Historical Aspects of Magnetoelectric Ferroics – with Some Personal Reminiscences

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5th European School on Multiferroics

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Centro Stefano Franscini, Monte Verità, Switzerland

Objectives of talk

1) Introduction - Understandig some terms:

ferroic(s), single phase multiferroic, type-I and type-II multiferroics, etc.

2) Some historical milestones of magnetoelectricit

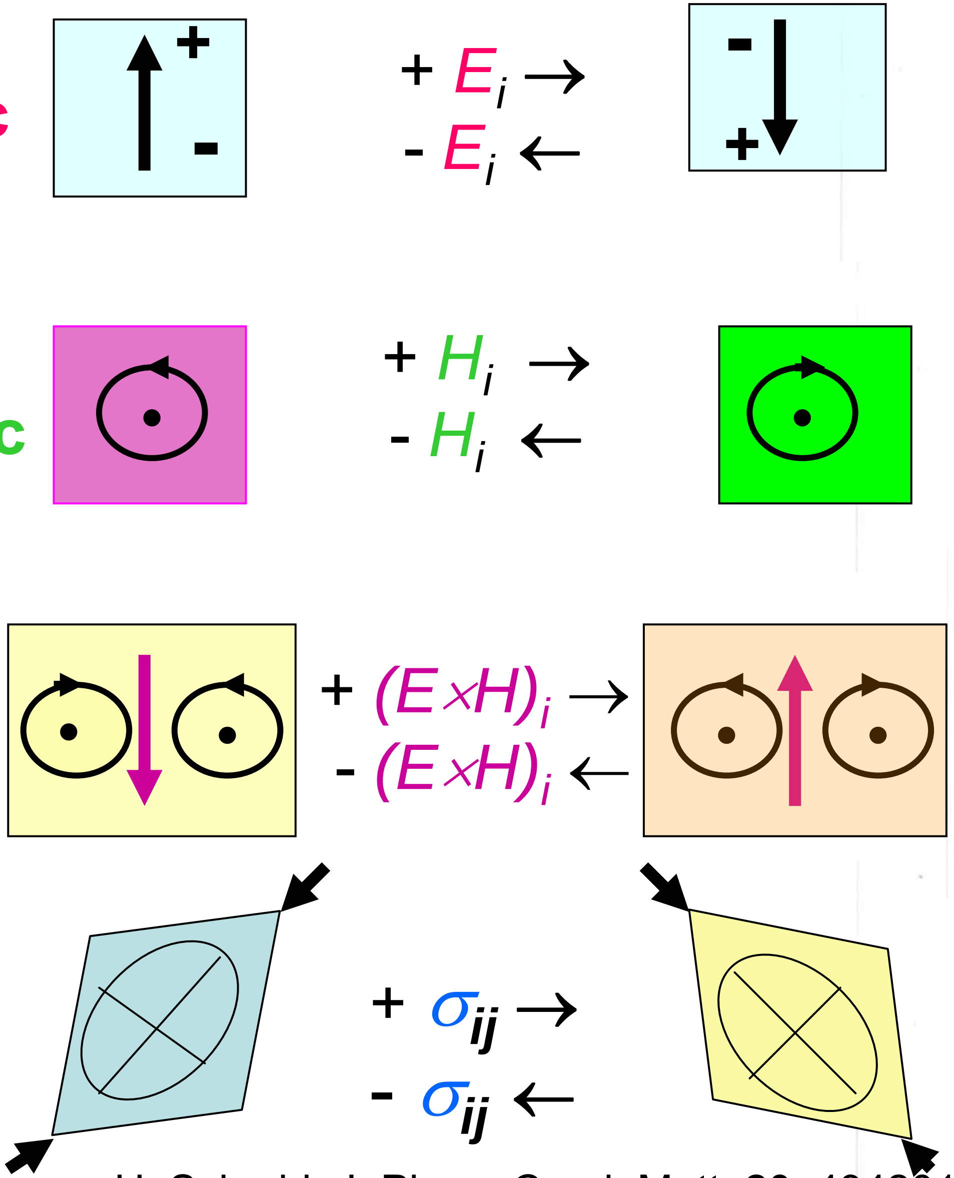
- The symmetry & thermodynamics approach
- The "chemical engineering" approach
- The first ferroelectric ferromagnets – some personal souvenirs of my Battelle Geneva period

3) Symmetry-based coupling between ferroics

- Role of ferroelasticity
- Ferroic domain control with applied fields.
- Toroidal moments and ferrotoroidic domains

"Ferroics": in common: domains and hysteresis loop

Term coined by *Kêitsiro Aizu* (Hitachi) in the 19sixties



Ferroelectric

$+ E_i \rightarrow$
$- E_i \leftarrow$

Ferromagnetic

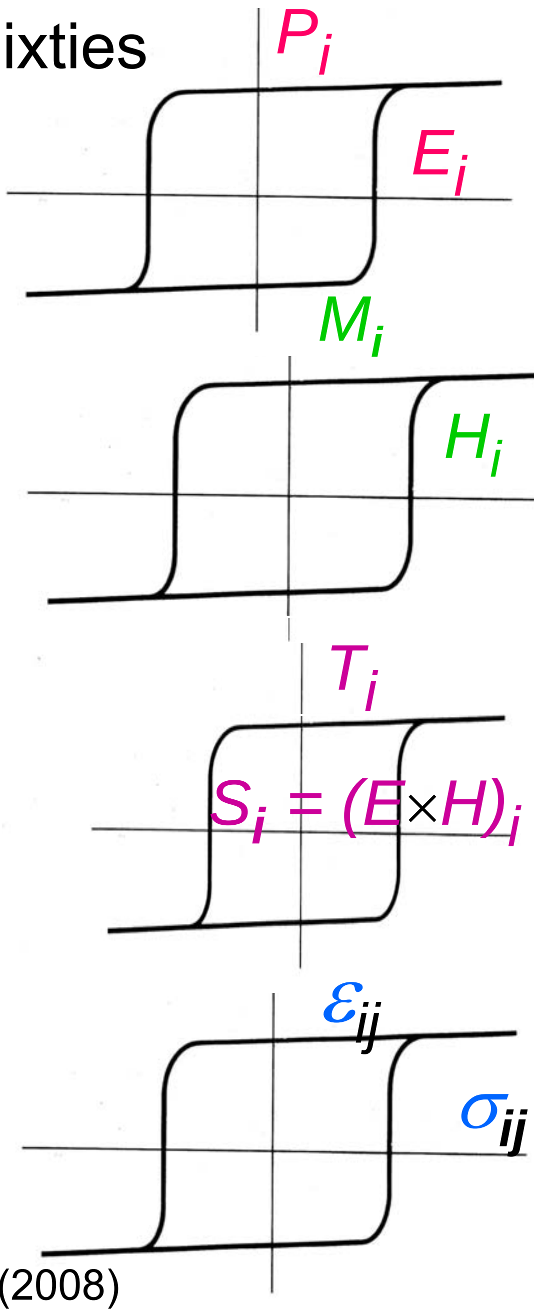
$+ H_i \rightarrow$
$- H_i \leftarrow$

Ferrotoroidic

$+ (E \times H)_i \rightarrow$
$- (E \times H)_i \leftarrow$

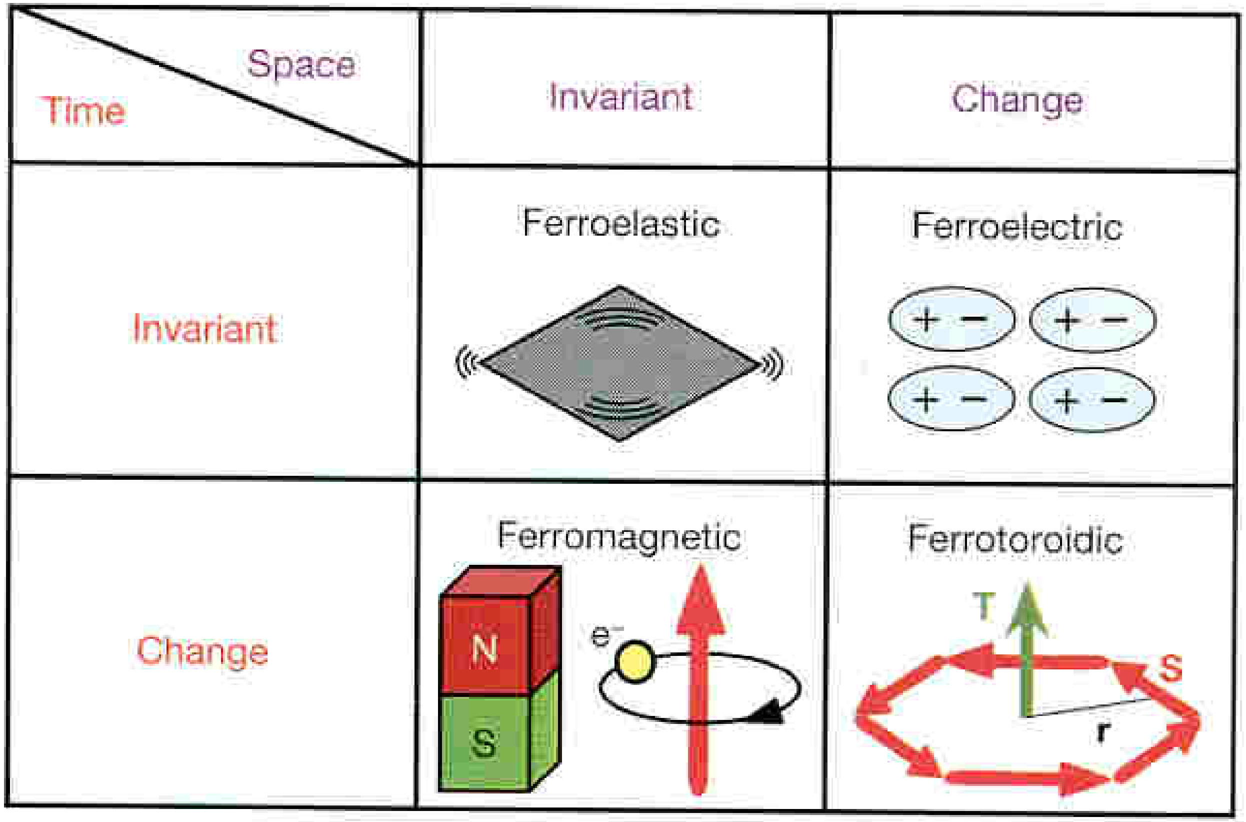
Ferroelastic

$+ \sigma_{ij} \rightarrow$
$- \sigma_{ij} \leftarrow$



H. Schmid, J. Phys.: Cond. Matt.,**20**, 434201(2008)

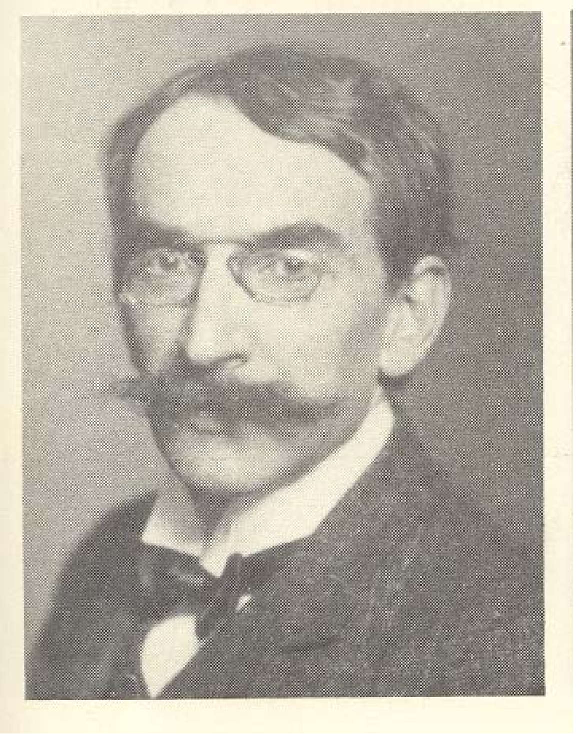
All forms of ferroic order under the parity operations of space and time



Time \ Space	Invariant	Change
Invariant	Ferroelastic	Ferroelectric
Change	Ferromagnetic	Ferrotoroidic

The red arrows are only a guide for the eyes!

B.B. Van Aken, J.-P. Rivera, H. Schmid and M. Fiebig,Nature, **449**, 702 (2007)



Pierre-Ernest Weiss
1865 - 1940

F.Bitter, Phys.Rev. **38**,1903-5 (1931)

In 1907 Pierre Weiss has the idea of ferromagnetic domains, later called « Weiss domains »

In 1931
F. Bitter and independantly
L. v. Hàmos & P.A. Thiessen
are proving Weiss' idea by revealing micro-patterns of domains and walls with an improved colloidal powder method.

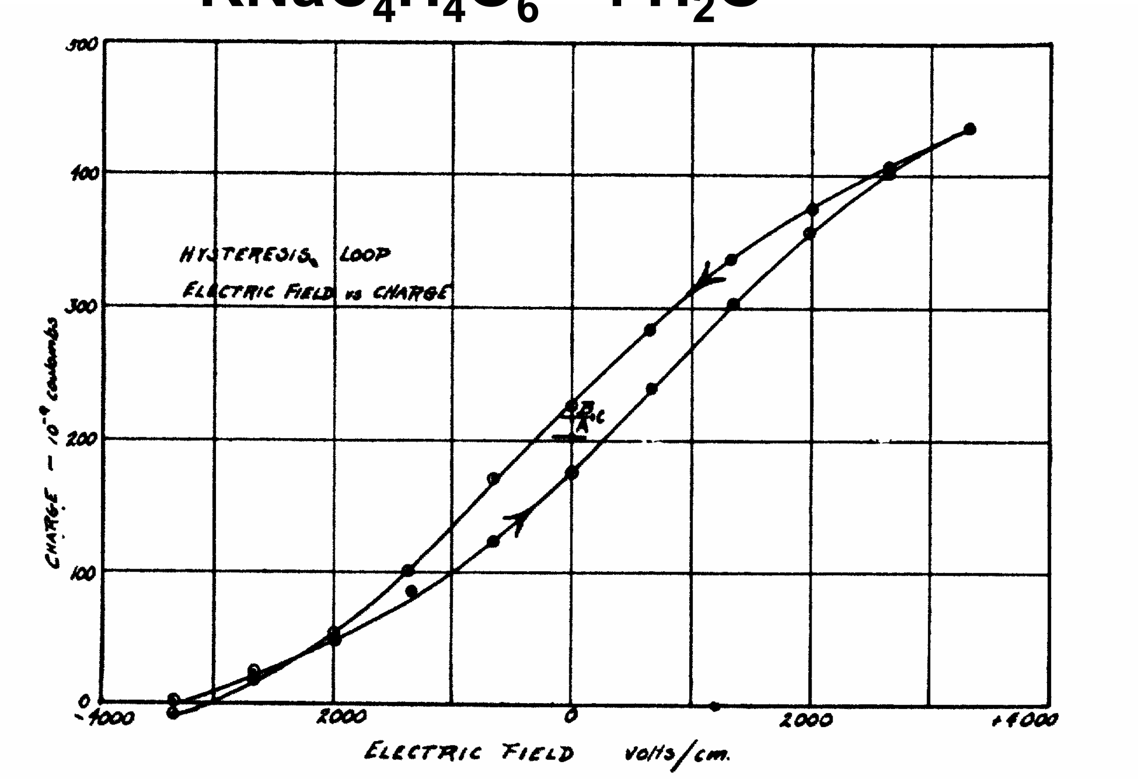
L. v.Hàmos &P.A.Thiessen
Z. Phys., **71**,442-4 (1931)

Pierre Weiss and Gabriel Foëx, Le Magnétisme, A.Colin,Paris, 1951
definitely introduce the term "domaines"

1920: Discovery of Ferroelectricity in Rochelle-(Seignette-) Salt

Joseph Valasek in 1922*)

$KNaC_4H_4O_6 \cdot 4\ H_2O$



Presented at the meeting of the American Physical Society, Washington, April 23/24 1920

***) J. Fousek, *Ferroelectrics*, 173, 3-5 (1995)**

MEIPIC-2, ASCONA, September 1993

The "virus" "multiferroic" is born !

What is a "Multiferroic" ?

- Original definition of a "Multiferroic":

  A material uniting two or more of the properties "ferroelectric", "ferromagnetic", "ferrotoroidic", "ferroelastic" in a *single phase*.

- Mutated definition:

  A ferromagnetic or antiferromagnetic ferroelectric permitting magnetoelectric effects; sometimes the term is even used for hetero-phase systems

Sir, my need is sore.
Spirits that I've cited
My commands ignore

Herr, die Not ist groß!
Die ich rief, die Geister,
Werd ich nun nicht los.

.
Johann Wolfgang von Goethe
(In: Der Zauberlehrling, The Sorcerer's Apprentice, 1779,
translation by Edwin Zeydel, 1955)

What kinds of magnetic multiferroics do exist?

"*Type-I*" multiferroics [*] [**]

(*Split-order-parameter* multiferroics [***])

- Ferroelectricity and magnetism have different origin and set on at different temperatures
- Medium and large spontaneous polarizations

"*Type-II*" multiferroics

(*Joint-order-parameter* multiferroics [***])

- Ferroelectricity and magnetic order due to spin system
- Extremely small spontaneous polarizations
- Rigid coupling between polarization and magnetic order

***)** J. Van den Brink and D.I. Khomskii, JPCM, **20** (2008) 434217

****)** D. Khomskii, Physics **2**, (2009) 20

*****)**Th. Lottermoser, D. Meier, R.V. Pisarev and M. Fiebig, PRB **80**, (2009) 100101(R)

History of the magnetoelectric (ME) effect

The symmetry + thermodynamics approach towards magnetoelectricity

History of the magnetoelectric (ME) effect

- **1894 Pierre Curie's conjecture:**

"Materials should exist, which can be polarised by a magnetic field and magnetised by an electric field "

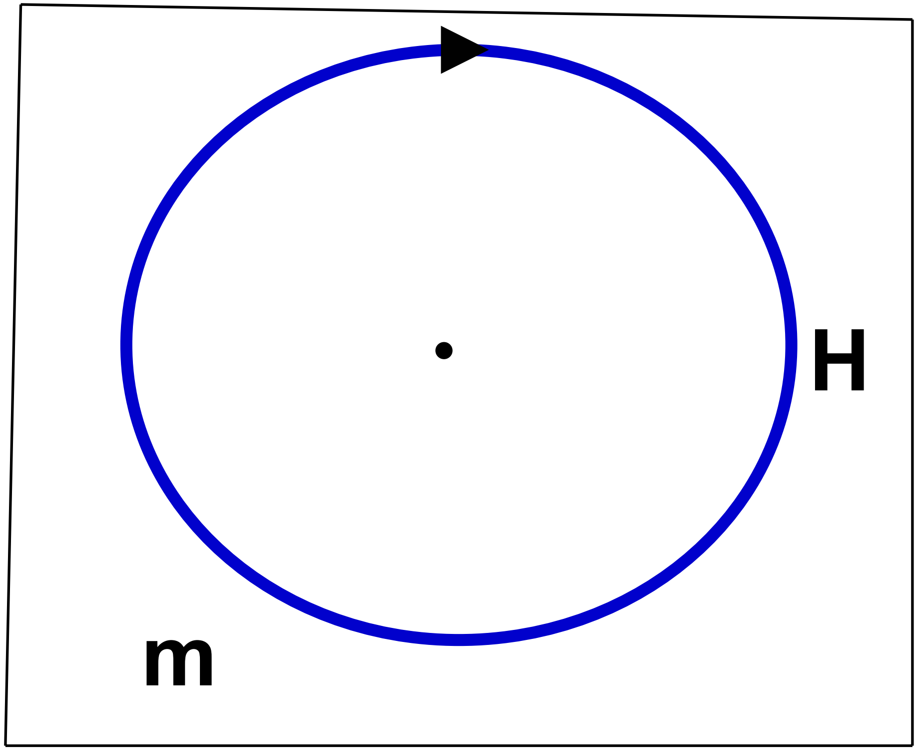
Journal de Physique, 3^e Série, **3**, 393 (1894)

Many unsuccessful experiments followed between 1922 and 1937 !

See: T.H. O'Dell, *The Electrodynamics of Magneto-electric Media*,
North Holland, Amsterdam, 1970

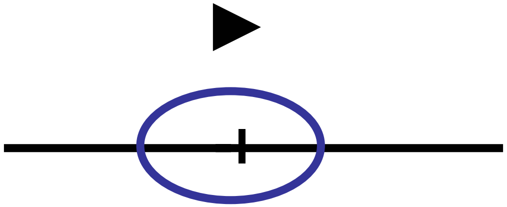
T.H. O'Dell, 1973

Pierre Curie was well aware of the symmetry of the magnetic and electric fields



1894

1859 - 1906



1932: Eugène **Wigner** (1902 – 1995) introduces the **"time reversal"** symmetry operator R (in crystallography we use: 1'):

A turning Point!

