0.5}Cr_{0.5}O_3$ exhibits magnetization reversal at low applied fields due to the competition between the single ion magnetic anisotropy and the antisymmetric Dzyaloshinsky–Moriya interaction. Below a compensation temperature (T_{comp}), a tunable bipolar switching of magnetization is demonstrated by changing the magnitude of the field while keeping it in the same direction. The present compound also displays both normal and inverse magnetocaloric effects above and below 260 K, respectively. These phenomena coexisting in a single magnetic system can be tuned in a predictable manner and have potential applications in electromagnetic devices. © *2011*



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July 2012

EPL, **99** (2012) 17008
doi: 10.1209/0295-5075/99/17008

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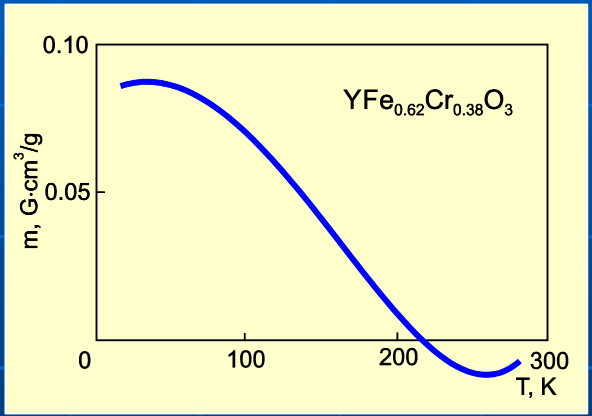
Weak ferromagnetism and magnetization reversal in $YFe_{1-x}Cr_xO_3$

Nagamalleswararao Dasari[1], P. Mandal[2], A. Sundaresan[2(a)] and N. S. Vidhyadhiraja[1(b)]



A.M. Kadomtseva et al.
Compensation of a weakly ferrimagnetic moment in yttrium ferrites–chromites, Sov. Phys. Solid State 20, 474 (1978)

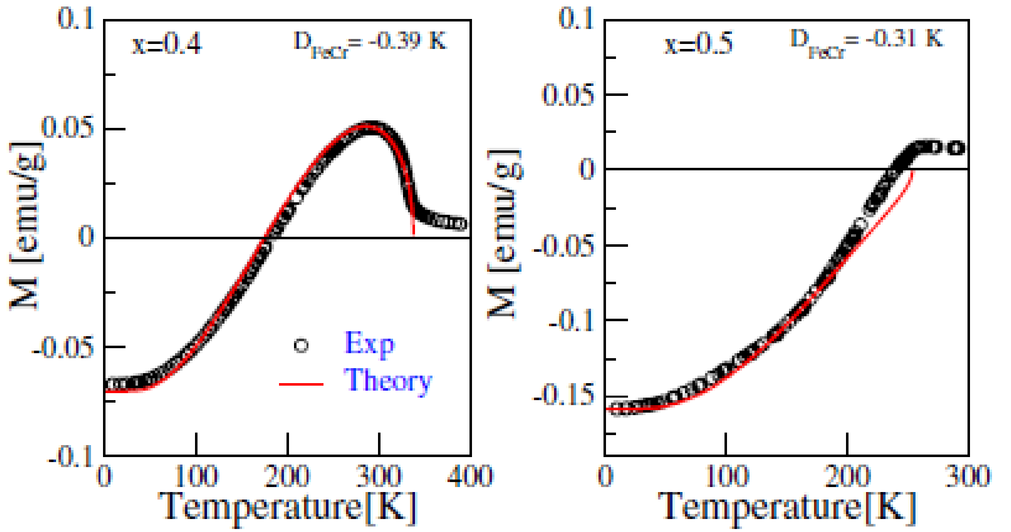
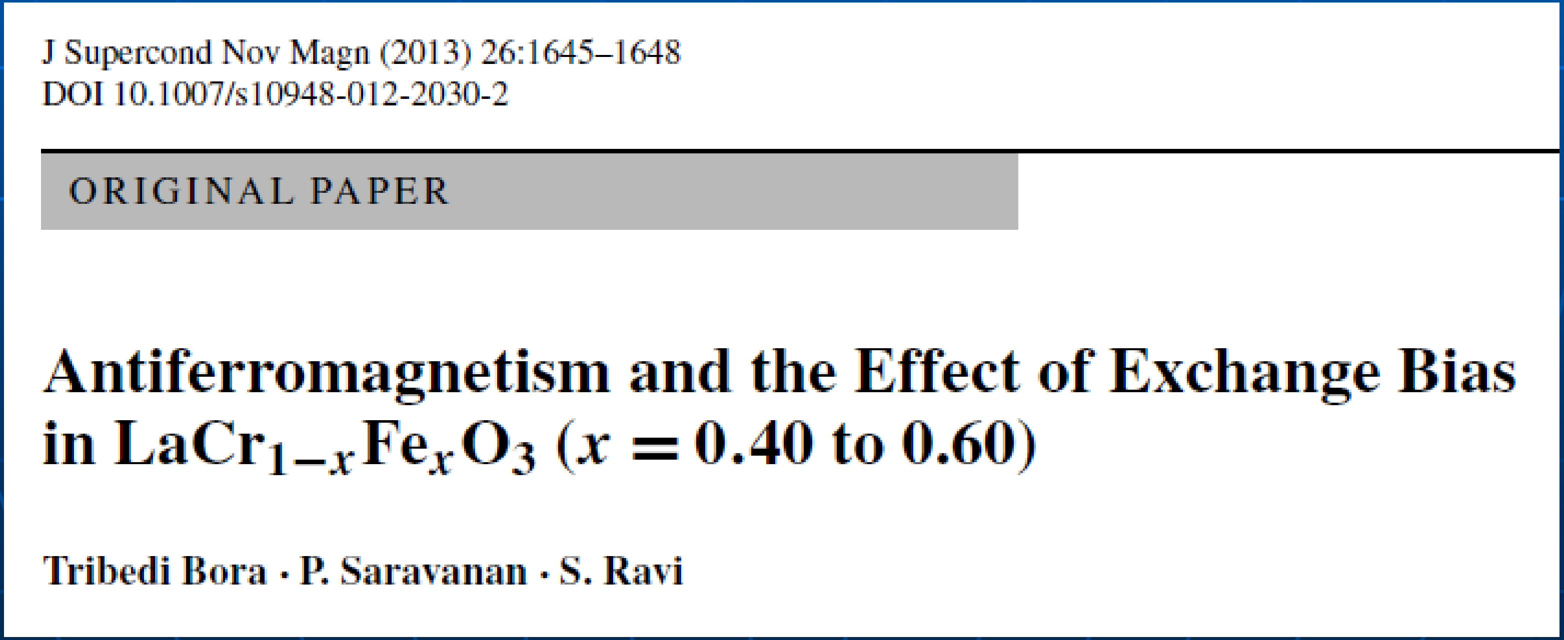


Fig. 6: (Colour on-line) Magnetization (experiment: black; theory: red) as a function of temperature for $x = 0.4$ (left) and 0.5 (right). Magnetization reversal is seen in this composition range.

Weak ferrimagnets can exhibit the tunable exchange bias effect



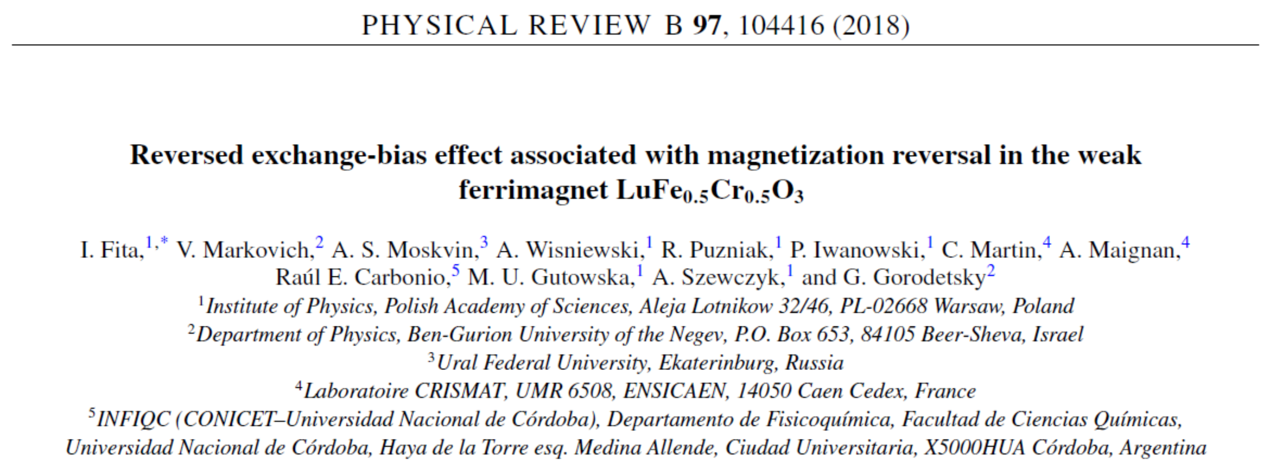
J Supercond Nov Magn (2013) 26:1645–1648
DOI 10.1007/s10948-012-2030-2

ORIGINAL PAPER

Antiferromagnetism and the Effect of Exchange Bias in $LaCr_{1-x}Fe_xO_3$ ($x = 0.40$ to 0.60)

Tribedi Bora · P. Saravanan · S. Ravi

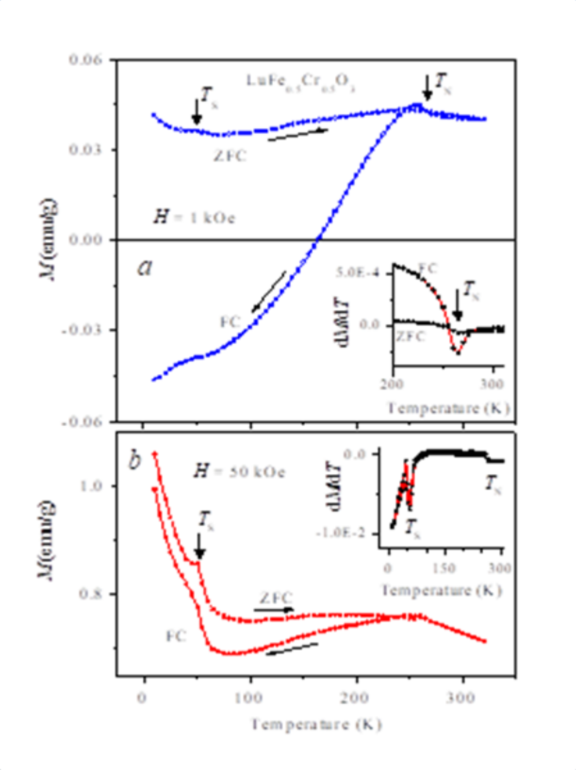
$LuFe_{0.5}Cr_{0.5}O_3$ after 40 years

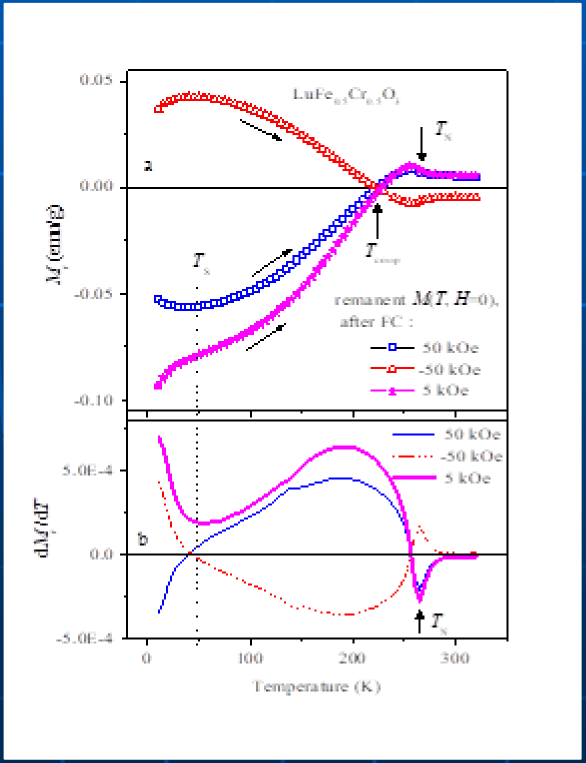


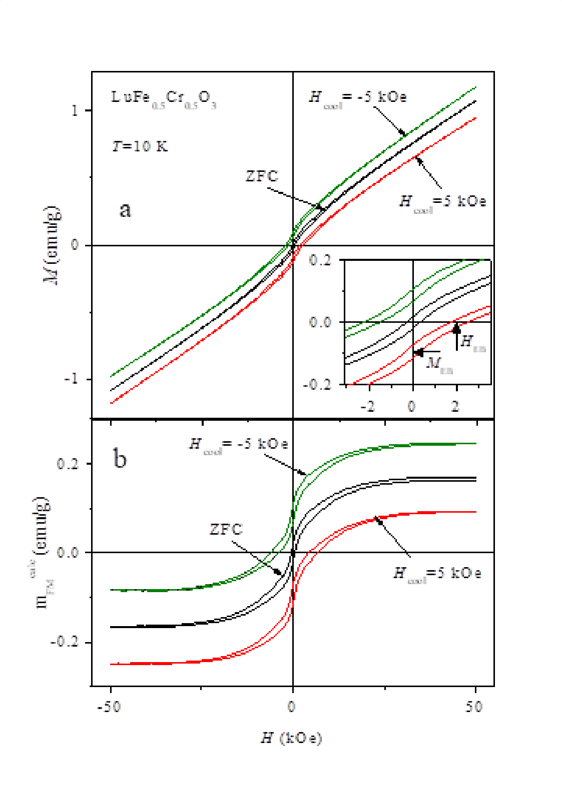
PHYSICAL REVIEW B **97**, 104416 (2018)

Reversed exchange-bias effect associated with magnetization reversal in the weak ferrimagnet $LuFe_{0.5}Cr_{0.5}O_3$

I. Fita,[1,*] V. Markovich,[2] A. S. Moskvin,[3] A. Wisniewski,[1] R. Puzniak,[1] P. Iwanowski,[1] C. Martin,[4] A. Maignan,[4]
Raúl E. Carbonio,[5] M. U. Gutowska,[1] A. Szewczyk,[1] and G. Gorodetsky[2]
[1] *Institute of Physics, Polish Academy of Sciences, Aleja Lotnikow 32/46, PL-02668 Warsaw, Poland*
[2] *Department of Physics, Ben-Gurion University of the Negev, P.O. Box 653, 84105 Beer-Sheva, Israel*
[3] *Ural Federal University, Ekaterinburg, Russia*
[4] *Laboratoire CRISMAT, UMR 6508, ENSICAEN, 14050 Caen Cedex, France*
[5] *INFIQC (CONICET–Universidad Nacional de Córdoba), Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Haya de la Torre esq. Medina Allende, Ciudad Universitaria, X5000HUA Córdoba, Argentina*







- Combining magnetization reversal effect with magnetoelectronics can exploit tremendous technological potential for device applications, for example, thermally assisted magnetic random access memories, thermomagnetic switches and other multifunctional devices, in a preselected and convenient manner.