History of the magnetoelectric (ME) effect

For space inversion $\bar{1}$:

$\bar{1}\mathbf{E} = -\mathbf{E}$

$\bar{1}\mathbf{H} = \mathbf{H}$

For time reversal R (1') :

- **Change of sign by applying** R:

velocity	$R\,\mathbf{v} = -\mathbf{v}$
electrical current density	$R\,\mathbf{j} = -\mathbf{j}$
spin density	$R\,\mathbf{S} = -\mathbf{S}$
magnetic field	$R\,\mathbf{H} = -\mathbf{H}$

- **No change of sign by applying** R:

charge density	$R\,\rho = \rho$
electric field	$R\,\mathbf{E} = \mathbf{E}$
spontaneous strain	$R\,\sigma = \sigma$

History of the magnetoelectric (ME) effect

1937 Landau

Lev Davidovich Landau
1908-1968

nonmagnetic crystals $j = 0$

magnetic crystals $R\ j = -j = \neq 0$

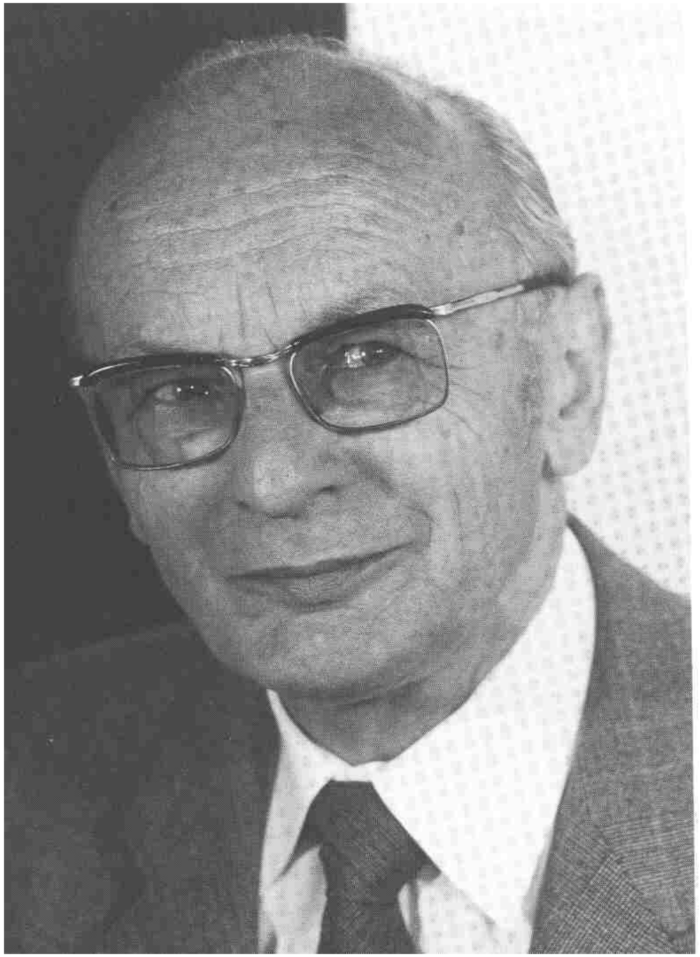
$R\ S = -S$

Landau and Lifshitz in:

The Electrodynamics of Continuous Media
Fizmatgiz, Moscow, 1959 (in Russian):

"The linear piezomagnetic effect and the linear magnetoelectric effect could exist in principle for certain magneto-crystalline classes."

Look into the Heesch–Shubnikov point groups



Heinrich Heesch
1906 - 1995

Alexey Vasilyevich Shubnikov
1887 - 1970

Point groups and space groups

Crystallo-physical phenomenology

32

Point groups (crystal classes)

J.F.C. Hessel 1830

A. Bravais 1848

"Time reversal" 1'

⇓

122 Heesch-Shubnikov ("black-white") point groups

H. Heesch 1930

A.V. Shubnikov 1951 (122 "antisymmetry"="colour" groups)

B.A.Tavger , V.M. Zaitsev 1956

Translation

⇒

Translation

⇒

Crystal structure, coordinates

230

Space groups

Fedorov 1890, Schönflies 1891

Heesch 1929

"Time reversal" 1'

⇓

1651 Heesch-Shubnikov ("black-white") space groups

A.M. Zamorzaev 1953

N.V. Belov, N.N. Neronova, T.S. Smirnova 1955

V.A. Koptsik 1966

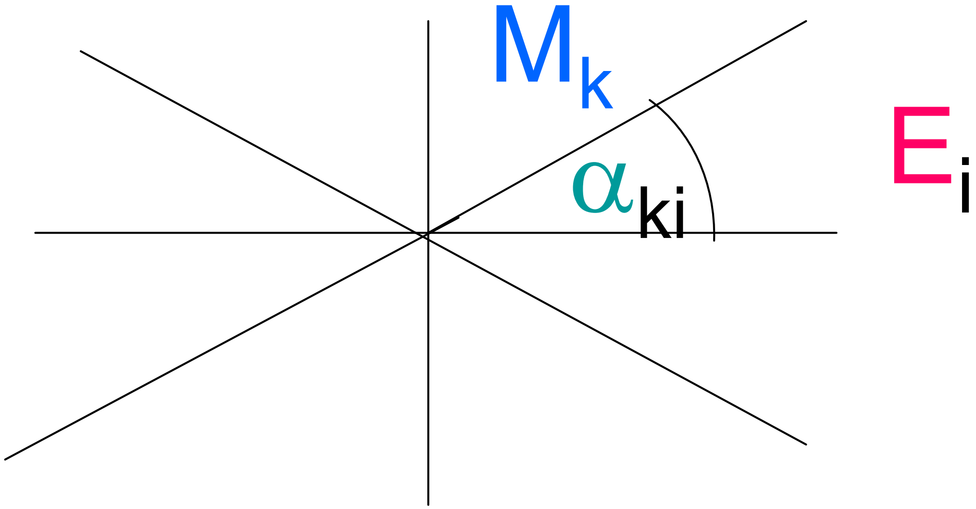
History of the magnetoelectric (ME) effect

- **1959** **Dzyaloshinsky** predicts the linear ME effect in a.f.m. Cr_2O_3 : **Point group $\bar{3}'m'$**

$$P_i = \alpha_{ik} H_k \quad \text{and} \quad M_k = \alpha_{ki} E_i$$

$$\alpha_{11} = \alpha_{22} \qquad \alpha_{33}$$

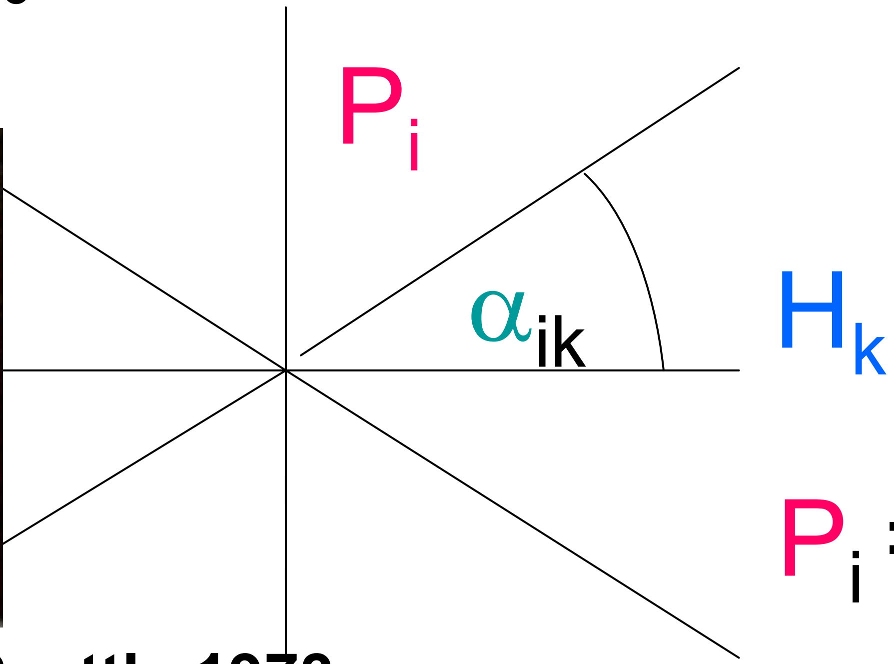
- **1960** **Astrov** measures the **$(ME)_E$** effect **on Cr_2O_3**



Dzyaloshinsky and Astrov, Ascona, MEIPIC-2, September 1993

History of the magnetoelectric (ME) effect

- **1961: Rado, Folen and Stalder** measure the **(ME)$_H$** effect on **Cr_2O_3 :**

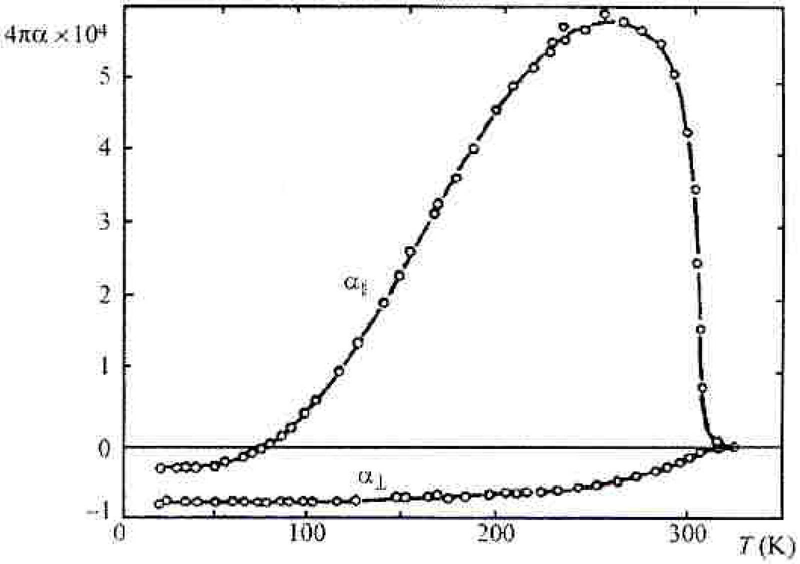


George T. Rado Seattle,1973

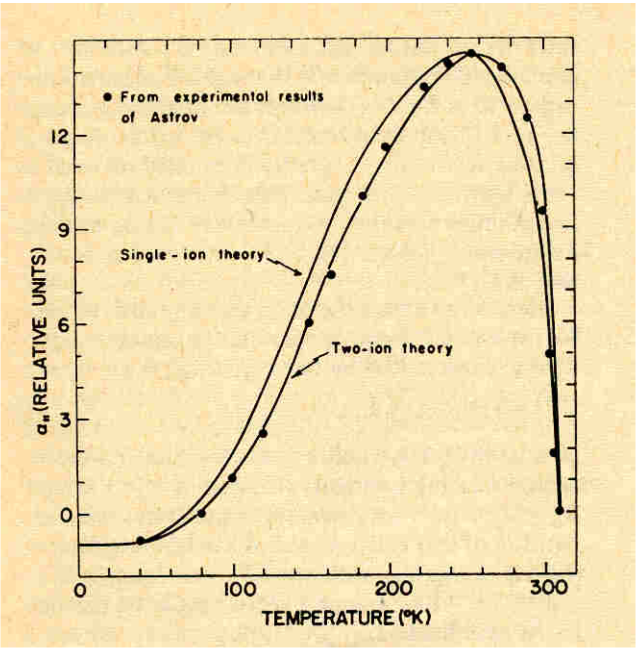
$$P_i = \alpha_{ik} H_k$$

V.N. Folen, Seattle,1973

History of the magnetoelectric (ME) effect



1960: Astrov
$(\mathrm{ME})_E$



1961: Rado et al.
$(\mathrm{ME})_H$

Linear ME-effect versus temperature

Density of stored free enthalpy for a single domain:

$$g(\mathbf{E},\mathbf{H},\boldsymbol{\sigma};T) = \ldots {}^{S}P_i\, E_i + {}^{S}M_i\, H_i + {}^{S}\varepsilon_{ij}\, \sigma_{ij}$$

$$+ \tfrac{1}{2}\, \varepsilon_0\, \varepsilon_{ik}\, E_i\, E_k + \tfrac{1}{2}\, \mu_0\, \mu_{ik}\, H_i\, H_k + \tfrac{1}{2}\, s_{ijkl}\, \sigma_{ij} \sigma_{kl}$$

$$+ \alpha_{ik}\, E_i\, H_k + d_{ijk}\, \sigma_{ij}\, E_k + g_{ijk}\, \sigma_{ij}\, H_k$$

$$+ \tfrac{1}{2}\, \beta_{ijk}\, E_i\, H_j\, H_k + \tfrac{1}{2}\, \gamma_{ijk}\, H_i\, E_j\, E_k$$

$$+ \tfrac{1}{2} \delta_{ijkl}\, E_i E_j H_k H_l \ldots$$

.

$$g = g_o - \varepsilon_o/2\, E^2 - \mu_o/2\, H^2$$

Which terms will be allowed ?

The derivatives

- $\mathrm{ME_{\mathbf{H}}}$ effects :

$P_k(\mathbf{E},\mathbf{H};T) = Q/S = -\,\partial g/\partial E_k =$

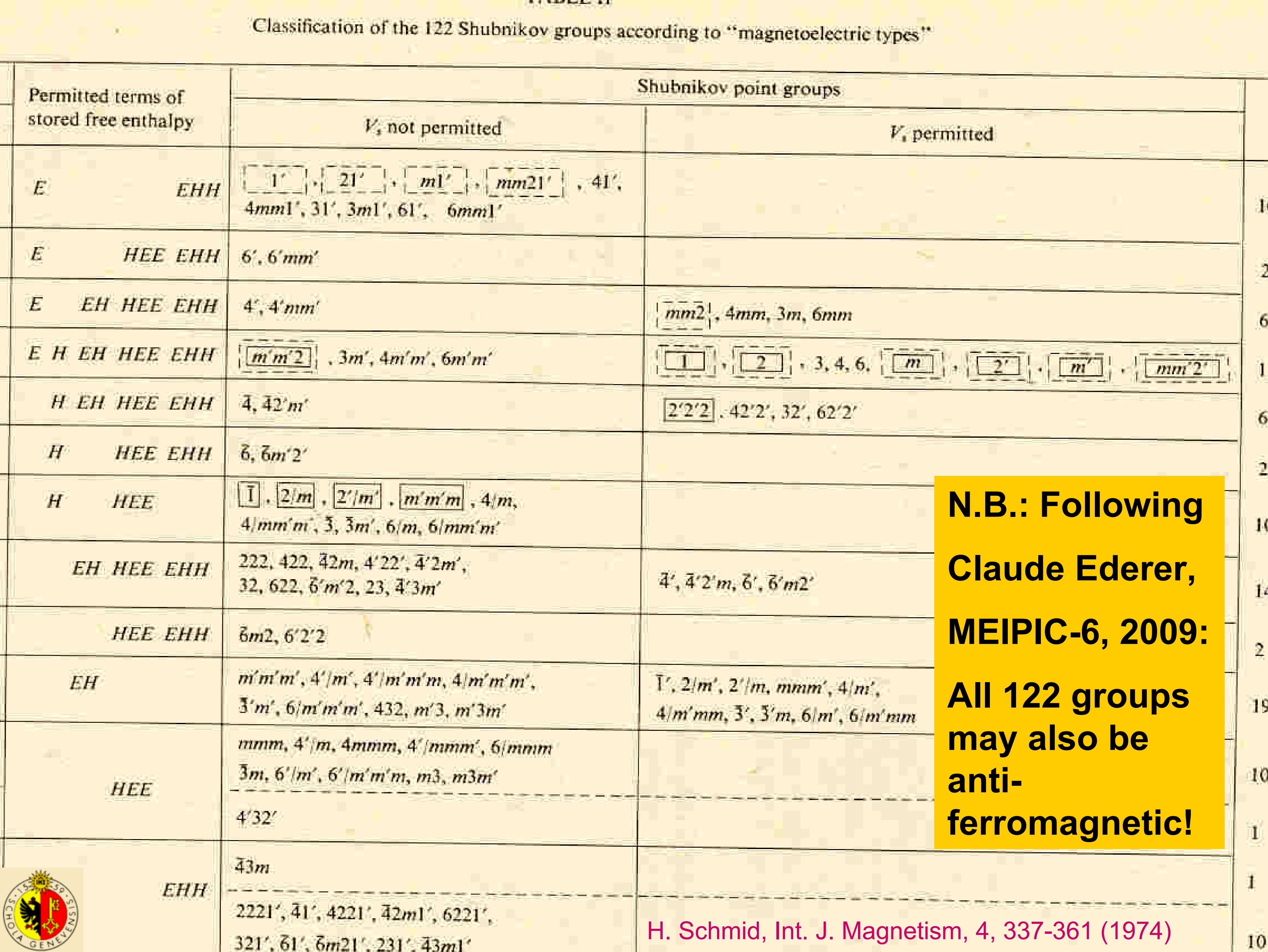
$\ldots {}^{S}P_k + \varepsilon_0\, \varepsilon_{ki}\, E_i + \alpha_{ki}\, H_i + \tfrac{1}{2}\, \beta_{kij}\, H_i\, H_j + \gamma_{ijk}\, H_i\, E_j + \ldots$

- $\mathrm{ME_{\mathbf{E}}}$ effects :

$M_k(\mathbf{E},\mathbf{H};T) = -\,\partial g/\partial H_k =$

$\ldots {}^{S}M_k + \mu_0\, \mu_{ki}\, H_i + \alpha_{ik}\, E_i + \beta_{ijk}\, E_i\, H_j + \tfrac{1}{2}\, \gamma_{kij}\, E_i\, E_j + \ldots$

Allowed terms: those remaining invariant under the symmetry operations of the point group



Classification of the 122 Shubnikov groups according to "magnetoelectric types"

Permitted terms of stored free enthalpy	Shubnikov point groups		
	V_s not permitted	V_s permitted	
E *EHH*	$\boxed{1'}$, $\boxed{21'}$, $\boxed{m1'}$, $\boxed{mm21'}$, 41′, 4*mm*1′, 31′, 3*m*1′, 61′, 6*mm*1′		1
E *HEE* *EHH*	6′, 6′*mm*′		2
E *EH* *HEE* *EHH*	4′, 4′*mm*′	$\boxed{mm2}$, 4*mm*, 3*m*, 6*mm*	6
E *H* *EH* *HEE* *EHH*	$\boxed{m'm'2}$, 3*m*′, 4*m*′*m*′, 6*m*′*m*′	$\boxed{1}$, $\boxed{2}$, 3, 4, 6, $\boxed{m}$, $\boxed{2'}$, $\boxed{m'}$, $\boxed{mm'2'}$	1
H *EH* *HEE* *EHH*	$\bar{4}$, $\bar{4}2'm'$	$\boxed{2'2'2}$, 42′2′, 32′, 62′2′	6
H *HEE* *EHH*	$\bar{6}$, $\bar{6}m'2'$		2
H *HEE*	$\boxed{\bar{1}}$, $\boxed{2/m}$, $\boxed{2'/m'}$, $\boxed{m'm'm}$, 4/*m*, 4/*mm*′*m*′, $\bar{3}$, $\bar{3}m'$, 6/*m*, 6/*mm*′*m*′		1
EH *HEE* *EHH*	222, 422, $\bar{4}2m$, 4′22′, $\bar{4}'2m'$, 32, 622, $\bar{6}'m'2$, 23, $\bar{4}'3m'$	$\bar{4}'$, $\bar{4}'2'm$, $\bar{6}'$, $\bar{6}'m2'$	1
HEE *EHH*	$\bar{6}m2$, 6′2′2		2
EH	*m*′*m*′*m*′, 4′/*m*′, 4′/*m*′*m*′*m*, 4/*m*′*m*′*m*′, $\bar{3}'m'$, 6/*m*′*m*′*m*′, 432, *m*′3, *m*′3*m*′	$\bar{1}'$, 2/*m*′, 2′/*m*, *mmm*′, 4/*m*′, 4/*m*′*mm*, $\bar{3}'$, $\bar{3}'m$, 6/*m*′, 6/*m*′*mm*	19
HEE	*mmm*, 4′/*m*, 4*mmm*, 4′/*mmm*′, 6/*mmm*, $\bar{3}m$, 6′/*m*′, 6′/*m*′*m*′*m*, *m*3, *m*3*m*′		10
	4′32′		1
EHH	$\bar{4}3m$		1
	2221′, $\bar{4}1'$, 4221′, $\bar{4}2m1'$, 6221′, 321′, $\bar{6}1'$, $\bar{6}m21'$, 231′, $\bar{4}3m1'$		10

N.B.: Following

Claude Ederer,

MEIPIC-6, 2009:

All 122 groups may also be anti-ferromagnetic!

H. Schmid, Int. J. Magnetism, 4, 337-361 (1974)

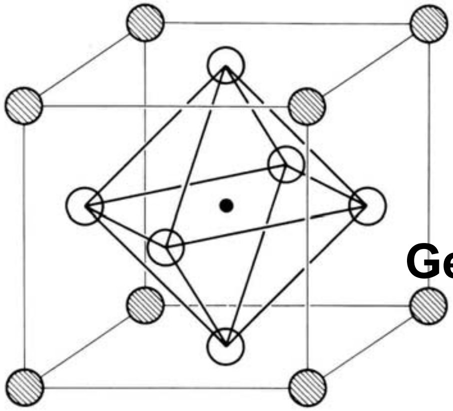
The chemical synthesis approach towards single phase ferroelectricity + (anti)ferromagnetism

First attempts at synthesizing ferroelectric ferromagnets:

2nd Int. Conference on Magnetism, Grenoble, **1958**
G.A. Smolenskii and V. A. Ioffe report on the first antiferromagnetic ferroelectrics, the perovskites

$Pb_3(Fe^{3+}\,2W^{6+})O_9$
$Pb(Fe^{3+}{}_{1/2}Nb^{5+}{}_{1/2})O_3$ in ceramic form
$Pb(Fe^{3+}{}_{1/2}Ta^{5+}{}_{1/2})O_3$

« Matthias-Smolensky rule » :
Ferroelectricity necessitates ions with rare gas configuration on oxy-octahedral sites (Nb^{5+}, Ta^{5+}, W^{6+}, Ti^{4+}, etc.)



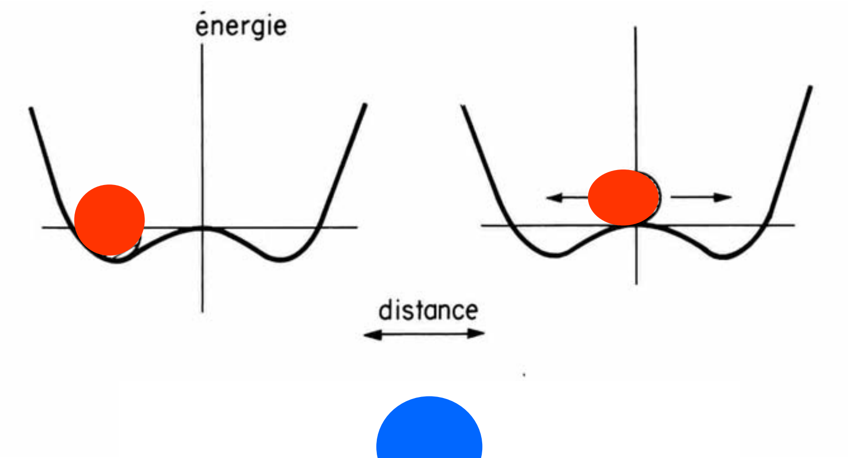
Perovskite cell

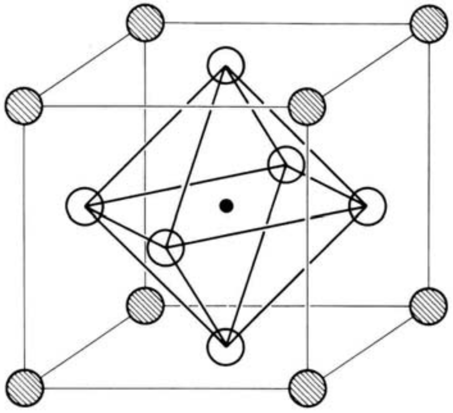
Georgii Anatolevich Smolensky
1910 – 1986

N.A.Hill,J.Phys.Chem.B **104**, 6694(2000)

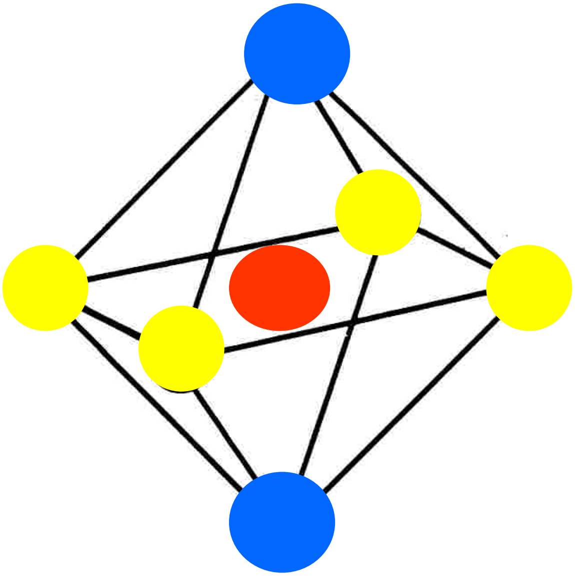
For avoiding the fatal « Smolenskii-Matthias rule » → double potential well idea by Aloysio Janner

Aloysio Janner





Perovskite cell



Anisotropic octahedron

First attempts at synthesizing oxygen-fluorine octahedra

The miracle: C.N.E.T. Bagneux/France finances our proposed project: "Attempts at synthesizing ferroelectric ferromagnets"

- Bogdan and Vera Zega try synthesizing $BaCr(O_2F)$, $BaFe(O_2F)$, $PbCr(O_2F)$, $PbFe(O_2F)$ without success
- Schmid synthesizes cobalt hydroxi-fluorides

H.S., Z. Anorg Allgem Chem., **334**,297-303 (1965)

Non-polar ! Of no interest !

BORACITE is finally discovered in literature !!!

T. Ito, N. Morimoto, and R. Sadanaga, *Acta Cryst.*, **4**, 310 (1951)

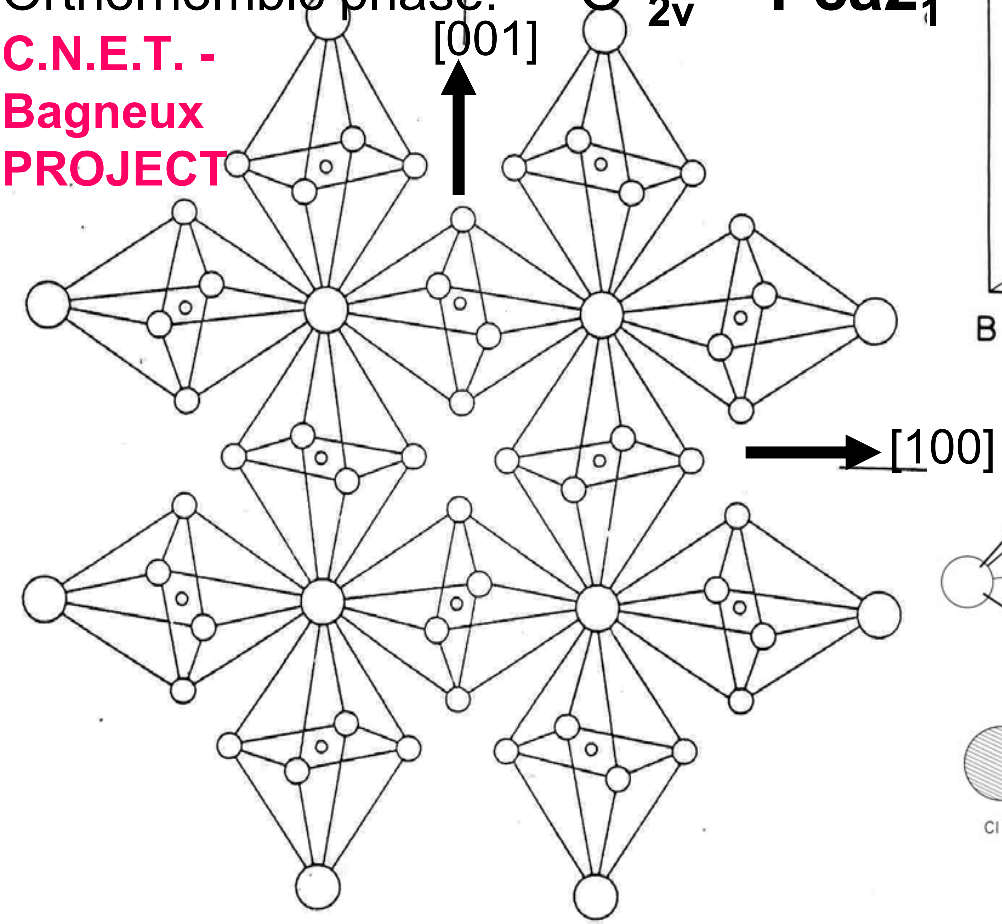
Boracite $Mg_3B_7O_{13}Cl$

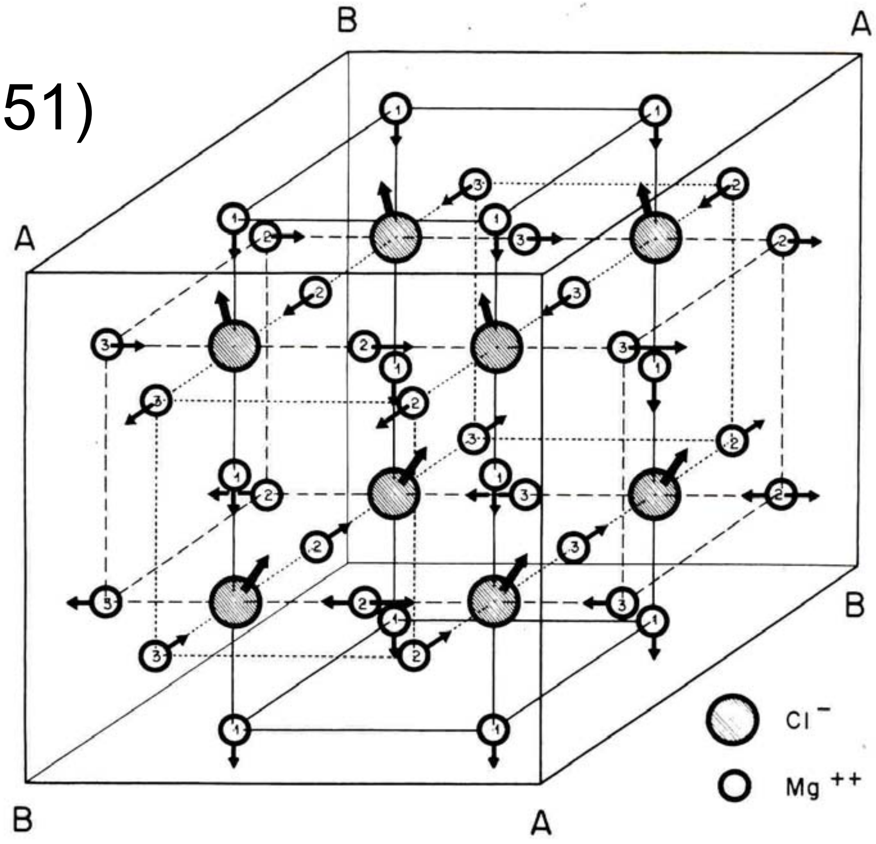
T_c = 265 ° C

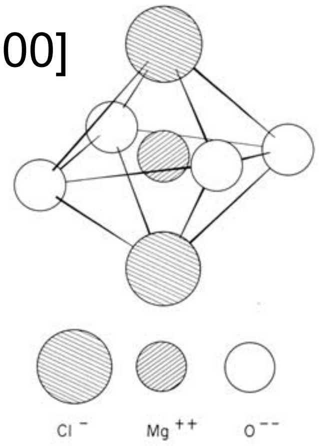
Cubic phase: T^5_d - $F\bar{4}3c$

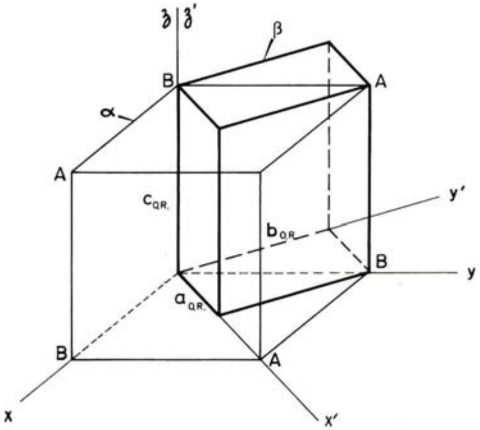
Orthorhombic phase: C^5_{2v} - $Pca2_1$

C.N.E.T. - Bagneux PROJECT









1962 First attempts at synthetizing single crystals:

- **Following W. Heintz and G.E. Richter, *(Pogg.) Ann.Phys*. 110, 613 (1860) for the synthesis of $Mg_3B_7O_{13}Cl$:**

« melting together » at 900°C:

$5\ NiO + NiCl_2 + 7\ B_2O_3 \rightarrow 2\ Ni_3B_7O_{13}Cl$

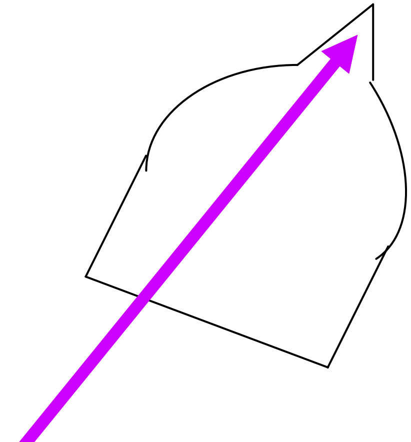
Great disapointment :

no reaction whatsoever !

However!!!

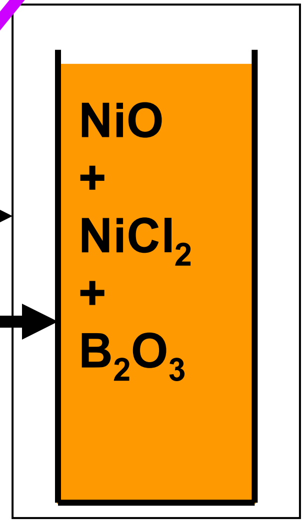
The mechanic Werner Kohli observes a yellow

0.1 mm crystal, "*differing from sublimed $NiCl_2$*"



evacuated quartz ampoule

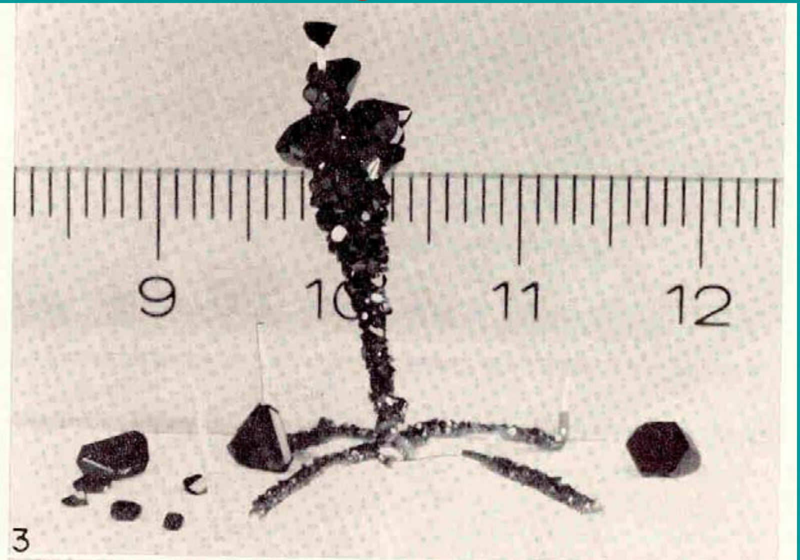
quartz crucible



No "melting together" but gas phase transport reactions

1962 The Synthesis

3



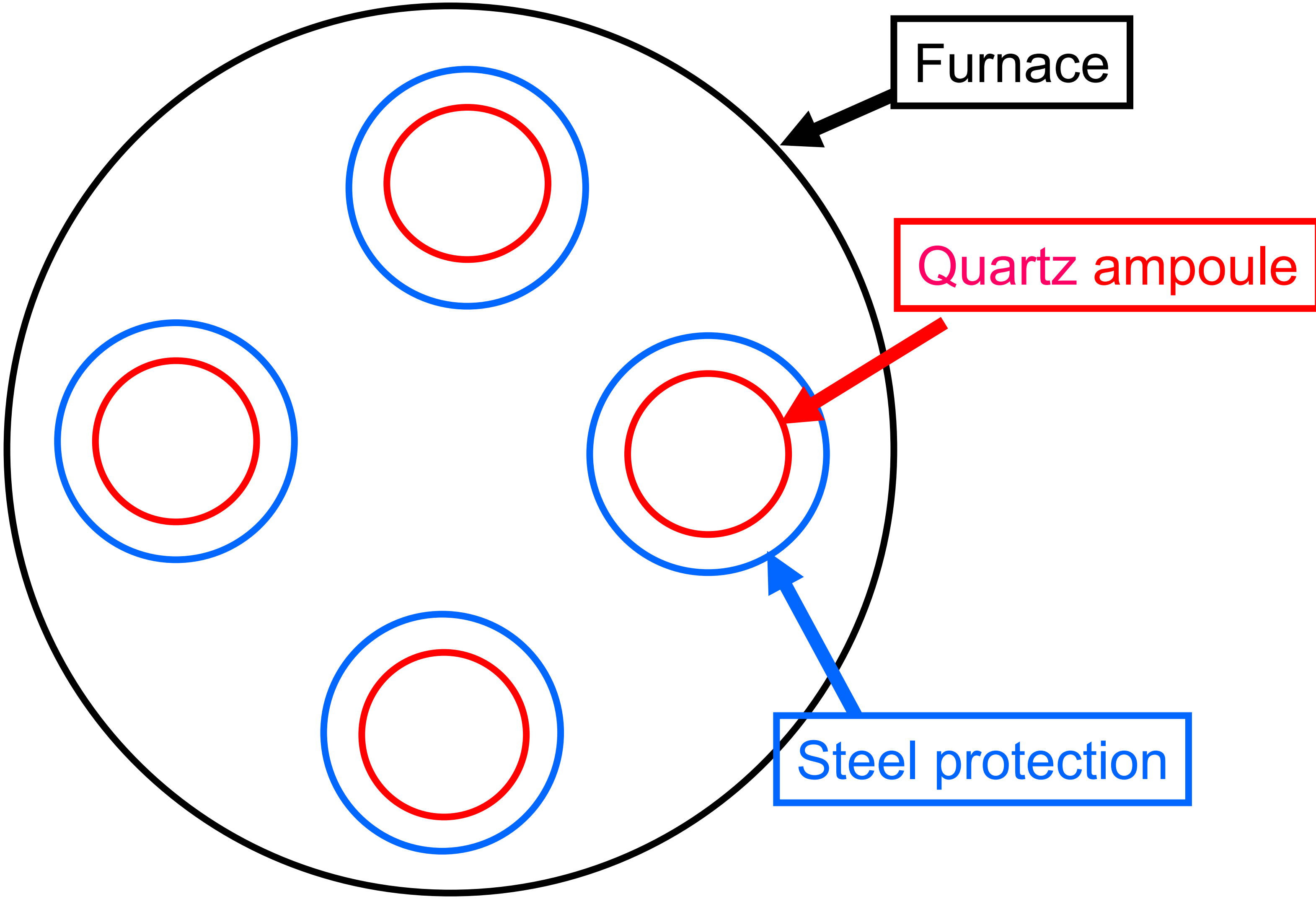
4

Abb. 3. Auf Platindraht aufgewachsene Nickel–Chlor-Borazitkristalle (Masstab in cm). Der Draht tauchte in die flüssige Borsäure ein.

Abb. 4. Im Quarztiegel gewachsene Nickel–Jod-Borazitkristalle (Masstab in cm).

H. Schmid, *J. Phys. Chem. Solids*,
26, 973-988 (1965)

The "Stalin Organ"



Furnace

Quartz ampoule

Steel protection

Is Ni-Cl-boracite ferroelectric ? Doubts come up

- Ascher's "maximal polar subgroup rule" fails

E. Ascher, *Phys. Lett.* **20** (1966) 352-4

Is the space group incorrect ?

- Sonin and Zheludev claim on symmetry grounds that boracite must be antiferroelectric

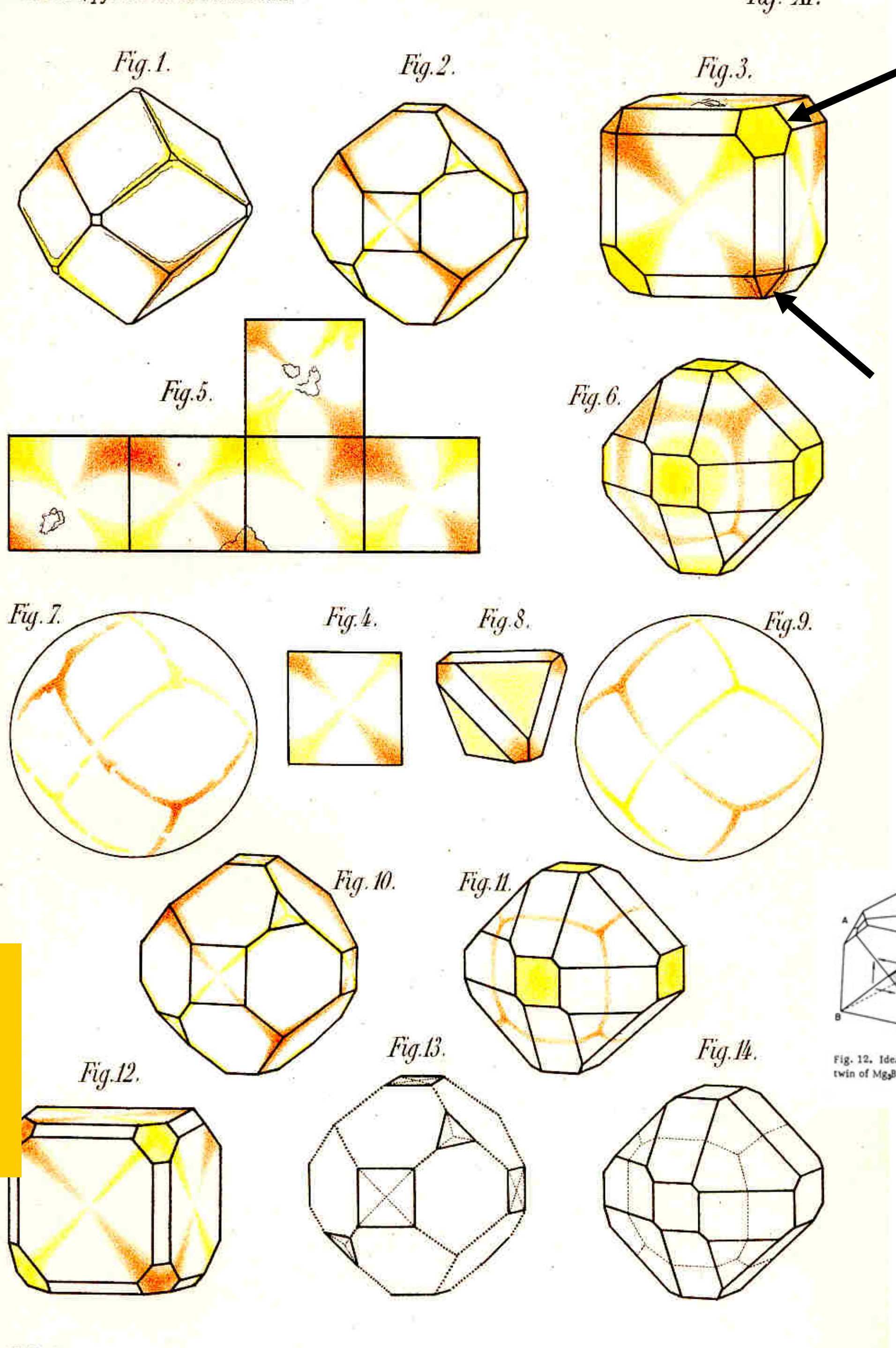
A.S. Sonin and I.S. Zheludev, *Sov. Phys.-Crystallogr.* **8** (1963) 283-285

K. MACK,
Z. Kryst.,
8, 503-522
(1884)

Proof of pyroelectric behaviour:

attraction of sulpur (yellow) and minium (red) powder

The polar space group must be correct !!