Other exchange-relativistic effects beyond simple Dzyaloshinskii -Moriya antisymmetric 3d-3d spin exchange coupling

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

Rare-earth-3d-ion antisymmetric exchange interaction

$$V_{DM}(4f\text{-}3d)=\mathbf{D}_{fd}\cdot[\mathbf{J}_f\times\mathbf{S}_d]$$

- D. V. Belov, A. K. Zvezdin, A. M. Kadomtseva, I. B. Krynetski, A. S. Moskvin, and A. A. Mukhin, Sov. Phys. Solid State 23, 1654 (1981)

Electron-nuclear Dzyaloshinskii -Moriya interaction

(antisymmetric supertransferred hyperfine interaction)

$$V_{DM}(ASTHF)=\mathbf{A}_{DM}\cdot[\mathbf{I}_{n}\times\mathbf{S}]$$

$$V(STHF)=A_{STHF}(\mathbf{I}_{n}\cdot\mathbf{S})$$

A.S. Moskvin, JETP, **63**, 1015, 1986

Electron-nuclear Dzyaloshinskii - Moriya interaction in orthoferrites

- $H_{ASTHFI} \approx (H_{DM}/H_{ex})\ H_{STHFI}$
- Orthoferrite YFeO3:

H_{STHFI}=58 T; H_{ASTHFI}=0.26 T

A.S. Moskvin, JETP, **63**, 1015, 1986

First experimental observation of the Dzyaloshinskii-Moriya electron-nuclear interaction

- **Electron-nuclear double resonance in $\mathbf{Pb_5Ge_3O_{11}:Gd^{3+}}$;**
- Antisymmetric ^{207}Pb-O^{2-}- Gd^{3+} supertransferred hyperfine interaction

- A. I. Rokeakh, A. S. Moskvin, N. V. Legkikh, and Yu. A. Sherstkov, Sov. Phys. JETP **66**, 1021 (1987)

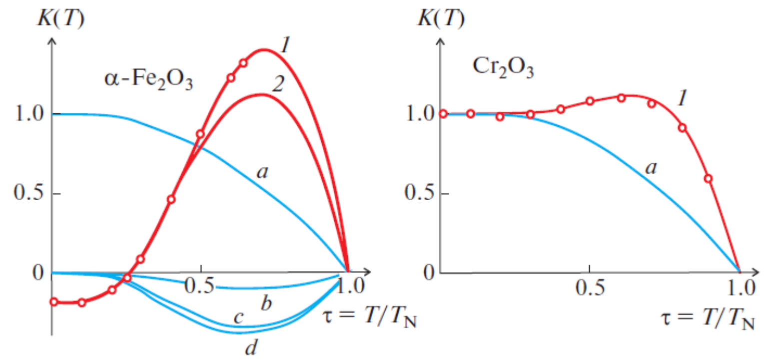
Exchange-relativistic two-ion spin anisitropy

$$V_{\text{an}} = \sum_{m,n,\alpha,\beta} K_{\alpha\beta}(mn) S_{m\alpha} S_{n\beta}$$

$$V_{\text{an}}(1,2) \sim \frac{V_{\text{so}}(1)V_{\text{ex}}(12)V_{\text{so}}(2)}{\Delta E^2} + \frac{V_{\text{so}}(1)V_{\text{so}}(2)V_{\text{ex}}(12)}{\Delta E^2} + \frac{V_{\text{so}}(1)V_{\text{ex}}(12)V_{\text{so}}(1)}{\Delta E^2} + \frac{V_{\text{so}}(1)V_{\text{so}}(2)V_{\text{ex}}(12)}{\Delta E^2}$$

$$E_{\text{an}} = \sum_{k_1 k_2} \rho_{k_1} \rho_{k_2} (k_{12}^2(k_1, k_2) \cdot [C^{k_1}(\hat{\mathbf{S}}_1) \times C^{k_2}(\hat{\mathbf{S}}_2)]^2),$$

$$K(T) = K(0)\rho_1^2 + K_{20}(\rho_2 - \rho_1^2) + K_{22}(\rho_2^2 - \rho_1^2) + K_{13}(\rho_1\rho_3 - \rho_1^2),$$



Spin-other-orbit antisymmetric exchange interaction and unconventional circular magnetooptics of weak ferromagnets

$$V_{DM}(LS)=\mathbf{D}_{12}\cdot[\mathbf{L}_1\times\mathbf{S}_2]$$

Gyration vector in weak ferromagnet

$$\mathbf{g} \propto A\,\mathbf{m} + [\mathbf{B}\times\mathbf{l}]$$

Antiferromagnetic contribution to circular magnetooptic (Faraday and Kerr) effects !

A.S. Moskvin, R.V. Pisarev et al., JETP, **69**, 792 (1989) – Experimental evidence in orthoferrite $YFeO_3$

Simple illustration of the mechanism of the circular and linear birefringeance

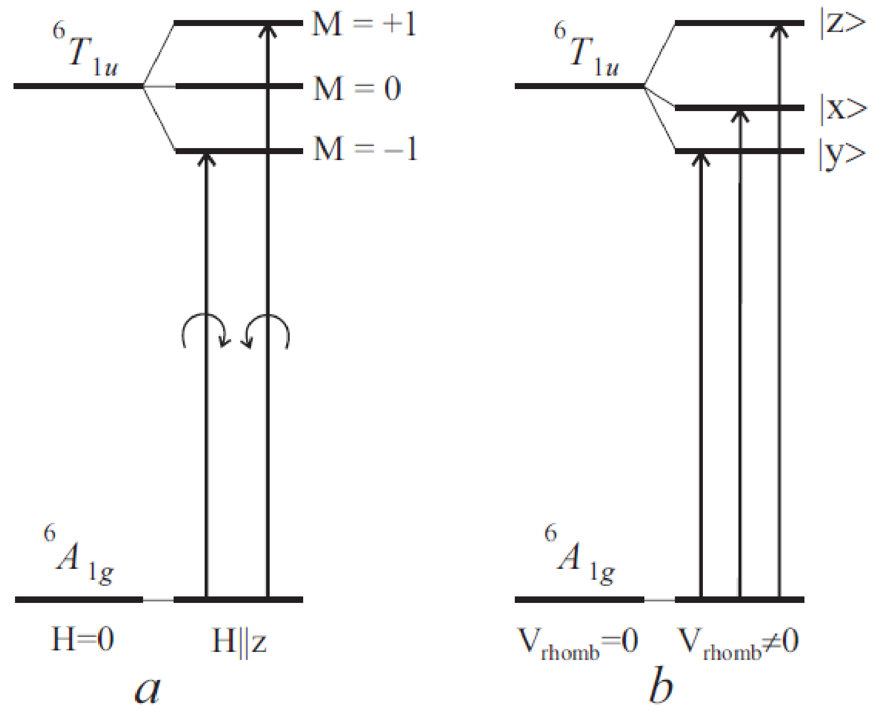


Figure 3. An illustration of the nature of circular and linear birefringence due to a splitting mechanism: (*a*) schematic for the dipole allowed CT transitions $^6A_{1g} \rightarrow {}^6T_{1u}$ for the light with right and left circular polarization under external magnetic field and orbital *Zeeman* splitting; (*b*) schematic for the CT transitions $^6A_{1g} \rightarrow {}^6T_{1u}$ for the light with a linear polarization in a low-symmetry (rhombic) crystal field and *Stark* splitting for excited $^6T_{1u}$ state. Note that we are dealing with finite current (a) and currentless (b) states, respectively.