Sulphur

Minium Pb_3O_4

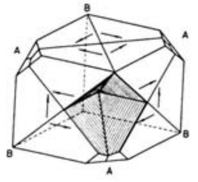


Fig. 12. Idealized schematic mimetic twin of $Mg_3B_7O_{13}Cl$ of the Stassfurt type.

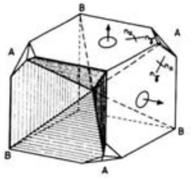
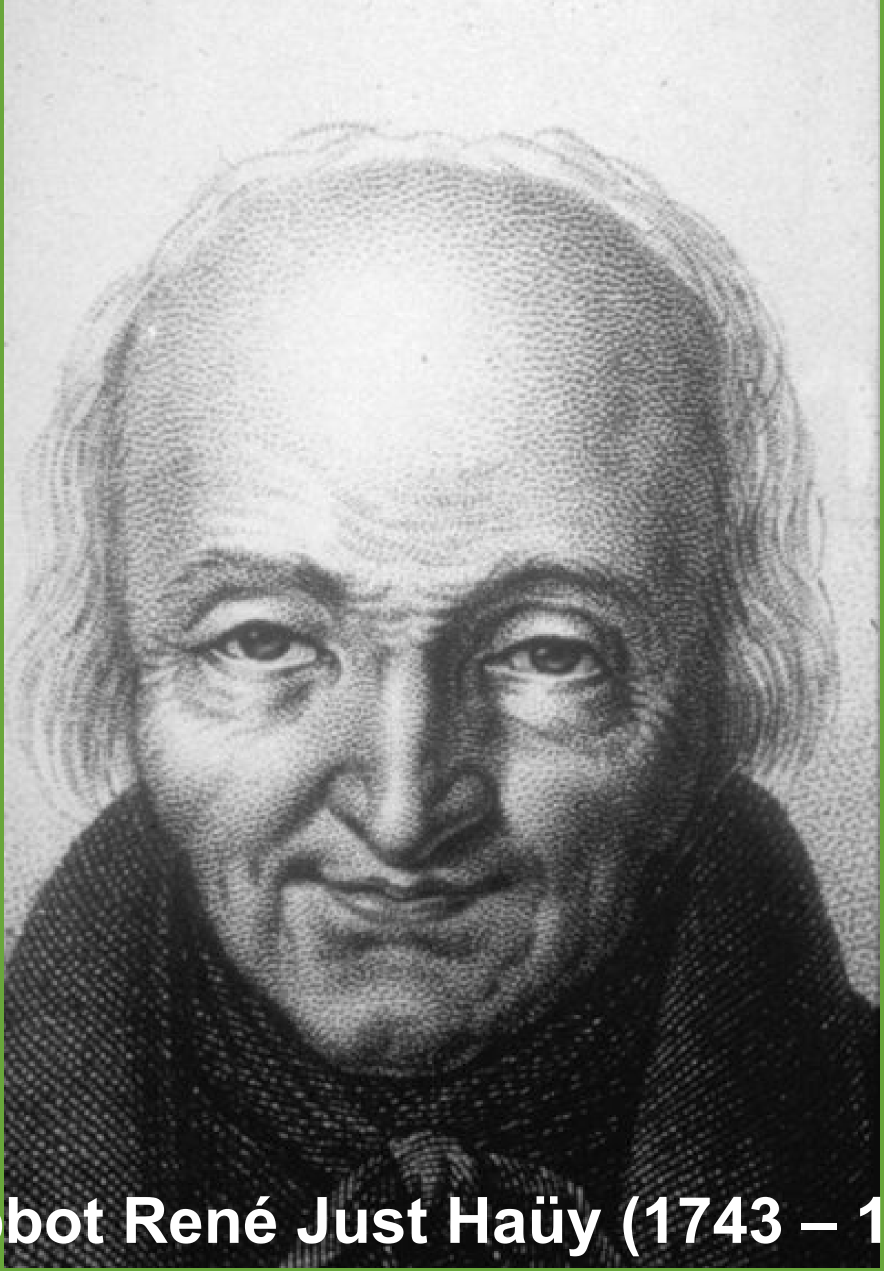


Fig. 13. Idealized schematic memetic twin of $Mg_3B_7O_{13}Cl$ of the Lüneburg type.



Abbot René Just Haüy (1743 – 1822)
discovered pyroelectricity in boracite in 1791

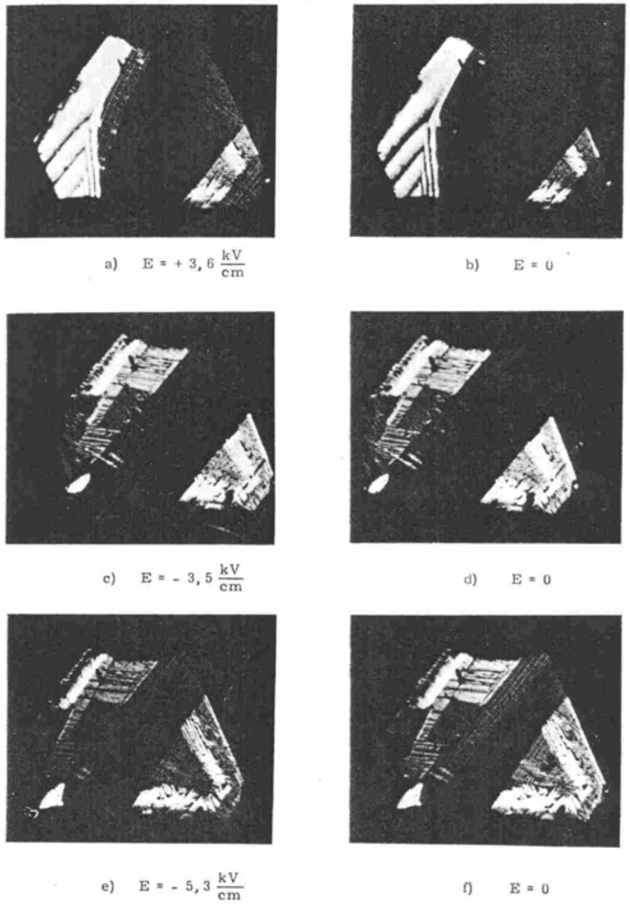
1963 And the walls did move

in $Ni_3B_7O_{13}Cl$

only at 10 degrees below T_c=610K in electric DC-field

High coercive field E_c!!

E. Ascher, H. Schmid and D. Tar, *Solid State Commun.*, **2**, 45-49 (1964)

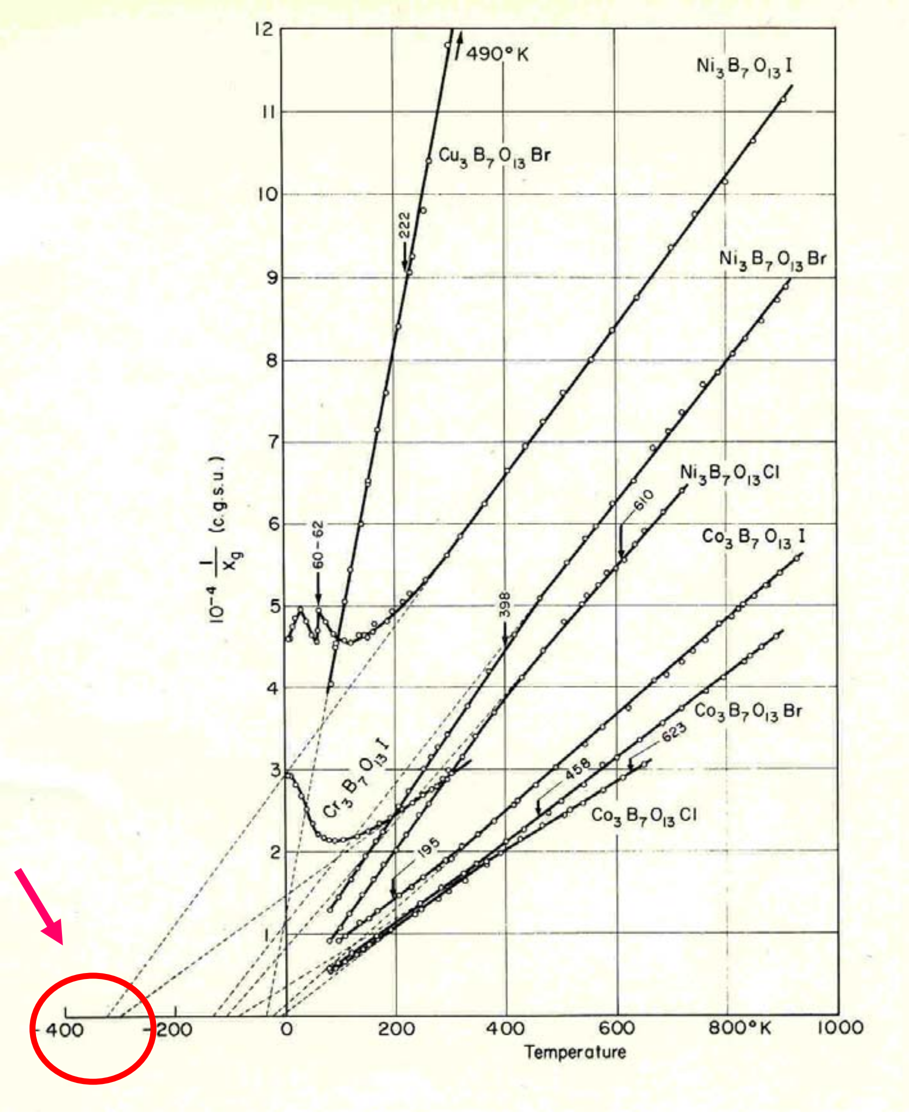


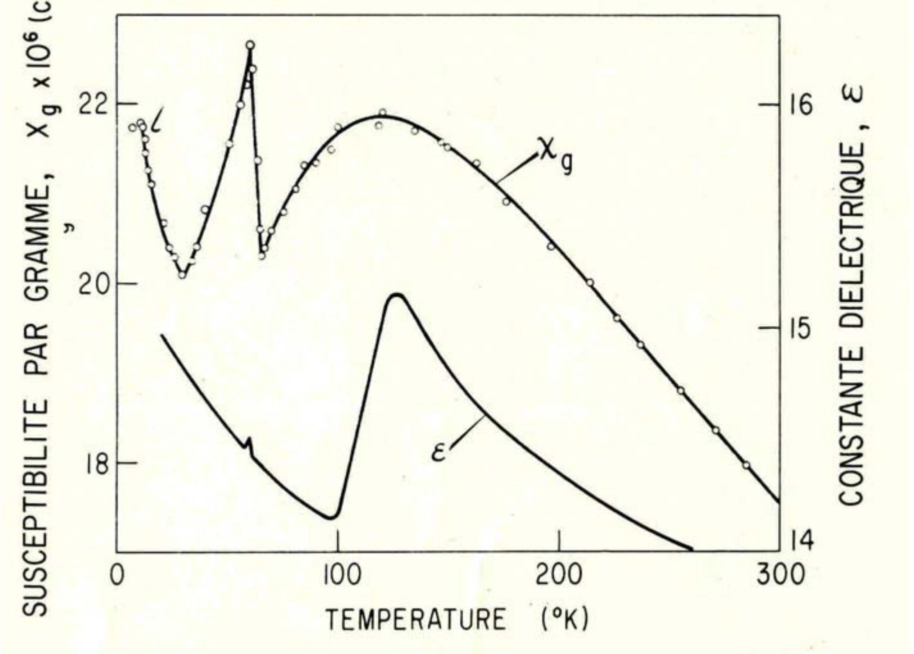
- And the ferroelectric walls did move!
- In polarized light: observation of sluggish motion of the ferroelectric walls of $Ni_3B_7O_{13}Cl$
- Ascher's "maximal polar subgroup rule does not hold !

  Sonin and Zheludev’s claim of *anti-ferroelectricity* does not hold !
- Euphoria !! But ephemeral only:
- C.N.E.T. turns down prolongation of financial support

•E. Ascher, H. Schmid and D. Tar, *Solid State Commun*., **2**, 45-49 (1964)

Magnetic susceptibility measurements with a Faraday balance





H. Schmid, H. Rieder and E. Ascher, *Solid State Commun.*, **3**, 327-329 (1965)

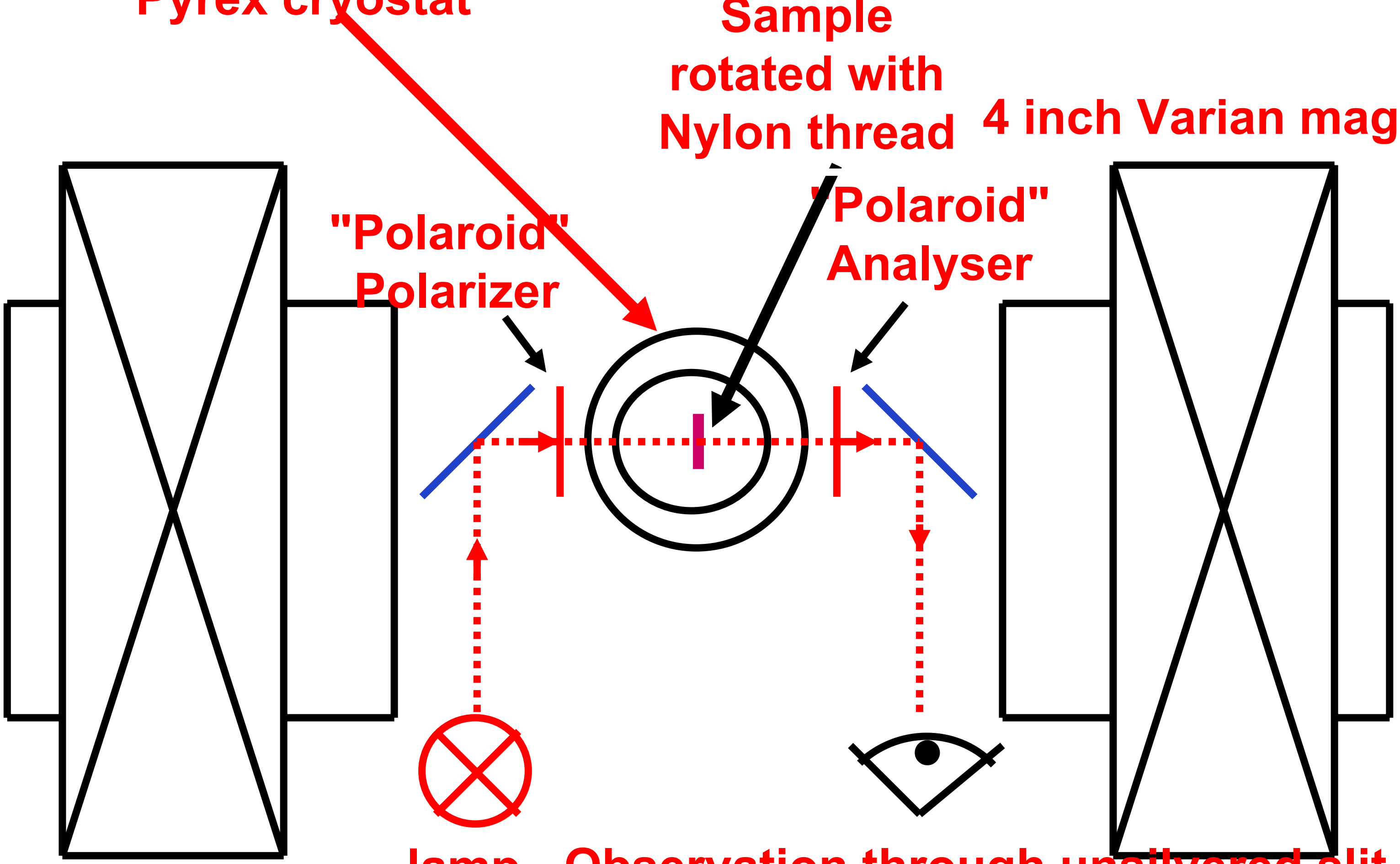
E. Ascher, H. Rieder, H. Stössel and H.Schmid, *J. Appl. Phys.*, **37**, 1404 (1966)

Dillon, Kamimura, Remeika, Magnetic rotation of visible light by ferro-magnetic $CrBr_3$, Phys. Rev. Letters, 9, 161-3 (1962) The Trigger !!!

Boracite $Ni_3B_7O_{13}I$, 40K, $(111)_c$, uncrossed polarizers, Faraday rotation contrast, superposed birefringence of growth sectors

Interpretation seemed hopeless !!!

Rudimentary equipment !



Pyrex cryostat

Sample rotated with Nylon thread

4 inch Varian magnet

"Polaroid" Polarizer

"Polaroid" Analyser

lamp

Observation through unsilvered slit with Improvised "microscope"

Domains moved both in electric and magnetic fields !

At 2:30 a.m., in a February night in 1964

Euphoria in the snowstorm !

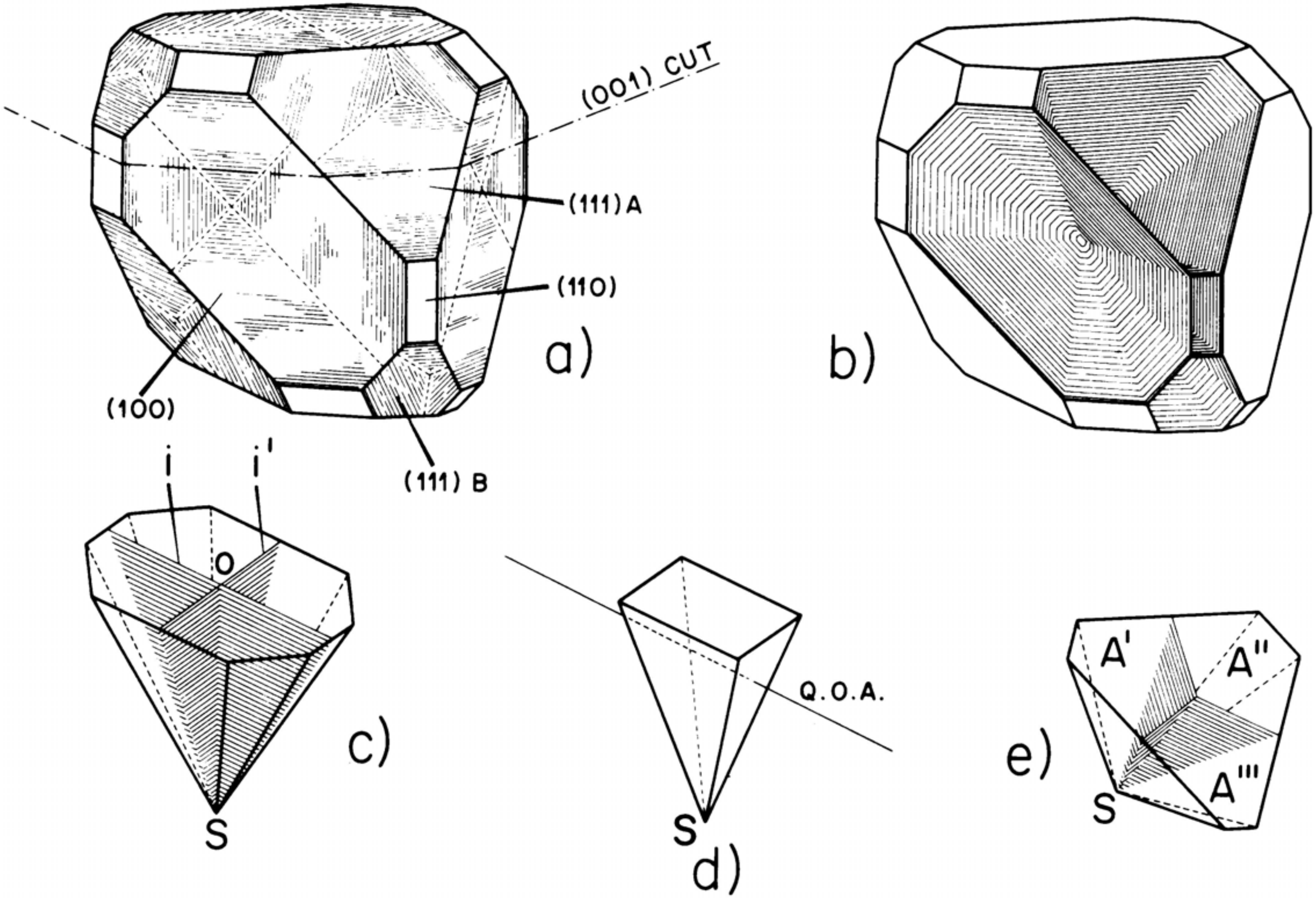
$Ni_3B_7O_{13}I$, 40 K, $(110)_c$, complex ferromagnetic/ferroelectric/ferroelastic domains , Faraday rotation contrast with superposed birefringence of growth sectors,

The hurdle

Superposition of

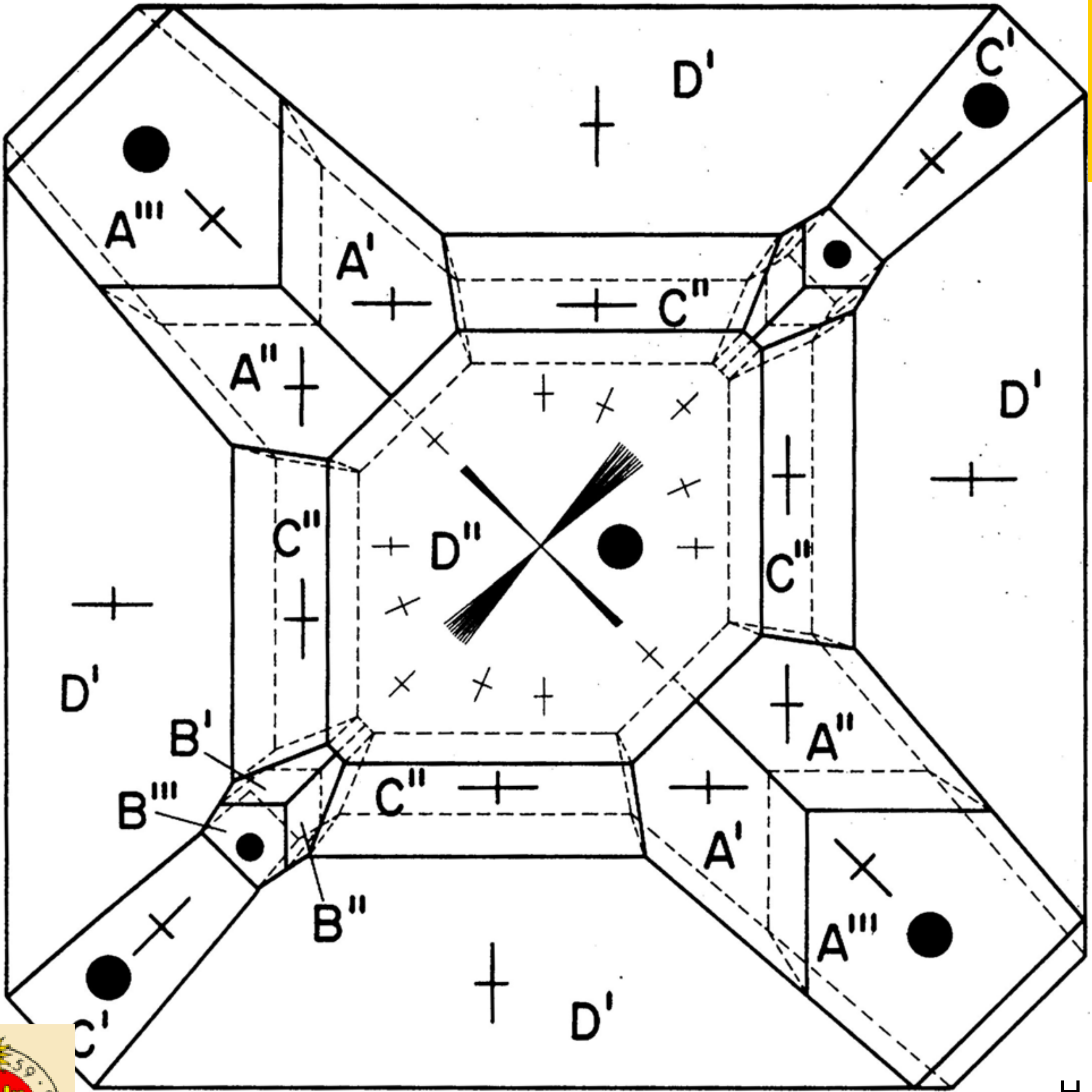
1) parasitic growth sector birefringence & dichroism+
2) ferroelastic domain birefringence/dichroism +
3) non-reciprocal Faraday rotation+
4) 3 types of ferroelastic walls + different ferromagnetic walls.

Growth sectors (growth pyramids) in boracites



H. Schmid, *Rost Kristallov*, **7**, 32-65 (1967) [*Crystal Growth*, **7**, 25-52 (1969)]

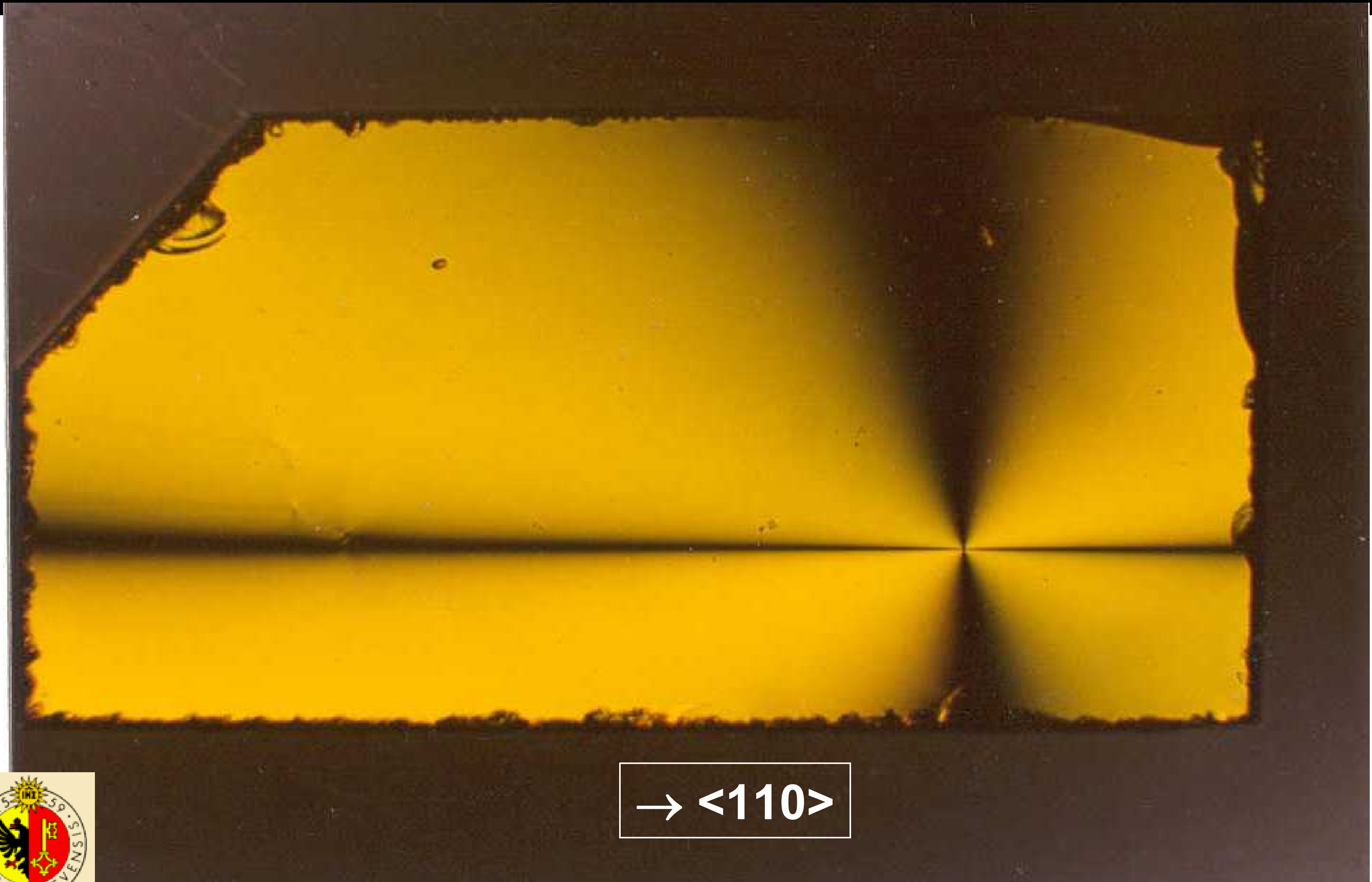
Birefringence in growth sectors



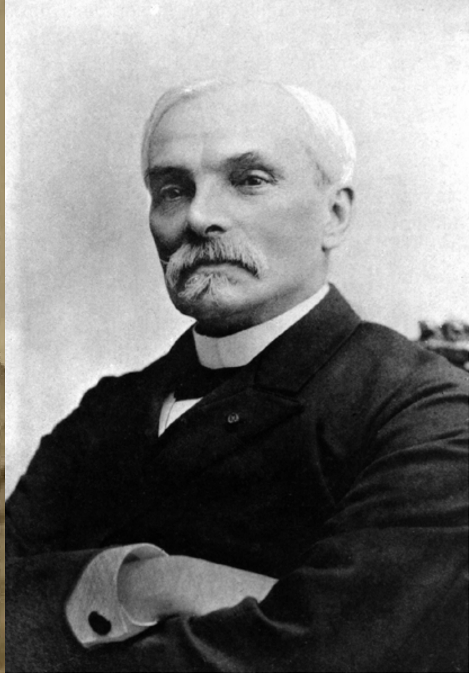
X-rays do not reveal these growth anomalies

H. Schmid, *Rost Kristallov,* **7**, 32-65 (1967) [*Crystal Growth*, **7**, 25-52 (1969)]

Stress-field of a growth dislocation of a $(100)_c$-growth pyramid of nickel-iodine boracite (crossed polarizers parallel $<110>_c$ / $<1\text{-}10>$, $(100)_c$-cut



Sir David Brewster
1781-1868
Edinburgh



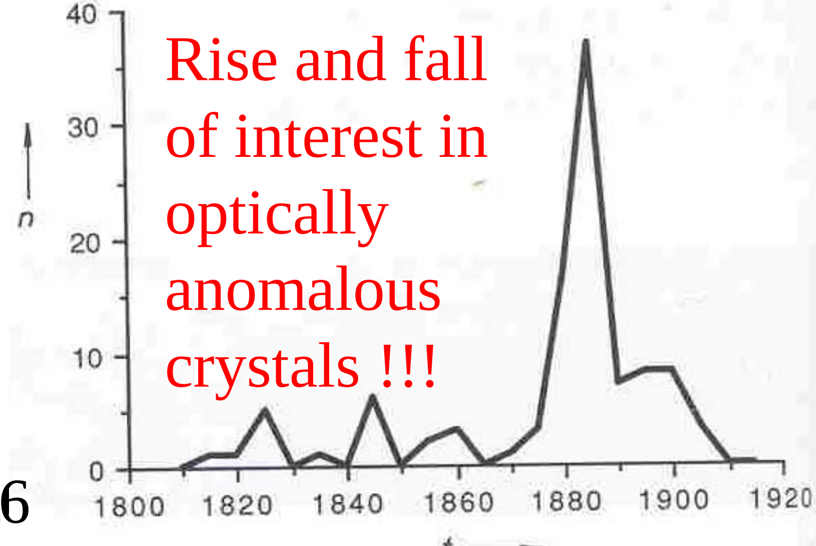
François Ernest
Mallard
1833-1894
Paris

Carl Klein
1842-1907
Göttingen

Reinhard Brauns
1861-1931
Bonn

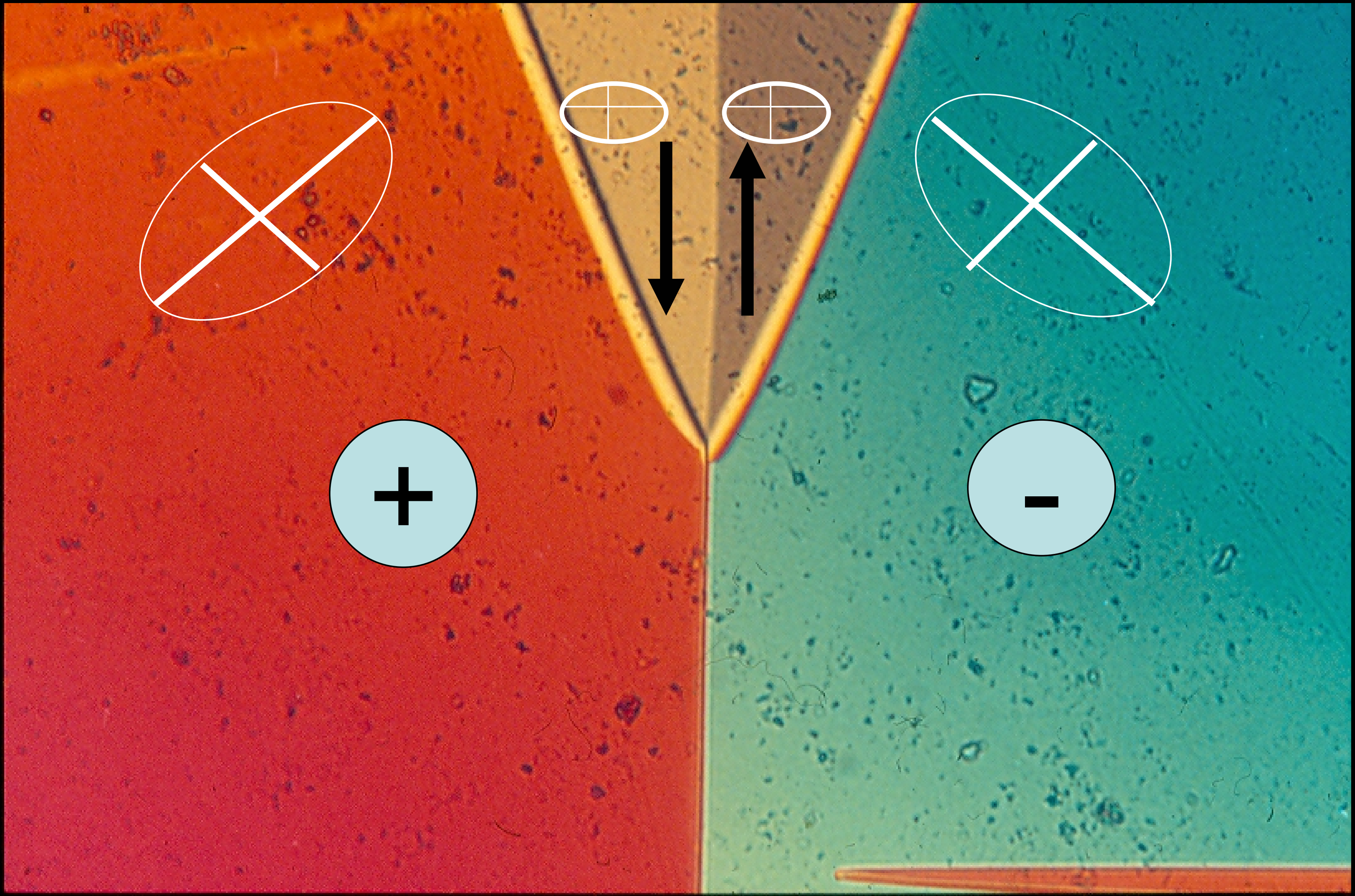
R. Brauns, Die optischen Anomalien der Krystalle, Leipzig: S. Hirzel, 1891

Bart Kahr and J. Michel McBride
Optically Anomalous Crystals,
Angew. Chem.Int.Ed.Engl. 21(1992) 1-26



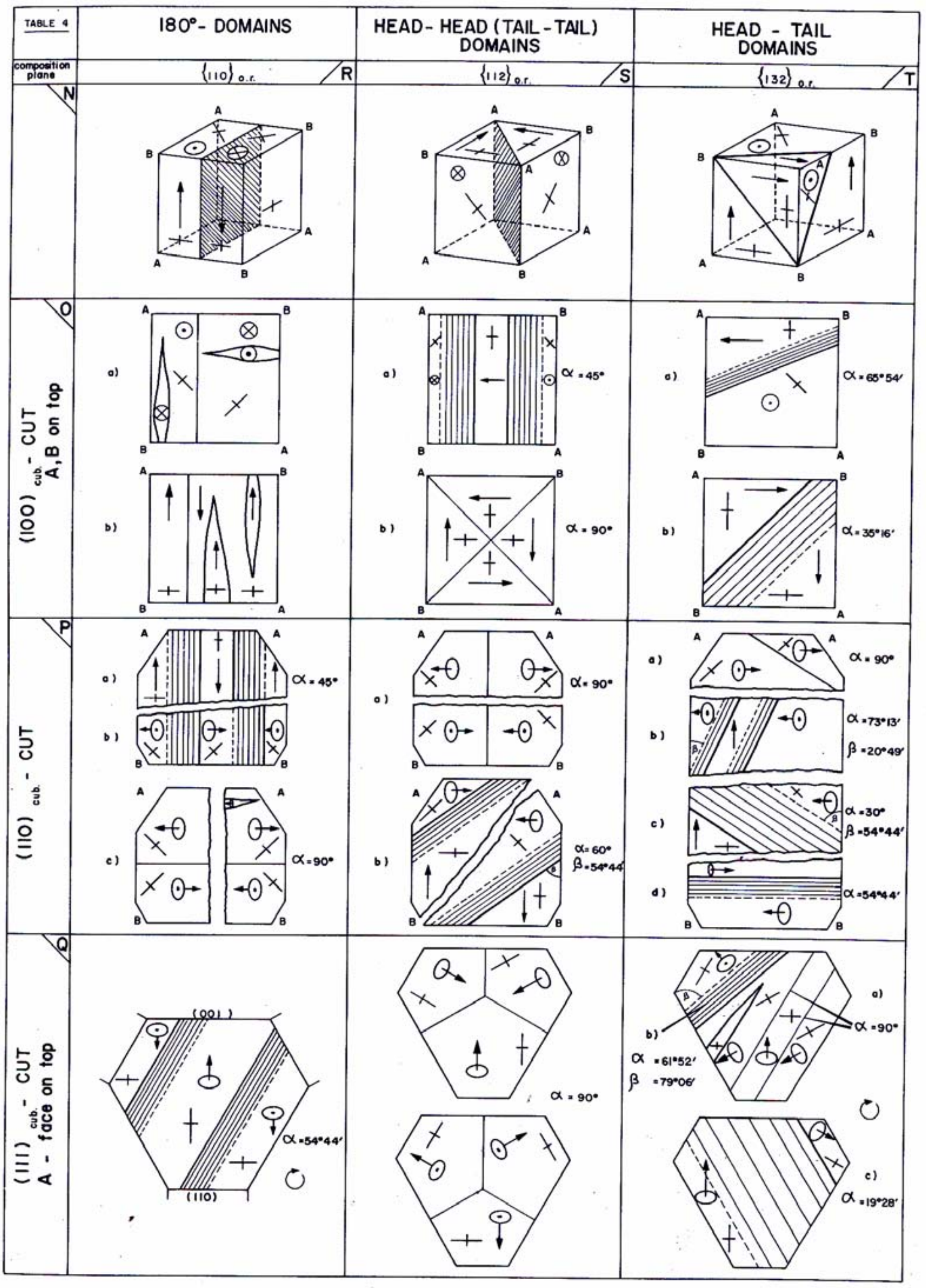
Rise and fall of interest in optically anomalous crystals !!!