Exchange-relativistic spin-orbital interaction

$$\hat{V}^{ex}_{SO} = \sum_{m,n} \lambda^{(0)}_{mn} (\mathbf{L}_m \cdot \mathbf{S}_n) + \sum_{m,n} (\boldsymbol{\lambda}_{mn} \cdot [\mathbf{L}_m \times \mathbf{S}_n]) + \sum_{m,n} (\mathbf{L}_m \overleftrightarrow{\boldsymbol{\lambda}}_{mn} \mathbf{S}_n)$$

$$\hat{S}_q(mn) = \hat{S}_q(n) + \gamma \left[\hat{V}^2 \left(s(m) \right) \times s^1(n) \right]^1_q = \\ \hat{S}_q(n) + \gamma \sum_{q_1, q_2} \begin{bmatrix} 2 & 1 & 1 \\ q_1 & q_2 & q \end{bmatrix} \hat{V}^2_{q_1} \left(s(m) \right) s_{q_2}(n) \, ,$$

$$V^{iso}_{SoO} = \sum_{mn} \lambda(mn) (\mathbf{L}(m) \cdot \mathbf{S}(n)) + + \sum_{m \neq n} \lambda'(mn) \Big(\mathbf{L}(m) \cdot \mathbf{S}(m) \Big) \Big(\mathbf{S}(m) \cdot \mathbf{S}(n) \Big)$$

Gyration vector in orthoferrites

$$\mathbf{g} = \hat{A}\,\mathbf{m} + \hat{B}\,\mathbf{l} + \hat{C}\,\mathbf{H}, \quad (m^2 + l^2 = 1)$$

$$\hat{A} = \begin{pmatrix} a_{xx} & 0 & 0 \\ 0 & a_{yy} & 0 \\ 0 & 0 & a_{zz} \end{pmatrix}, \quad \hat{B} = \hat{B}^s + \hat{B}^a = \begin{pmatrix} 0 & 0 & b_{xz} \\ 0 & 0 & 0 \\ b_{zx} & 0 & 0 \end{pmatrix},$$

$$a_{xx} \neq a_{yy} \neq a_{zz}\,, \quad b_{zx} \neq b_{xz}\,.$$

$$A_{zz}m_z = (0.95 \pm 0.55) \cdot 10^{-3};\ B_{zx}|l_x| = (3.15 \pm 0.55)) \cdot 10^{-3};$$

$$A_{xx}m_x = (0.2 \pm 0.7) \cdot 10^{-3};\ B_{xz}|l_z| = (-2.1 \pm 1.0)) \cdot 10^{-3};$$

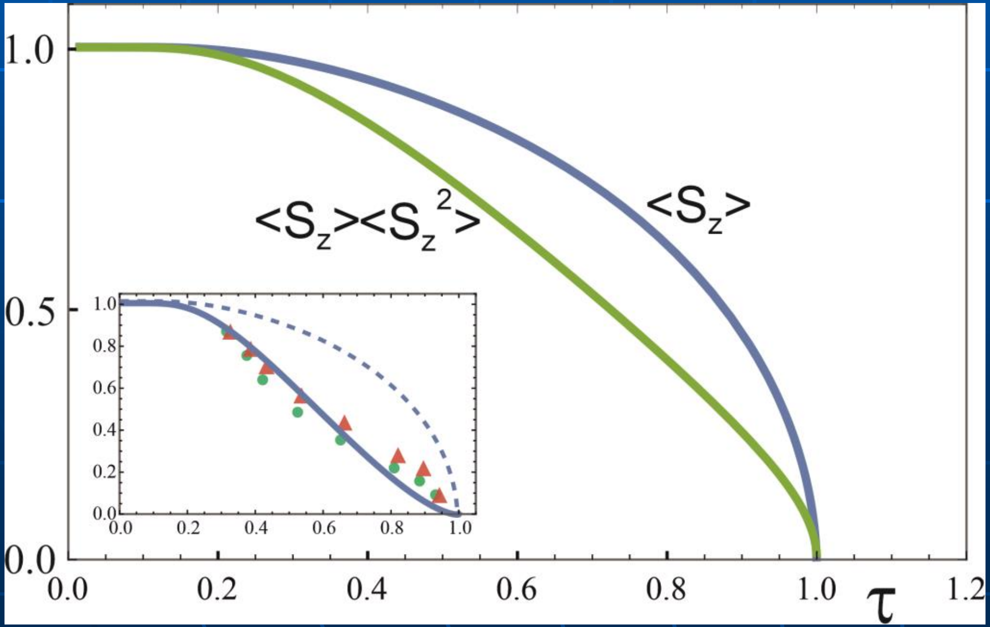
$$C_{zz} \approx C_{xx} = (-1.1 \pm 2.8) \cdot 10^{-6}\,kOe^{-1}\,,$$

Rather large measurement errors allow for certain to determine only the fact of a large if not a dominant antisymmetric antiferromagnetic contribution related with antisymmetric spin-other-orbit coupling.

In rhombohedral weak ferromagnets (α-Fe_2O_3 , $FeBO_3$, FeF_3)

$$\mathbf{g} = \hat{A}\,\mathbf{m} + \hat{B}\,\mathbf{l} + \hat{C}\,\mathbf{H}, \quad (m^2 + l^2 = 1)$$

$$\hat{A} = \begin{pmatrix} a_\perp & 0 & 0 \\ 0 & a_\perp & 0 \\ 0 & 0 & a_\parallel \end{pmatrix}, \quad \hat{B} = \hat{B}^a = \begin{pmatrix} 0 & b_{xy} & 0 \\ b_{yx} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$



Temperature dependence of the normalized thermodynamic quantities determining the temperature dependence of the circular MOE. The inset shows an example of fitting the experimental data on the temperature dependences of the equatorial Kerr effect in hematite α-Fe2O3 using the contribution of the antisymmetric spin-other-orbit coupling

Some recent papers on orthoferrites

A.S. Moskvin, Microscopic theory of Dzyaloshinskii-Moriya coupling and related exchange-relativistic effects, **JMMM, 400**, pages 117–120, 15 February 2016.

A. S. Moskvin, Dzyaloshinskii–Moriya Coupling in 3d Insulators, **Condens. Matter** 2019, 4(4), 84,

А. С. Москвин, ВЗАИМОДЕЙСТВИЕ ДЗЯЛОШИНСКОГО И ОБМЕННО-РЕЛЯТИВИСТСКИЕ ЭФФЕКТЫ В ОРТОФЕРРИТАХ, **ЖЭТФ**, 2021, том 159, вып. 4, стр. 607–643 (**JETP**, **132**, #4, 517-547, 2021).

Moskvin, A. Structure–Property Relationships for Weak Ferromagnetic Perovskites. Magnetochemistry 2021, 7, 111.

Moskvin, A.; Vasinovich, E.; Shadrin, A. Simple Realistic Model of Spin Reorientation in 4f-3d Compounds. **Magnetochemistry** 2022, 8, 45.

DM coupling

“Cuprate” epoch

Microscopic theory of DM coupling in La_2CuO_4

- D. Coffey, T.M. Rice, and F.C. Zhang, Phys. Rev. 44, 10112, (1991).
- L. Shekhtman, O. Entin-Wohlman, and A. Aharony, Phys. Rev. Lett. 69, 836 (1992).
- W. Koshibae, Y. Ohta, and S. Maekawa, Phys. Rev. B 47, 3391 (1993); Phys. Rev. B 50, 3767 (1994).
- N. E. Bonestel, Phys. Rev. 47, 11302 (1996).
- J. Stein, O. Entin-Wohlman, and A. Aharony, Phys. Rev. 53, 775 (1996).