$Ni_3B_7O_{13}Cl$ at room temperature, phase mm21', pseudo-cubic (100)-cut



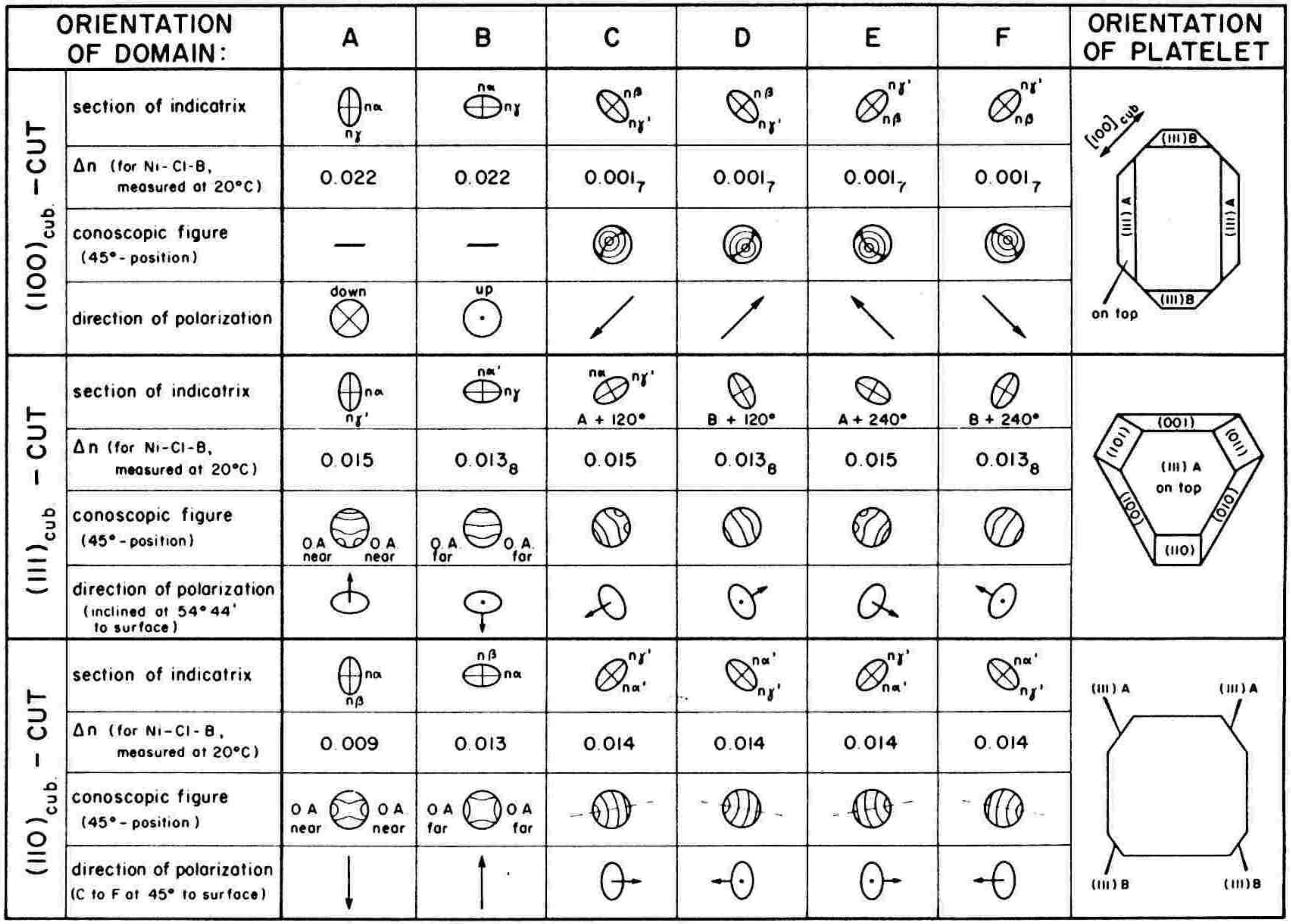
Three types of domain wall:

(100)$_C$
(110)$_C$
(hkl)



H. Schmid,
Rost Kristallov,
7, 32-65 (1967)
[*Crystal Growth*,
7, 25-52 (1969)]

TABLE 2. Chart for the Determination of the Polarization Directions of β-Phase Twins on {100}, {110}, and $\{111\}_{cub}$-Cuts. Generally Applicable to Boracites. For Details of Birefringence, see Appendix to Table 2.



ORIENTATION OF DOMAIN:		A	B	C	D	E	F	ORIENTATION OF PLATELET
$(100)_{cub.}$ -CUT	section of indicatrix	n_α n_γ	n_α n_γ	n_β $n_{\gamma'}$	n_β $n_{\gamma'}$	$n_{\gamma'}$ n_β	$n_{\gamma'}$ n_β	$[100]_{cub}$ (111)B (111) A (111) A (111)B on top
	Δn (for Ni-Cl-B, measured at 20°C)	0.022	0.022	0.001_7	0.001_7	0.001_7	0.001_7	
	conoscopic figure (45°-position)	—	—					
	direction of polarization	down	up					
$(111)_{cub}$ – CUT	section of indicatrix	n_α $n_{\gamma'}$	$n_{\alpha'}$ n_γ	n_α $n_{\gamma'}$ A + 120°	B + 120°	A + 240°	B + 240°	(001) (011) (101) (111) A on top (100) (010) (110)
	Δn (for Ni-Cl-B, measured at 20°C)	0.015	0.013_8	0.015	0.013_8	0.015	0.013_8	
	conoscopic figure (45°-position)	O A near O A near	O A far O A far					
	direction of polarization (inclined at 54°44' to surface)							
$(110)_{cub.}$ – CUT	section of indicatrix	n_α n_β	n_β n_α	$n_{\gamma'}$ $n_{\alpha'}$	$n_{\alpha'}$ $n_{\gamma'}$	$n_{\gamma'}$ $n_{\alpha'}$	$n_{\alpha'}$ $n_{\gamma'}$	(111) A (111) A (111) B (111)B
	Δn (for Ni-Cl-B, measured at 20°C)	0.009	0.013	0.014	0.014	0.014	0.014	
	conoscopic figure (45°-position)	O A near O A near	O A far O A far					
	direction of polarization (C to F at 45° to surface)							

H. Schmid, *Rost Kristallov*,**7**, 32-65 (167) [*Crystal Growth*, **7**, 25-52 (1969)]

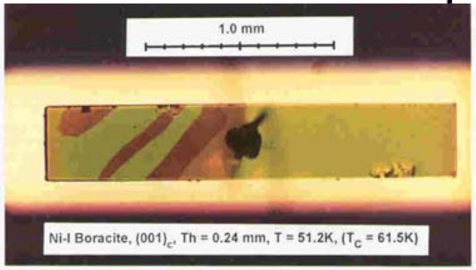
1966

Switching of $Ni_3B_7O_{13}$ I is Interpreted by Species $\bar{4}3m1'Fm'm2'$

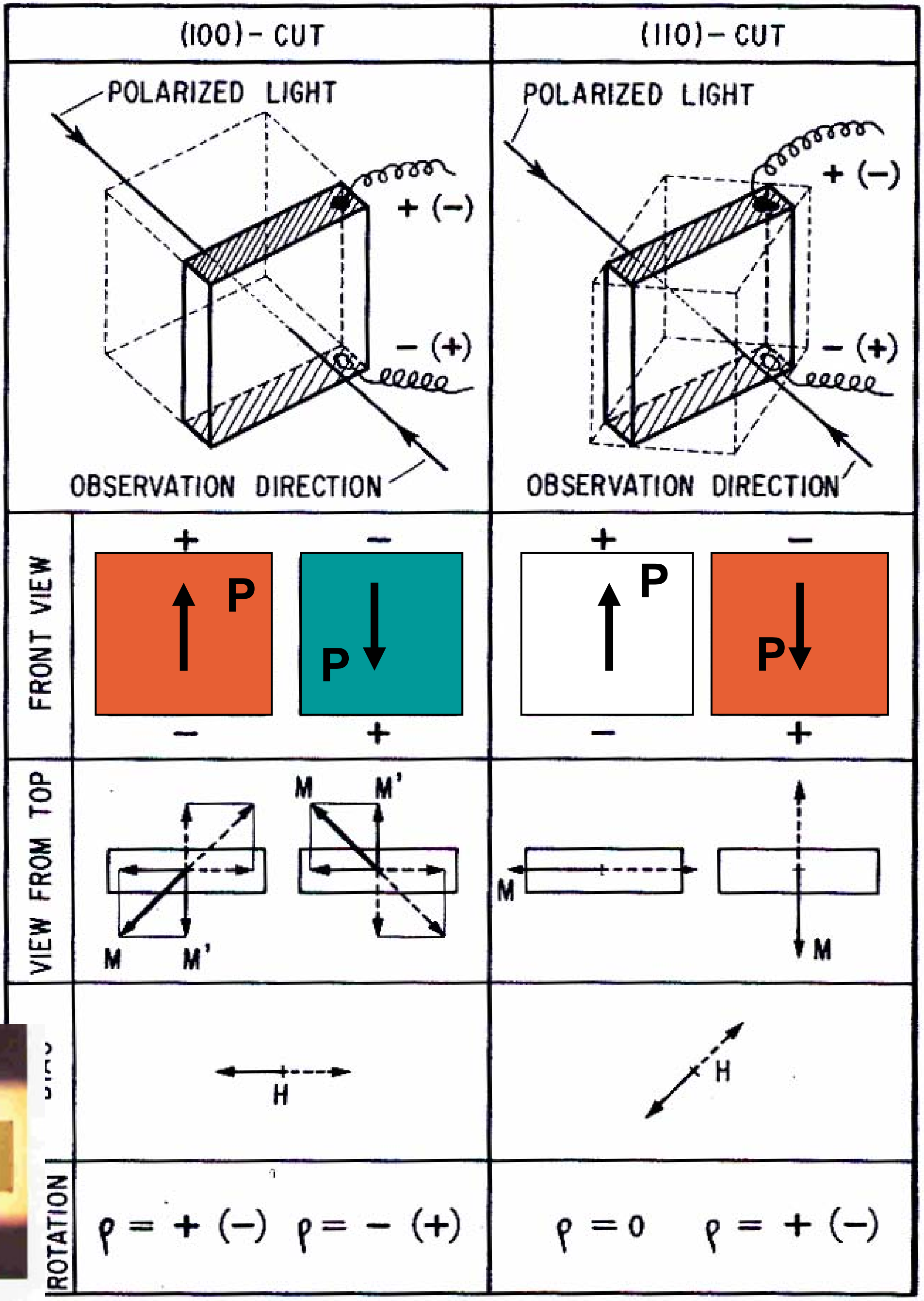
Later recognized as:

$\bar{4}3m1'Fm'$

J.-P. Rivera and H. Schmid, *Ferroelectrics*, **36**, 447 (1981)

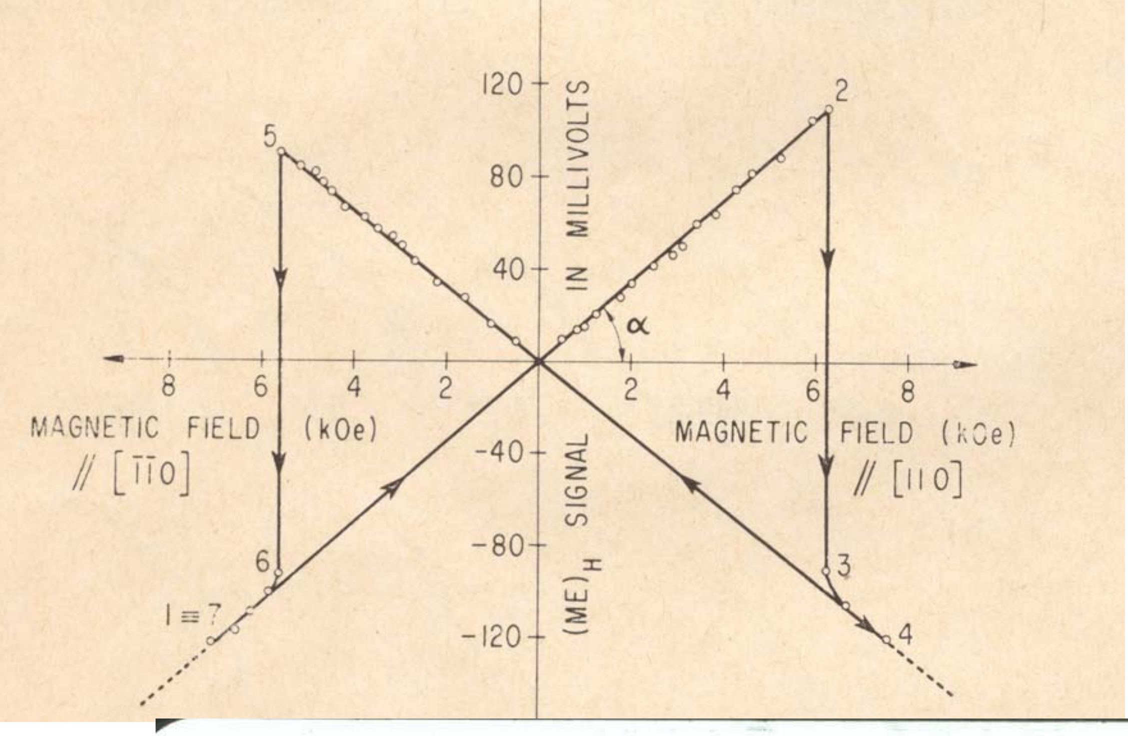


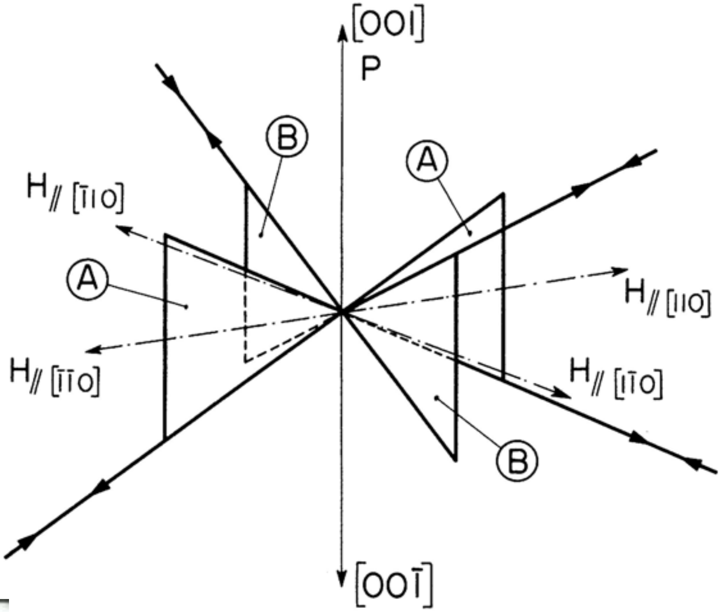
COLOR PLATE XI. See H. Schmid, Figure 1.
FERROELECTRICS, Volume 162(1–4).



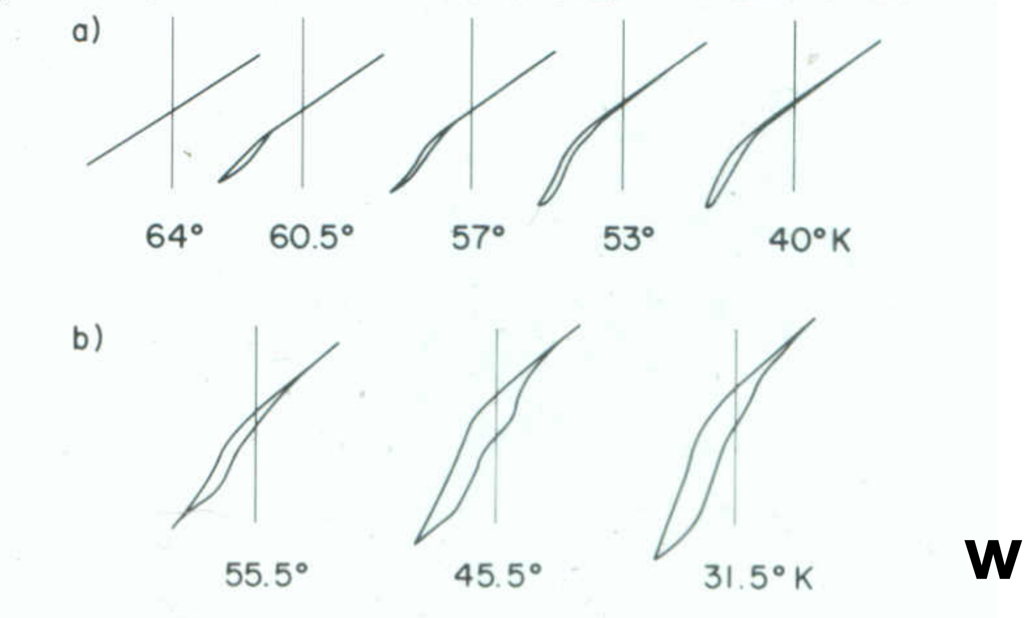
H. Schmid, *Rost Kristallov*, **7**, 32-65 (1967) [*Crystal Growth*, **7**, 25-52 (1969)]

Int. Conf. of Crystallography Moscow 1966





H. Schmid, *Rost Kristallov*, **7**, 32-65 (1967) [*Crystal Growth*, **7**, 25-52 (1969)]



Assumed point group:
$\bar{4}$3m1'Fm'm2'

STOP
with experiments!

E. Ascher, H. Rieder, H. Stössel and H.Schmid, *J. Appl. Phys.*, **37**, 1404 (1966)

Frustrations

- 1st Proposal to Battelle Advanced Study Center: March 1965: **Rejection**
- "Your program is too chemical in nature"

2nd Proposal to Battelle Advanced Study Center: 20 October 1965: **Rejection**

- "Your topic is not sufficiently advanced"

- Proposal to FNS, Sept. 1969

  1st **Rejection:**19/02/70 2nd **Rejection:** 08/04/70

  "Your crystals have too many applications"

- Proposal to CERS, Sept 1970 **Rejection**: 27/11/70

  "The Swiss industry does not see any applications"

1968/1969 A Franco-Swiss project, encouraged by Prof. Bertaut, is distroyed by a speech of the General

Prof. Erwin Félix Lewy-Bertaut

Le Général De Gaulle

- Aizu species
- Full and partial coupling of domains with fields
- Coupling of order parameters via ferro-elasticity

In the 19-sixties Kêitsiro Aizu introduces

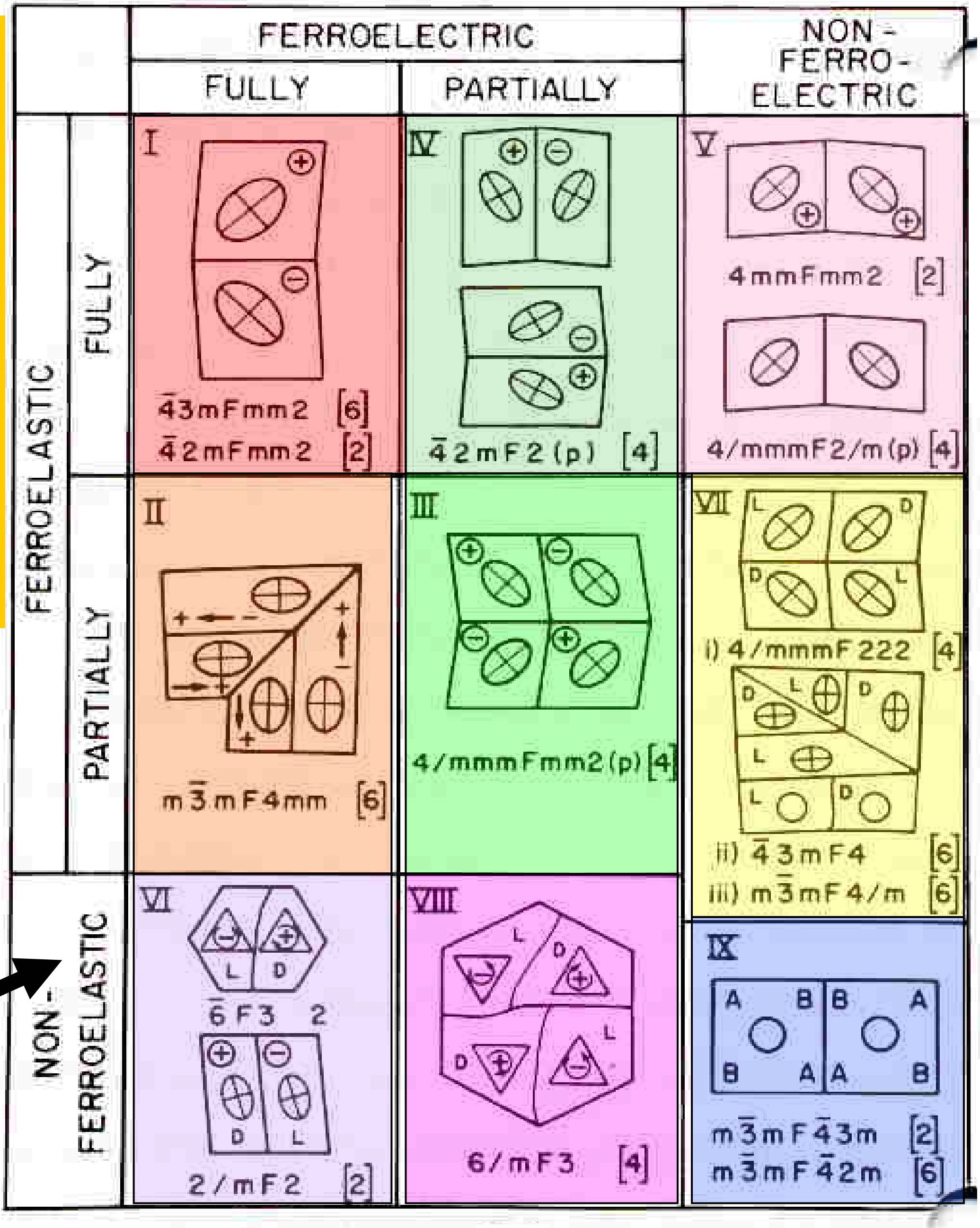
- The notion of "ferroelasticity" *)**)
- The term "ferroic(s)"
- The notion of "species", Example mmm1'Fmm21' (prototype F ferroic phase)
- The notions "Full" and "Partial" ferroelectrics, ferroelastics and ferromagnetics (coupling of external fields with domains)
- Specification of maximal number n of domain states

*)non-equi-class phase transitions → ferroelastic

equi-class phase transitions → co-elastic (E. Salje)

**) Klassen Neklyudova M.V., *Mechanical Twinning of Crystals*, (New York: Consultants Bureau), 1960

The 212 non-magnetic Aizu species, split into 9 ensembles



Ensembles of the 773 magnetic and non-magnetic species, H. Schmid, Ferroelectrics, 221,9-17 (1999)

Extension to the toroidic species D. Litvin, Acta Cryst., A64,316-20 (2008)

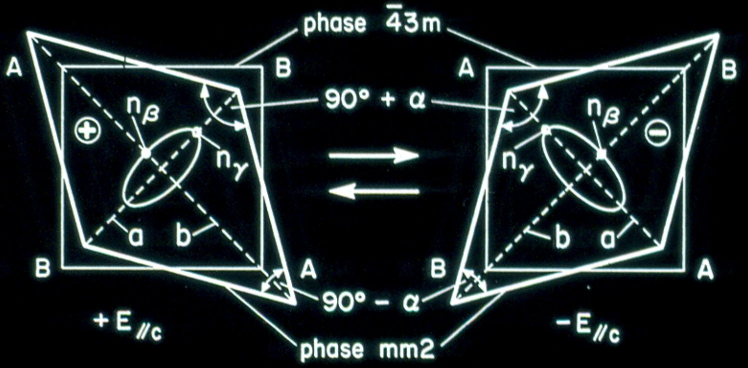
"Co-elastic" (Salje, 1990)

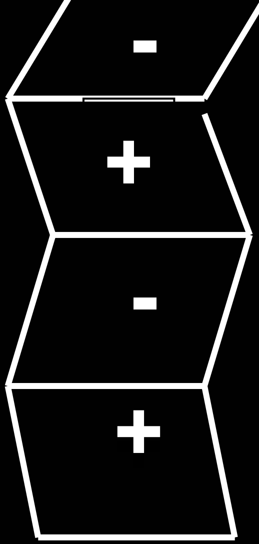
H. Schmid, in: N. Setter and E.L. Colla, Eds., *Ferroelectric ceramics*, Birkhäuser, 1993

Example of ferroelectric = ferroelastic domains

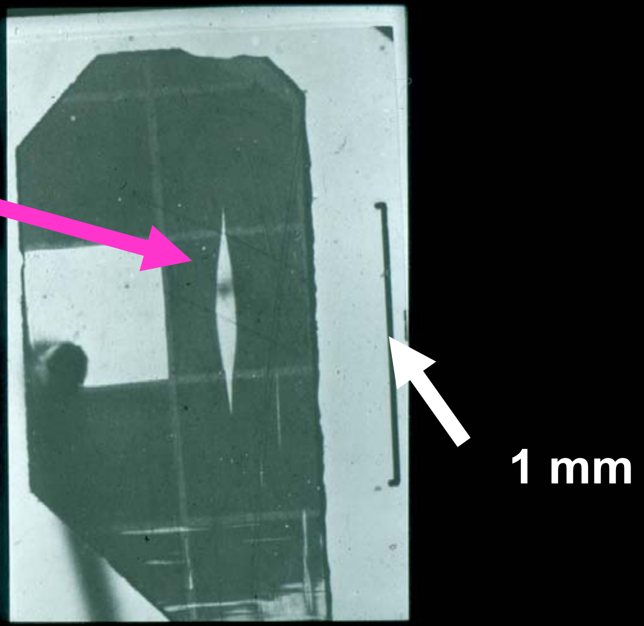
Species $\bar{4}3m1'Fmm21'$ $Fe_3B_7O_{13}I$

Time of the "all-optical computer"





Mechanical cross-talk



Fe-I-Boracite plate with transparent gold elctrodes, room temperature

L.A. Pétermann and H. Schmid, *Revue de Physique*, **11**, 449-466 (1976)

Some ferroelastic shear angles α

$\alpha = |90° - 2\mathrm{tg}^{-1}\, a/b|$ [mn] , normalized for different symmetries

- « Mechanical twinning » e.g., calcite $\alpha > 10$ deg
- « Ferroelastic » phases - YBCO $\alpha \approx 1$ deg.
  - – $BiFeO_3$ $m\bar{3}m1'F3m1'$ $\alpha \approx 30$ mn
  - - $Ni_3B_7O_{13}Cl$ $\bar{4}3m1'Fmm21'$ $\alpha = 30$ mn
- - $BaTiO_3$ $m\bar{3}m1'F4mm1'$ $\alpha = 17$ mn
- - $Fe_3B_7O_{13}I$ $\bar{4}3m1'Fmm21'$ $\alpha = 2.5$ mn
- - $Bi_4Ti_3O_{12}$ $4/mmm1'Fm(s)1'$ $\alpha = 1.5$ mn
- « Spontaneous magnetostriction » ≡ «Ferroelastic»
  - – Ni $m\bar{3}m1'F\bar{3}m'$ $\alpha = 0.13$ mn
  - – α-Fe , $m\bar{3}m1'F4/mm'm'$, $\alpha = 0.017$ mn
  - – $CoFe_2O_4$ $m\bar{3}m1'F4/mmm$ $\alpha = 0.38$

Fatigue in $BiFeO_3$

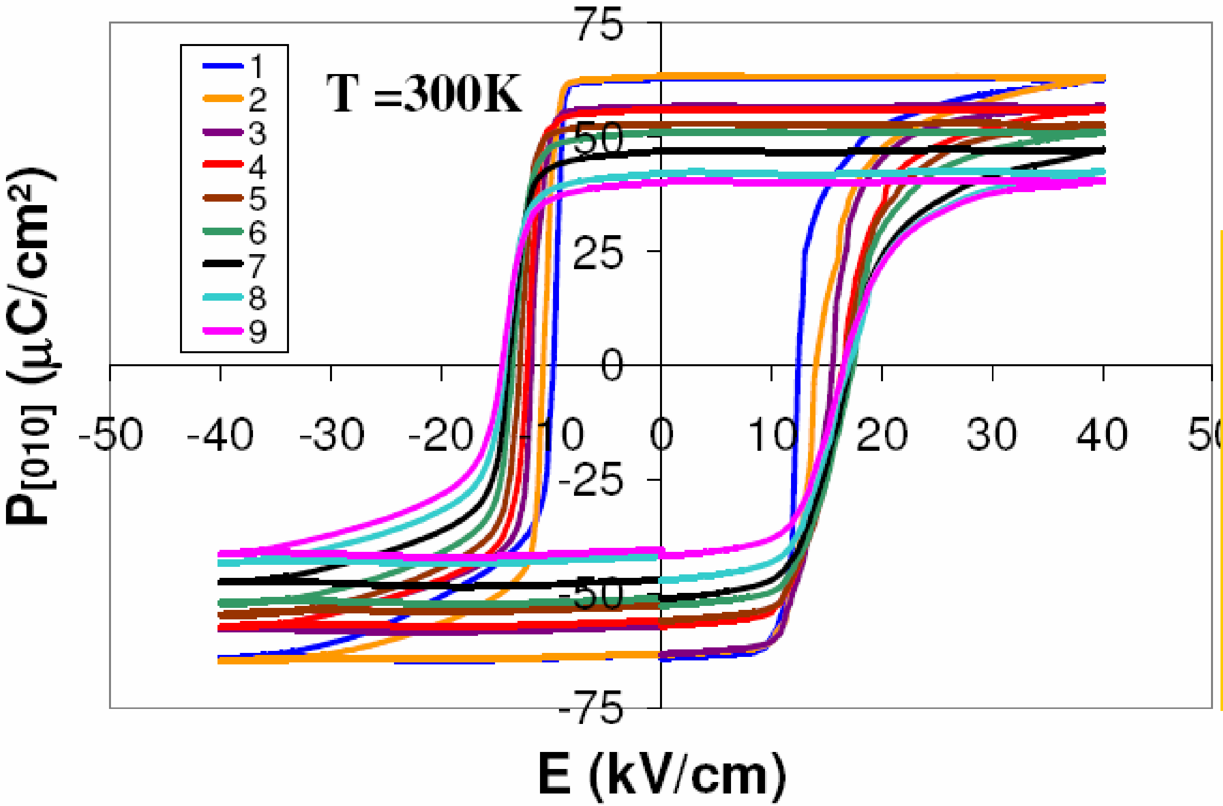
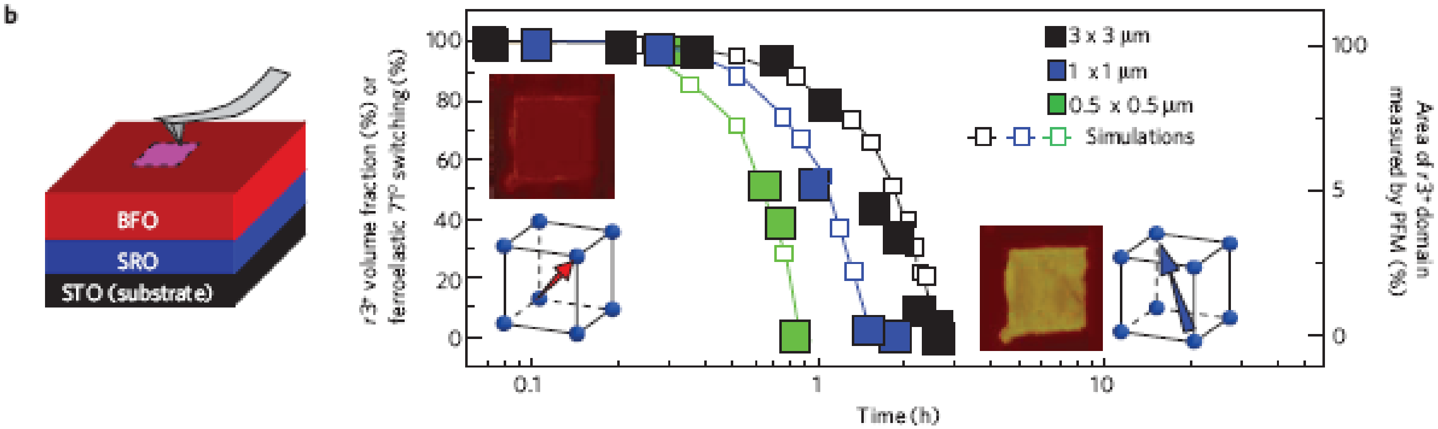
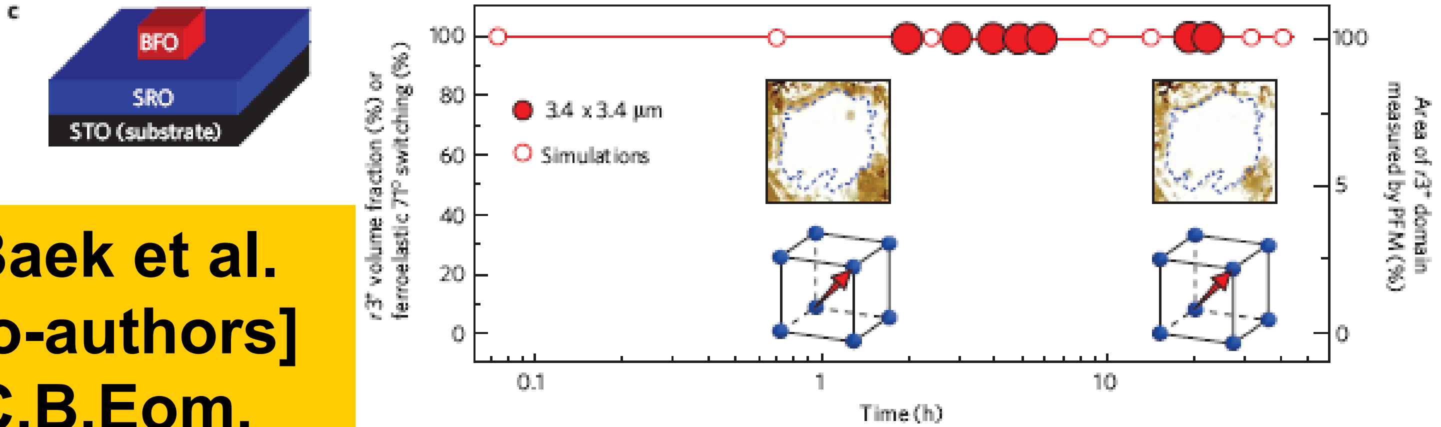


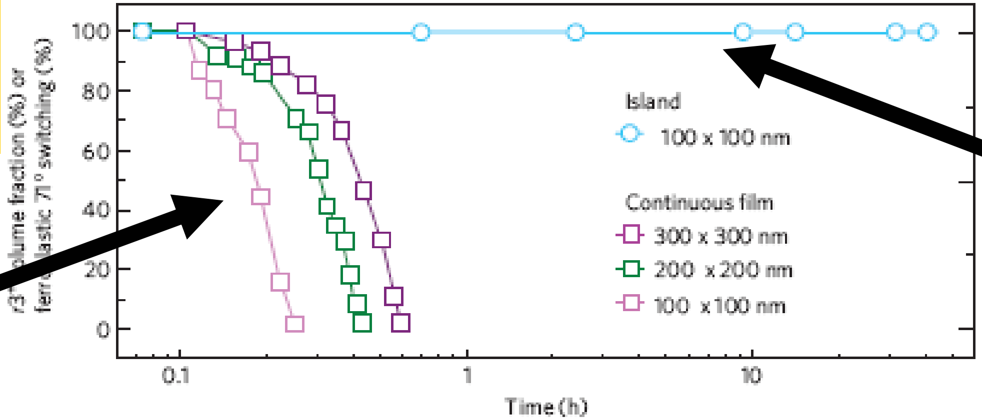
Figure 46 : Modification graduelle des cycles d'hystérésis P(E) au cours du cyclage électrique. Les mesures sont faites à température ambiante sur un monocristal de $BiFeO_3$ de 40µm d'épaisseur.

D. Lebeugle, Thèse de Doctorat, Université Paris XI Orsay, 2007





S.H.Baek et al. [14 co-authors] and C.B.Eom, Nature Materials 9, 309 (2010)



Island

Continuous film

Disadvantages associated with ferroelastic coupling

- Mechanical fatigue, fracture of crystals
- Back-switching
- Only *reorientation*-switching of directions of M_s (P_s), induced by E (H) fields, are possible
- Ferroic phases with centro-symmetric prototype allow less coupling than ferroic phases with non-centro-symmetric prototype

The axio-polar (time-odd polar) vector and ferrotoroidicity

E. Ascher, *Helv. Phys. Acta*, 39, 40-48 (1966),

determines

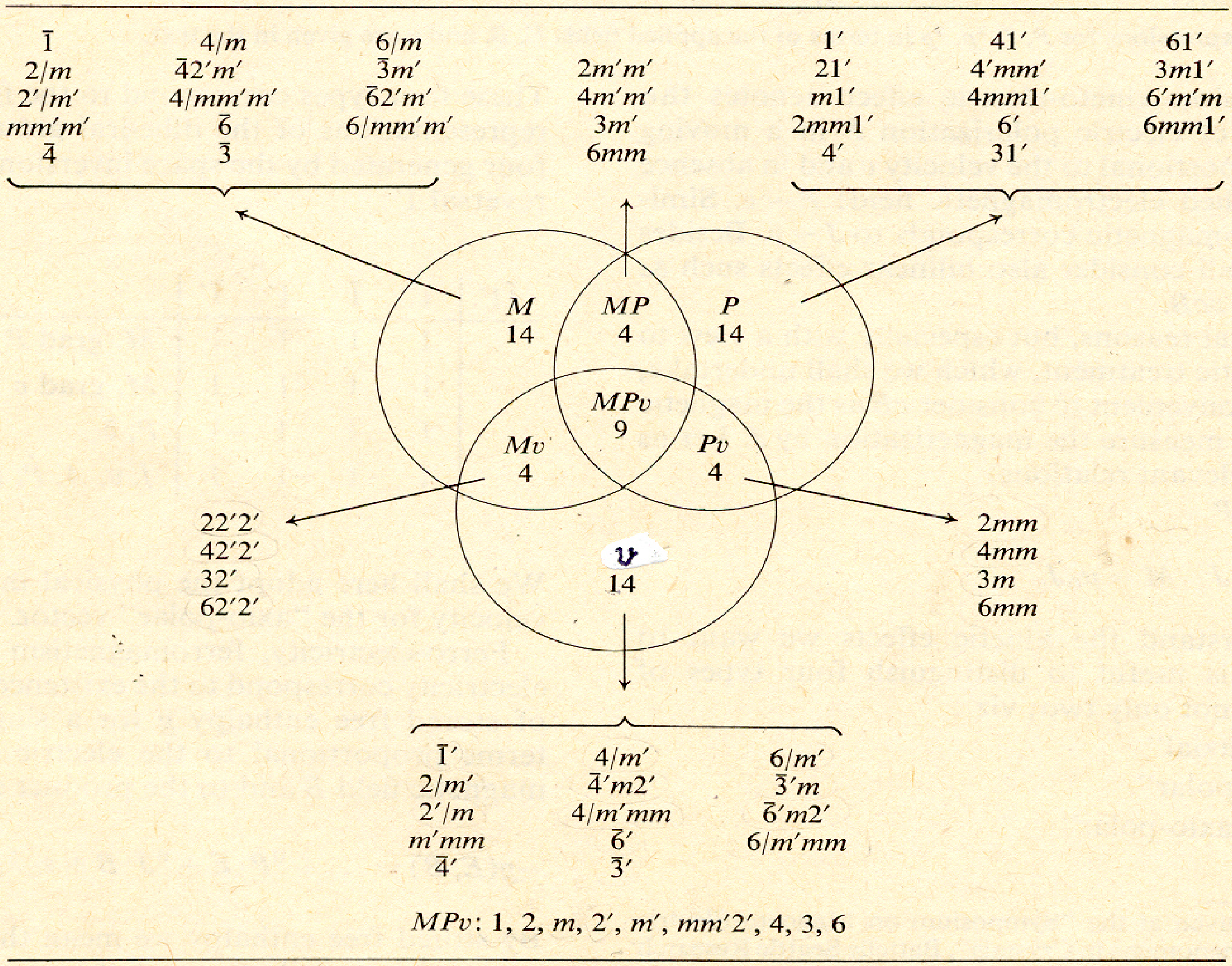
- the **31 magnetic point groups** permitting a **"spontaneous current"** # (i.e., in the absence of an external electric field)

changing sign under **space and time** reversal, hence it is an **axio-polar (time-odd polar) vector**

B.C.S.-theory in 1957. Initially, Ascher did not believe in it!