Some recent papers on the theory of DM coupling in 1D and 2D systems

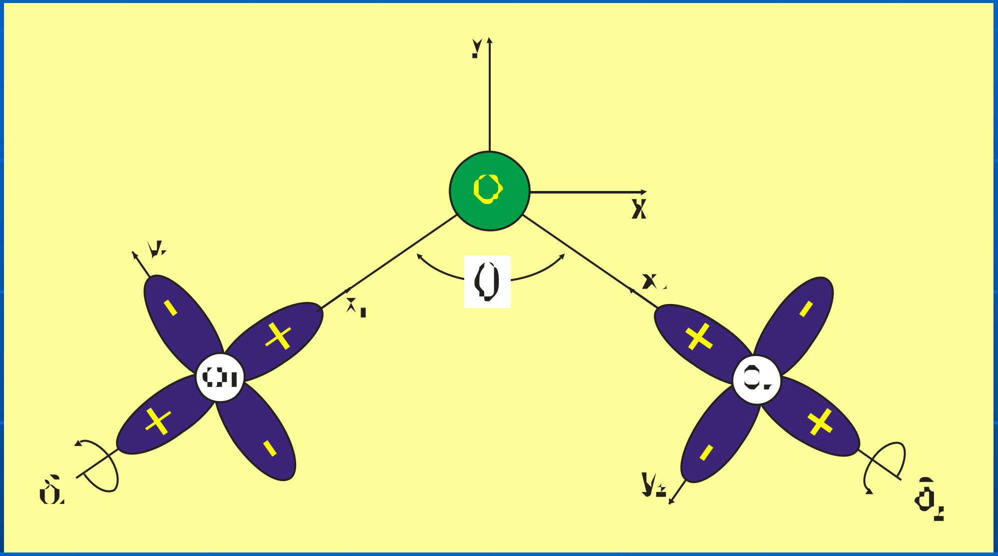
- I. Affleck and M. Oshikawa, Phys. Rev. Lett. 79, 2883 (1997).
- V. Yushankhai, M. Wolf, K.-H. Mueller, R.Hayn, and H. Rosner, Phys. Rev. B **62**, 14229 (2000).
- V.N. Kotov, M. Elhajal, M.E. Zhitomirsky, and F. Mila, Phys. Rev. B **72**, 014421 (2005).
- A.L. Chernyshev, Phys. Rev. B **72**, 174414 (2005).

Dzyaloshinsky-Moriya coupling in cuprates

A. S. Moskvin, Field induced staggered magnetization and ^{17}O Knight shift anomaly in La_2CuO_4, **Phys. Rev**. B **75**, 054505 (2007).

A. S. Moskvin, Dzyaloshinsky-Moriya antisymmetric exchange coupling in cuprates: Oxygen effects, **JETP**, 2007, Vol. **104**, No. 6, pp. 911–925.

DM coupling in cuprates



$\theta \approx 180^0$ – corner-shared

$\approx 90^0$ – edge-shared

cuprates

$$\vec{D}_{12} = \vec{D}_{12}^{(1)} + \vec{D}_{12}^{(O)} + \vec{D}_{12}^{(2)}$$

All three Dzyaloshinskii vectors can be of different direction and magnitude !

Copper contribution to Dzyaloshinskii vector in cuprates

$$D^{(1)}_{12x} = \sqrt{2}\xi_{3d}c_{200}({}^1A_{1g})[c_{200}({}^3E_g)\cos\delta_1 - 2c_{200}({}^3A_{2g})\sin\delta_1]\cos\frac{\theta}{2};$$

$$D^{(1)}_{12y} = -\sqrt{2}\xi_{3d}c_{200}({}^1A_{1g})[c_{200}({}^3E_g)\cos\delta_1 - 2c_{200}({}^3A_{2g})\sin\delta_1]\sin\frac{\theta}{2};$$

$$D^{(1)}_{12z} = -\sqrt{2}\xi_{3d}c_{200}({}^1A_{1g})[c_{200}({}^3E_g)\sin\delta_1 - 2c_{200}({}^3A_{2g})\cos\delta_1];$$

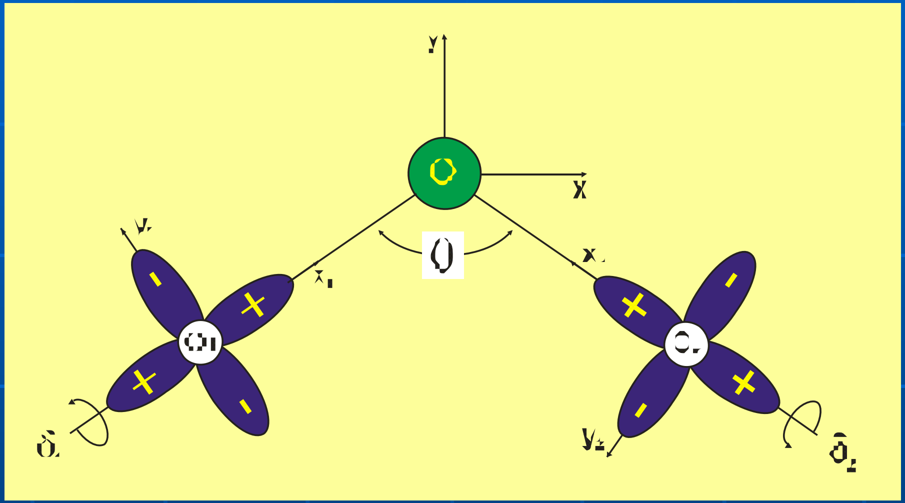
$$c_{200}({}^1A_{1g}) = -\frac{3t^2_{pd\sigma}}{2\sqrt{2}}\frac{1}{E_{{}^1A_{1g}}}\left[\frac{\sin^2\frac{\theta}{2}}{\varepsilon_x} - \frac{\cos^2\frac{\theta}{2}}{\varepsilon_y}\right]$$

$$c_{200}({}^{1,3}A_{2g}) = -\frac{\sqrt{3}}{4}t_{pd\sigma}t_{pd\pi}\frac{1}{E_{{}^{1,3}A_{2g}}}\left(\frac{1}{\varepsilon_x} + \frac{1}{\varepsilon_y}\right)\sin\theta\cos\delta_1$$

$$c_{200}({}^{1,3}E_g) = -\frac{\sqrt{3}}{4}t_{pd\sigma}t_{pd\pi}\frac{1}{E_{{}^{1,3}E_g}}\left(\frac{1}{\varepsilon_x} + \frac{1}{\varepsilon_y}\right)\sin\theta\sin\delta_1$$

Nonmagnetic anions as contributors to DM coupling

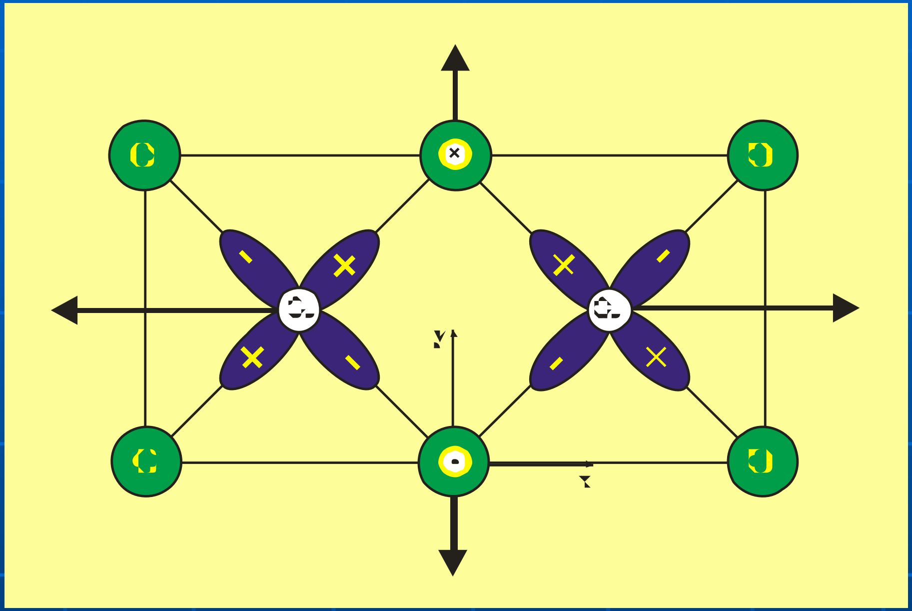
Anomalous oxygen contribution to DM coupling in cuprates



$$\mathbf{D}_O = \mathrm{D}_O(\theta)[\mathbf{r}_1 \times \mathbf{r}_2]$$

$$D_O(\theta) = \frac{9\zeta_{2p}t_{pd\sigma}^4}{16}\frac{1}{E_t(p_x p_y)}\left(\frac{1}{\varepsilon_x}+\frac{1}{\varepsilon_y}\right)\left[\frac{\cos^2\frac{\theta}{2}}{\varepsilon_x E_s(p_x^2)}-\frac{\sin^2\frac{\theta}{2}}{\varepsilon_y E_s(p_y^2)}\right]$$

Anomalous oxygen contribution to weak antiferromagnetism in edge-shared cuprates ($LiCu_2O_2$, $LiVCuO_4$, $LiZr_2CuO_4$,…)



Net Dzyaloshinskii vector **turns into zero**, however, due to different spatial location the oxygen contributions result in a **nonzero weak antiferromagnetic ordering** !

Anionic contribution to Dzyaloshinskii vector needs in a detailed experimental and theoretical examination

Anionic contribution to Dzyaloshinskii vector is crucial for the very existence of the DM coupling in the pair of rare-earth ions (see, e.g., Yb^{3+}-As^{4-}-Yb^{3+} triads in Yb_4As_3 – M. Oshikawa et al., J. Phys. Soc. Japan, 68, 3181 (1999)) because very strong spin-orbital coupling for rare-earth ions is diagonalized within a ground state multiplet and does not contribute to DM coupling.

Antiferromagnetism induced by external uniform field

$$\vec{L} = -\frac{1}{J^2}\left[\vec{D}\times\vec{H}\right] = \overset{\leftrightarrow}{\chi}_s \vec{H}$$

A.S. Moskvin, **Sov. Phys. Solid State 32**, 959 (1990) – **FeF_3**

- R. E. Walstedt, B. S. Shastry, and S. W. Cheong, **Phys. Rev. Lett. 72**, 3610 (1994); R. E. Walstedt and S. W. Cheong, **Phys. Rev. B 64**, 014404 (2001) -- **La_2CuO_4, experiment**
- A. S. Moskvin, Field induced staggered magnetization and ^{17}O Knight shift anomaly in La_2CuO_4, **Phys. Rev**. B **75**, 054505 (2007)

-- **La_2CuO_4, theory**

- A.U.B. Wolter, P. Wzietek, S. Sullow, F.J. Litterst, A. Honecker, W. Brenig, R. Feyerherm, and H.-H. Klauss, **Phys. Rev. Lett. 94**, 057204 (2005) - copper pyrimidine dinitrate

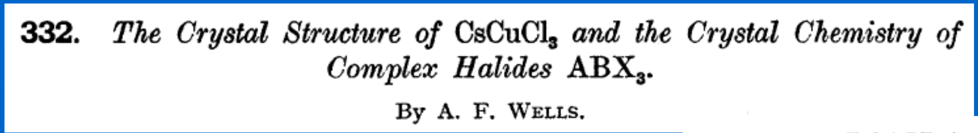
DM coupling in helimagnetic $CsCuCl_3$

… in collaboration with **Hiroyasu Matsuura**, Department of Physics,

The University of Tokyo

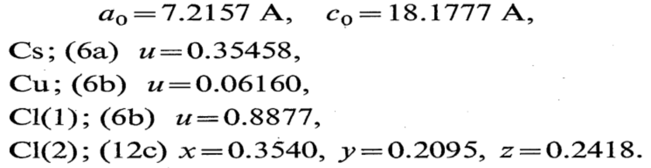
$CsCuCl_3$ is the first compound having a helical magnetic structure due to the DM coupling.

Structure



332. *The Crystal Structure of* CsCuCl$_3$ *and the Crystal Chemistry of Complex Halides* ABX$_3$.

By A. F. Wells.



$a_0 = 7.2157$ A, $c_0 = 18.1777$ A,

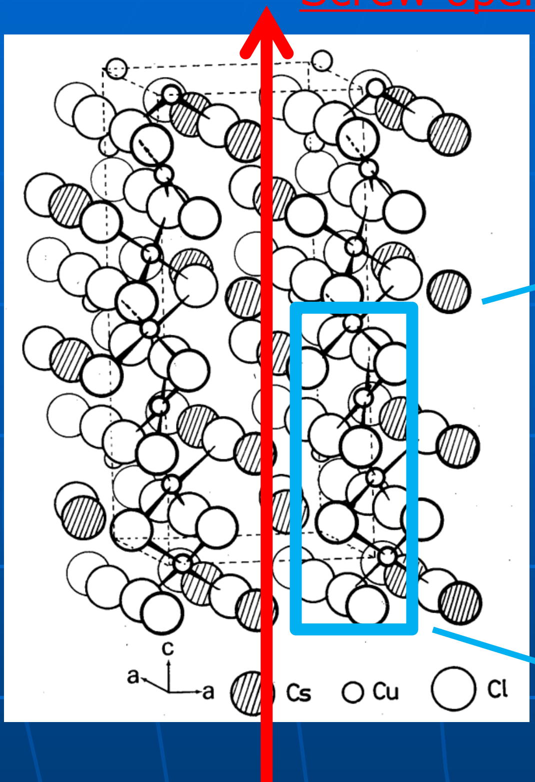
Cs; (6a) $u = 0.35458$,

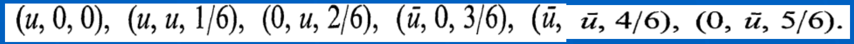
Cu; (6b) $u = 0.06160$,

Cl(1); (6b) $u = 0.8877$,

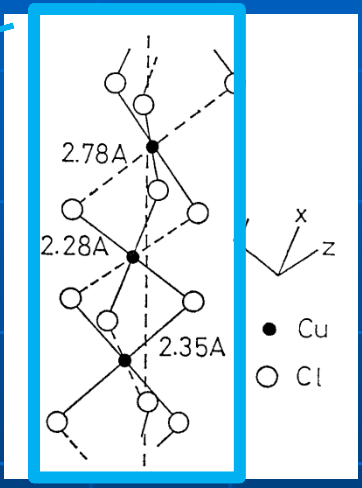
Cl(2); (12c) $x = 0.3540$, $y = 0.2095$, $z = 0.2418$.

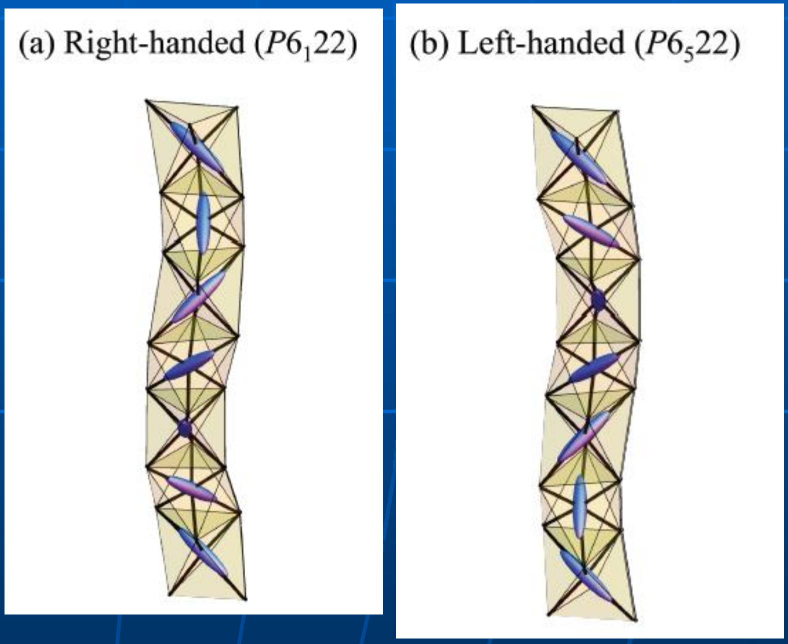
Screw operation





$(u, 0, 0)$, $(u, u, 1/6)$, $(0, u, 2/6)$, $(\bar{u}, 0, 3/6)$, $(\bar{u}, \bar{u}, 4/6)$, $(0, \bar{u}, 5/6)$.





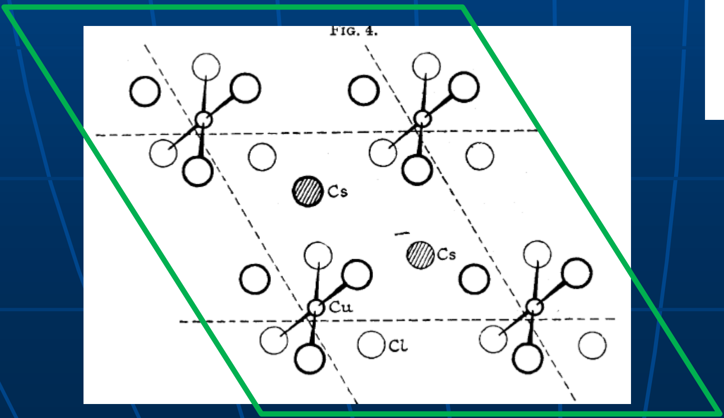
(a) Right-handed ($P6_122$)

(b) Left-handed ($P6_522$)

Kousaka (2012)

ab-plane

FIG. 4.



Some predictions on the Dzyaloshinskii vector direction

1. K. Adachi, N. Achiwa, M. Mekata, J. Phys. Soc. Japan 49 (1980) 545.

2. V.P. Plakhty, J. Wosnitza, J. Kulda, Th. Brückel, W. Schweika, D. Visser, S.V. Gavrilov, E.V. Moskvin, R.K. Kremer, M.G. Banks, Physica B 385-386 (2006) 288294

The net Dzyaloshinskii vector $\mathbf{D}_{nn+1}$ for Cu_n-Cu_{n+1} pair is a superposition of three contributions

$$\mathbf{D}_{nn+1} = \mathbf{D}_n + \mathbf{D}_{Cl} + \boldsymbol{D}_{n+1}$$

attached to the respective sites. All the vectors are oriented differently. Interestingly, the projection *of* the Dzyaloshinskii vector onto the Cu_n-Cu_{n+1} direction gives rise to a helical spin ordering along *c*-axis with spins in *ab*-plane, while perpendicular components compete for the spin canting upward and downward from the *ab*-plane with a periodicity of six Cu^{2+} ion spacings along the *c*-axis.

A.S. Moskvin, H. Matsuura, I.G. Bostrem, to be published

Antisymmetric exchange and multiferroicity

- H. Katsura, N. Nagaosa, and A.V. Balatsky, Phys. Rev. Lett. 95, 057205 (2005).
- I.E. Sergienko and E. Dagotto, Phys. Rev. B 73, 094434 (2006); cond-mat/0508075.

Exchange-relativistic mechanism of multiferroicity

- A.S. Moskvin, S.-L. Drechsler, PRB, 78, 2008; EPJ, 71,2009

Spin structure of electric polarization in crystals

$$\vec{P}_a = \sum_{mn} \left[\vec{\Pi}^{a}_{mn} \times \left[\vec{S}_m \times \vec{S}_n \right] \right]$$

relativistic bilinear antisymmetric coupling derived any case from antisymmetric Dzyaloshinskii-Moriya exchange

Effective spin-operators: spin-dependent polarisation against effective spin Hamiltonians

$$\vec{P}_{ex} = \vec{\Pi}_s\left(\vec{s}_1 \cdot \vec{s}_2\right)$$

$$\vec{P}_{ex-rel} = -\frac{1}{J}\vec{\Pi}_s\left(\vec{D}\cdot\left[\vec{s}_1 \times \vec{s}_2\right]\right)$$

$$V_{ex} = J\left(\vec{s}_1 \cdot \vec{s}_2\right)$$

$$V_{ex-rel} = \left(\vec{D}\cdot\left[\vec{s}_1 \times \vec{s}_2\right]\right)$$

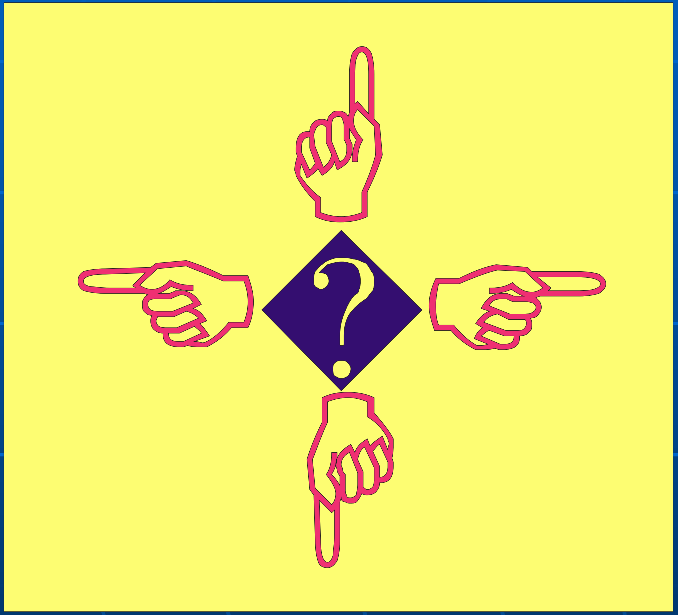
At present there is no reliable theoretical justifications and experimental evidences for dominating of the antisymmetric over conventional symmetric isotropic contribution to spin-dependent polarization

Large variety of weak ferro- and antiferromagnets

- α-Fe_2O_3, $MnCO_3$, $MnCO_3$, $CoCO_3$, NiF_2, $RFeO_3$, $RCrO_3$, FeF_3, $FeBO_3$, CoF_2, β-MnS, MnSi, $CuCl_2\cdot 2H_2O$, La_2CuO_4, $Ba_3Cu_2O_4Cl_2$, $Ba_2CuGe_2O_7$, $NaCu_2O_2$, $CsCuCl_3$, $K_2V_3O_8$, Yb_4As_3, Cu benzoate, magnetic molecules (Mn_{12},…), …….

Dzyaloshinskii-Moriya antisymmetric exchange coupling remains to be in the focus of experimental and theoretical studies…

Problems to be solved



Location of Dzyaloshinsky vector

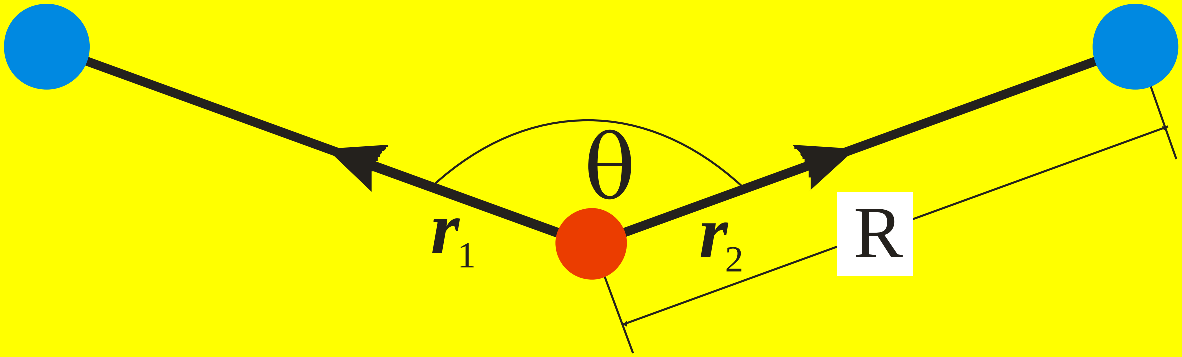
Sense of Dzyaloshinsky vector

Oxygen contribution to Dzyaloshinsky vector

……

- Thank you!

Superexchange coupling



$$V_{DM} = \vec{d}_{12}(\theta)\cdot\left[\vec{S}_1 \times \vec{S}_2\right]$$

$$\vec{d}_{12}(\theta) = (d'_{12}(R) + d''_{12}(R)\cos\theta)\left[\vec{r}_1 \times \vec{r}_2\right]$$

Dzyaloshinskii factor $d_{12}(\theta) = d'_{12}(R) + d''_{12}(R)\cos\theta$ does not depend on the choice of 1-2 ion numeration and has a certain sign!

Simple spin pair Hamiltonian in a weak ferromagnet

$$H_S = J\,(\mathbf{S}_1 \cdot \mathbf{S}_2) + \mathbf{D} \cdot [\mathbf{S}_1 \times \mathbf{S}_2]$$

$$E_S = JS^2(\mathbf{m}^2 - \mathbf{l}^2) + \mathbf{D}S^2[\mathbf{m} \times \mathbf{l}]$$

Magnetization in a weak ferromagnet:

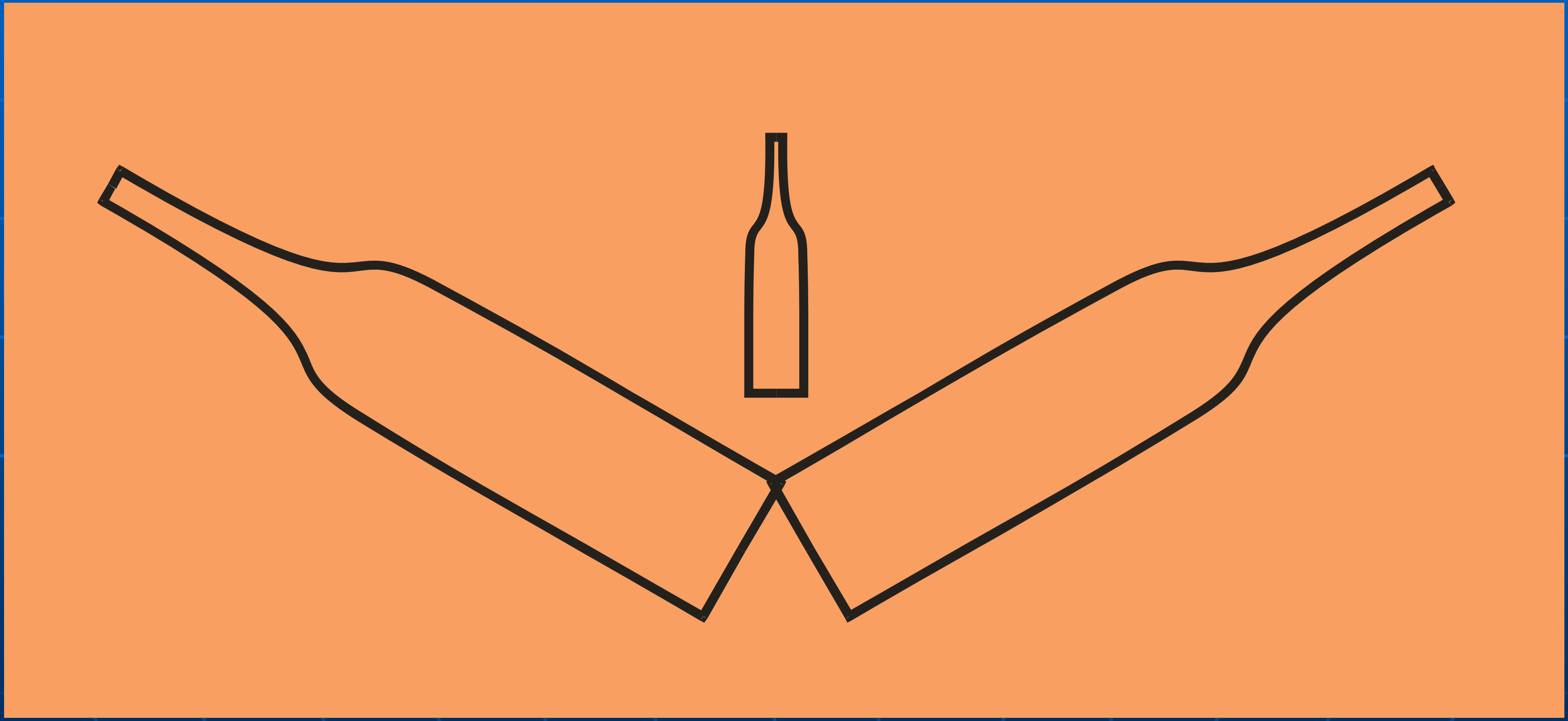
$$\mathbf{M} \propto [\mathbf{D} \times \mathbf{L}]/2J$$

Spin kinematics for a spin pair

- Three types of vector operators for a composite two-spin ½ pair:
- $\mathbf{S}=\mathbf{s}_1+\mathbf{s}_2$; $\mathbf{V}=\mathbf{s}_1-\mathbf{s}_2$; $\mathbf{T}=2[\mathbf{s}_1\times\mathbf{s}_2]$
- $\langle 00|V_m|1n\rangle=\langle 1n|V_m|00\rangle=\delta_{mn}$
- $\langle 00|T_m|1n\rangle=-\langle 1n|T_m|00\rangle=i\delta_{mn}$

$$\boxed{V_{DM}=1/2\ J\ \mathbf{S}^2+1/2\ (\mathbf{D}\cdot\mathbf{T})}$$

Russian vision of canting



Dzyaloshinskii term (Dzyaloshinskii interaction) in free energy for α-Fe_2O_3:

$$E_D = d_1 m_x l_y + d_2 m_y l_x$$

- $\mathbf{m} = \mathbf{m}_1 + \mathbf{m}_2$ – ferromagnetic vector
- $\mathbf{l} = \mathbf{m}_1 - \mathbf{m}_2$ – antiferromagnetic vector

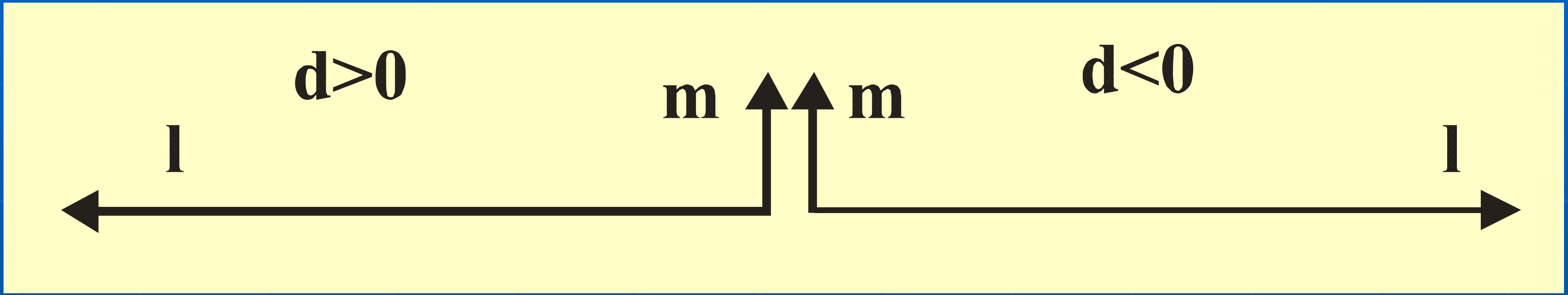
Two types of Dzyaloshinskii interaction

- Dzyaloshinskii interaction in free energy for α-Fe_2O_3:

$$
\boxed{\begin{gathered}E_D=d_1m_xl_y+d_2m_yl_x=\\ \tfrac{1}{2}(d_1+d_2)(m_xl_y+m_yl_x)+\\ \tfrac{1}{2}(d_1-d_2)(m_xl_y-m_yl_x)\end{gathered}}
$$

Sum of symmetric and antisymmetric terms – symmetric anisotropy and antisymmetric exchange

Sign of Dzyaloshinskii vector



Whether it has a “sign”?

The answer is YES !

RFeO$_3$:Relative orientation of F,C,A, and G vectors