Edgar Ascher (1921 – 2006)

TABLE I



$\bar{1}$, $2/m$, $2'/m'$, $mm'm'$, $\bar{4}$

$4/m$, $\bar{4}2'm'$, $4/mm'm'$, $\bar{6}$, $\bar{3}$

$6/m$, $\bar{3}m'$, $\bar{6}2'm'$, $6/mm'm'$

$2m'm'$, $4m'm'$, $3m'$, $6mm$

$1'$, $21'$, $m1'$, $2mm1'$, $4'$

$41'$, $4'mm'$, $4mm1'$, $6'$, $31'$

$61'$, $3m1'$, $6'm'm$, $6mm1'$

$22'2'$, $42'2'$, $32'$, $62'2'$

$2mm$, $4mm$, $3m$, $6mm$

$\bar{1}'$, $2/m'$, $2'/m$, $m'mm$, $\bar{4}'$

$4/m'$, $\bar{4}'m2'$, $4/m'mm$, $\bar{6}'$, $\bar{3}'$

$6/m'$, $\bar{3}'m$, $\bar{6}'m2'$, $6/m'mm$

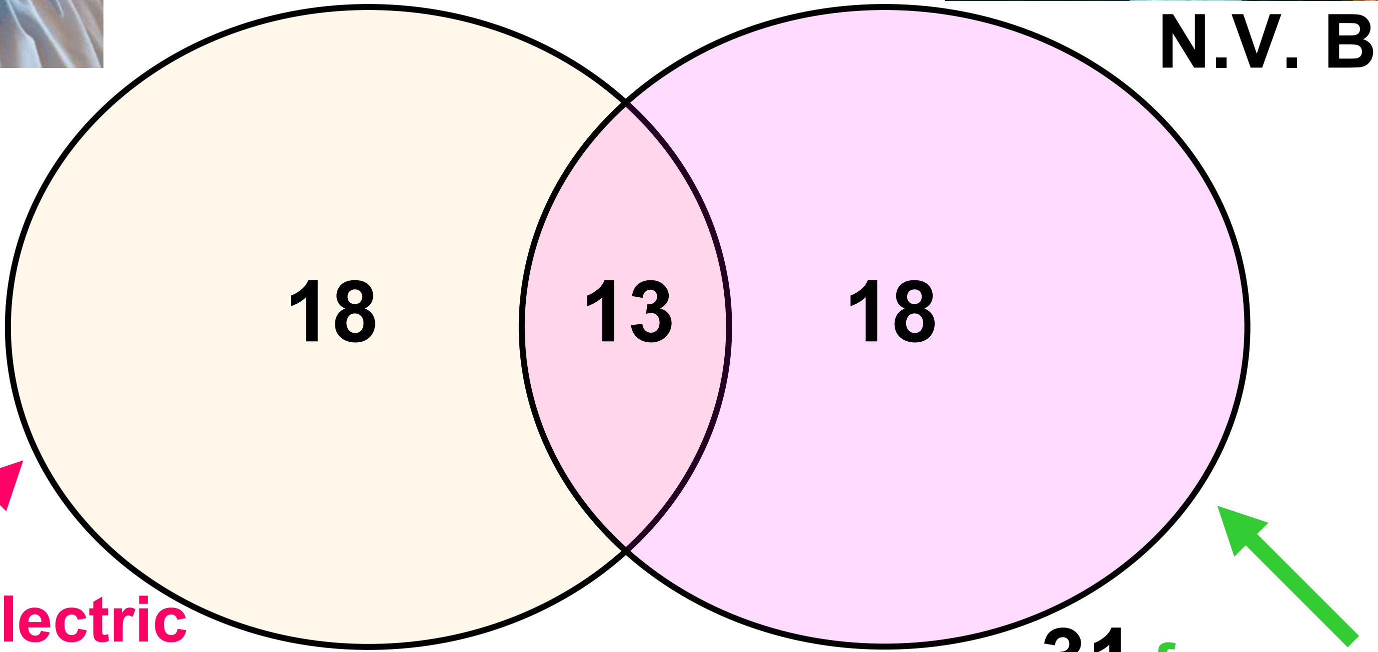
MPv: 1, 2, *m*, 2′, *m*′, *mm*′2′, 4, 3, 6

Hans Schmid

E. Ascher, *Int. J. Magnetism*, **5**, 287-295 (1974)

Lev A. Shuvalov

N.V. Belov

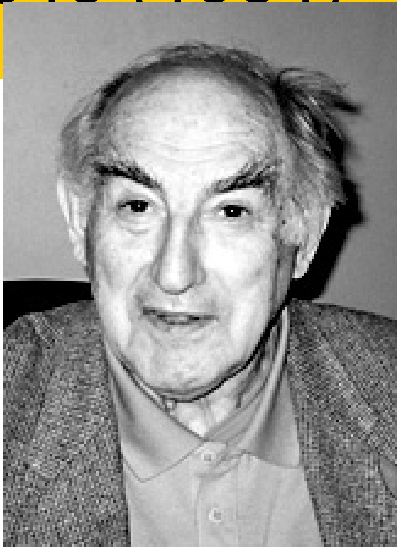


31 ferroelectric
point groups

31 ferromagnetic
point groups

L.A. Shuvalov and N.V. Belov, Kristallografiya, 7, 192 (1962)
[Sov. Physics-Crystallogr., 7, 150 (1962)]

V.L. Ginzburg, A.A. Gorbatsevich, Yu.V. Kopaev and V.A. Volkov, *Solid State Commun*., **50**, 339-343 (1984)



V.L. Ginzburg

- They give the **31 magnetic point groups*), permitting a non-zero toroidal moment density**.
- "…one should bear in mind that **in a toroidal state a magnetoelectric effect must be observed…"** , i.e., the 31 groups must allow the linear magnetoelectric effect.

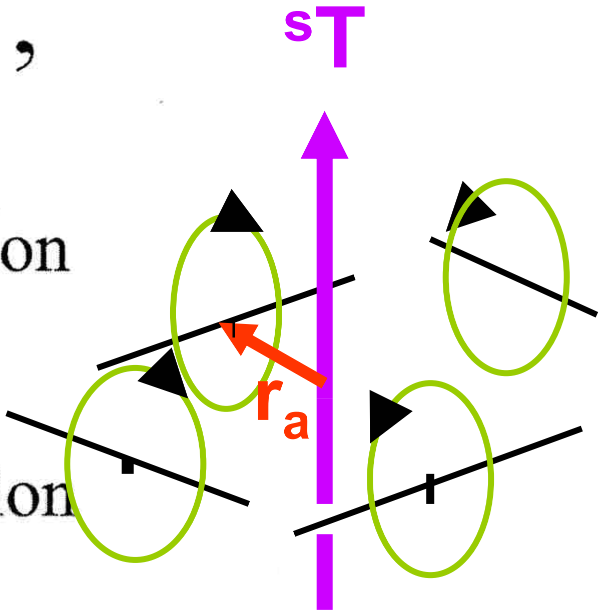
*) E. Ascher, *Helv. Phys. Acta*, **39**, 40-48 (1966);

Definition of spin part of a toroidal moment

$$ {}^{S}\mathbf{T} = \tfrac{1}{2}\mu_B \sum_{a} \mathbf{r}_a \times \mathbf{S}_a , $$

$\mathbf{S}_a$ = spin moment of magnetic cation « a »

$\mathbf{r}_a$ = radius vector of magnetic cation « a » from the unit cell's center



A.A. Gorbatsevich and Yu.V. Kopaev, *Ferroelectrics*, **161**, 321 (1994) (see "MEIPIC-2")

Ferrotoroidic Domains and Ferrotoroidic Domain Switching ?

Toroidal moment contribution to stored free enthalpy

1) $\sim -\boldsymbol{T} \times \mathrm{curl}\,\boldsymbol{H}$

A.A. Gorbatsevich and Yu.V. Kopaev, 1994

2) $\sim -\boldsymbol{T}\, S_i$, where $S_i = (E \times H)_i$

A.A. Gorbatsevich, Yu.V. Kopaev and V.V. Tugushev, 1983

Magnetoelectric switching of antiferromagnetic domains of Cr_2O_3 (J.C. Martin and J.C. Anderson, 1966)

$$g^{+} = \tfrac{1}{2}\,\chi_{ik}\, H_i H_k + \tfrac{1}{2}\,\kappa_{ik}\, E_i E_k + \alpha_{ik}\, E_i H_k$$

$$g^{-} = \tfrac{1}{2}\,\chi_{ik}\, H_i H_k + \tfrac{1}{2}\,\kappa_{ik}\, E_i E_k - \alpha_{ik}\, E_i H_k$$

$g^{+} - g^{-} = 2\,\alpha_{ik}\, E_i H_k$ switching energy for the total hysteresis loop

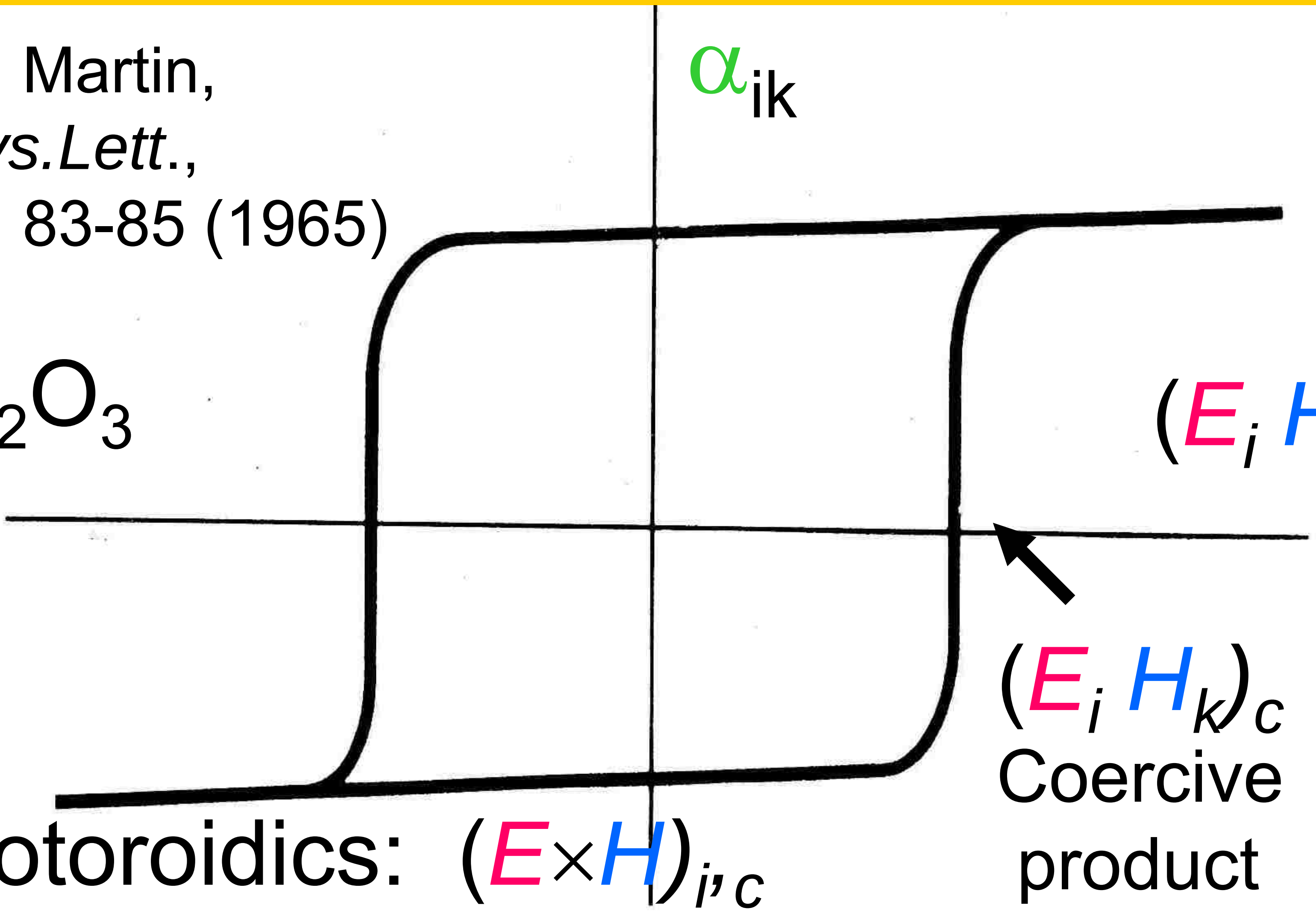
Condition for ferrotoroidic domain switching :

$\alpha_{ik} \neq \alpha_{ki}$ and $E_i \times H_k$

Secondary ferroic, magnetoelectric

T.J. Martin,
Phys.Lett.,
17, 83-85 (1965)

Cr_2O_3



α_{ik}

$(E_i\,H_k)$

$(E_i\,H_k)_c$

Coercive product

Ferrotoroidics: $(E \times H)_{i,c}$

$MnPS_3$, first example of a "pure" antiferromagnetic ferrotoroidic ?

Domain switching observed and claimed by application of the product (ExH).

Magnetic point group: 2'/m, i.e. allowing no spontaneous magnetization and no spontaneous polarization; ferrotoroidic and antiferromagnetic domains are identical

However, no test for the presence of a (weak) ferromagnetic moment was made!!

E. Ressouche et al., Phys. Rev. B, **82**, 100408 (2010)

Ferrotoroidic/weakly ferromagnetic domains in $LiCoPO_4$

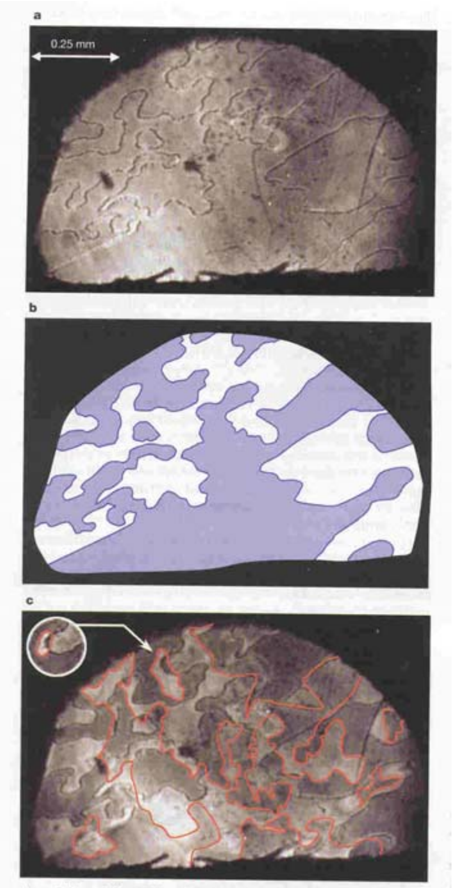


Figure 5 | Coexisting AFM and FTO domains of a $LiCoPO_4$(100) sample at 10 K imaged with SHG light at 2.197 eV. a, Obtained using light from χ_{yyz}. Dark lines are the AFM domain walls. **b,** Distribution of the AFM domains in **a**. **c,** Obtained using interfering light from χ_{yyz} and χ_{zyy}. Bright and dark areas are caused by the interference of AFM and FTO contributions to SHG (see text). Red lines indicate the FTO domain walls. Inset, FTO domain movement caused by a temperature cycle below T_N.

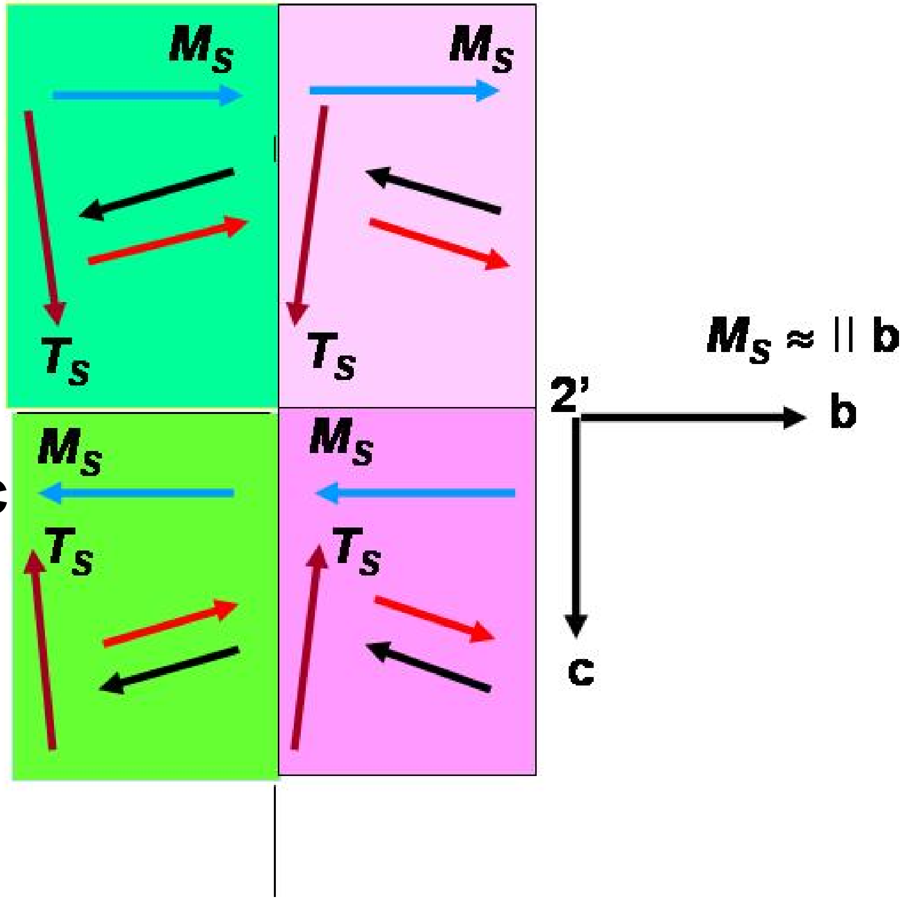
Species mmm1'F2'

Ferroelastic
Partial: absent

Ferroelectric
Partial: absent

Ferromagnetic
Partial

Ferrotoroidic:
Full



Van Aken B B , Rivera J-P, Schmid H and Fiebig M
Nature **449** (2007) 702-5

Schmid H, *J. Phys.:Cond. Matt.* **20** (2008) 434201

Example of ferroelectric = ferroelastic and ferromagnetic = ferrotoroidic domains

Aizu species

$$\bar{4}3m1'Fm'm2'$$

Prototype phase

Ferroic phase

Number of domain states	Ferroelectric	≡ Ferroelastic	Ferromagnetic	≡ Ferrotoroidic
6 × 2	**Full**	**Full**	**Full**	**Full**

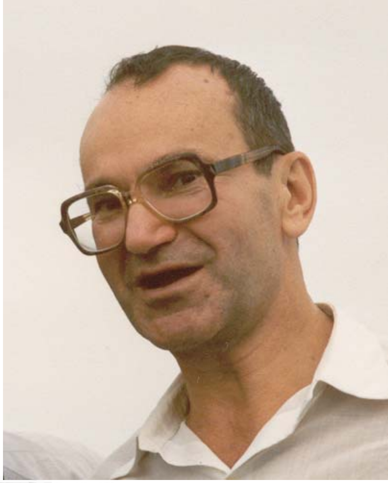
Split!!

Typical Type-I multiferroic

K. Aizu, Phys.Rev. B **2**, 754-772 (1970)

D.E. Sannikov, *Ferroelectrics*, **219**, 177-181 (1998)

Sannikov explains singularity of linear magnetoelectric coefficient α_{32} phenomenologically by a toroidal moment



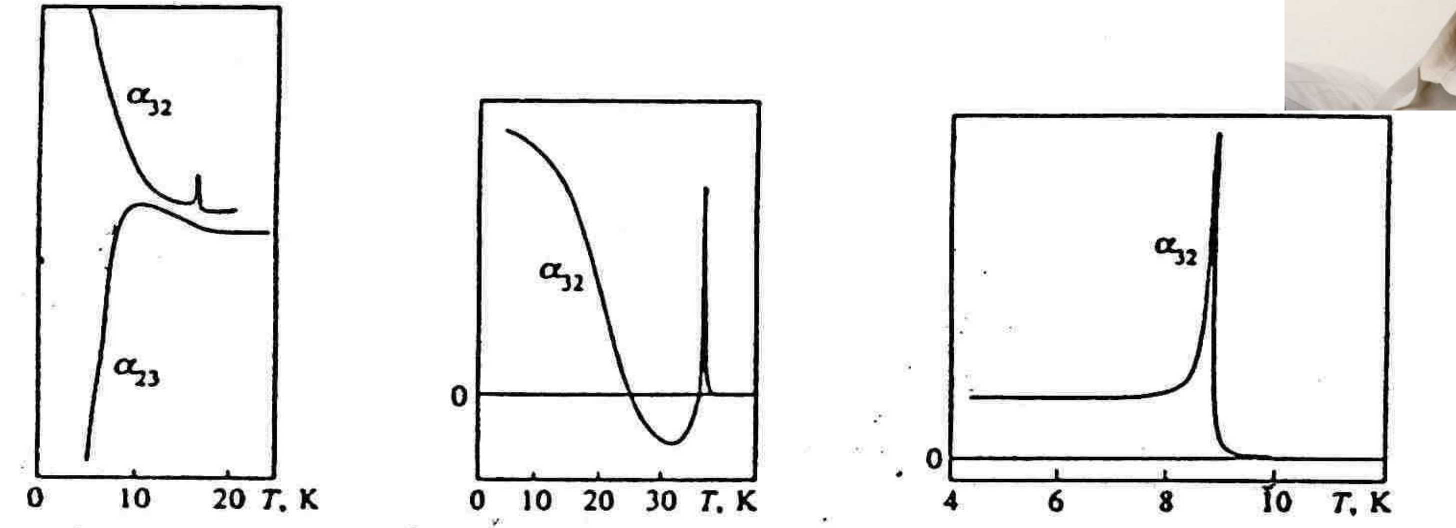


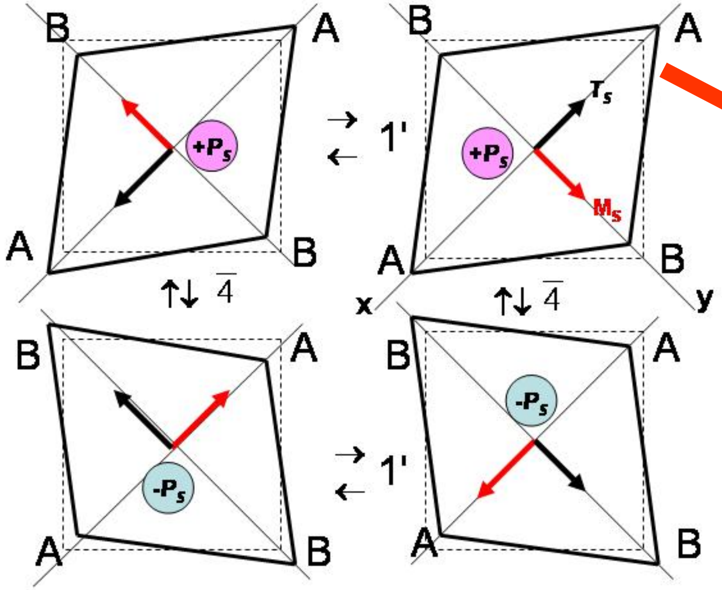
FIGURE 1 Temperature dependences of the components α_{32} and α_{23} of the magnetoelectric tensor in C_2 phase of Co–Br[1] (1), Co–I[2] (2), and Ni–Cl[3] (3) boracites.

Magnetic point group m'm2' : only coefficients α_{23} and α_{32}

$$\alpha_{32} = \frac{DaP_0}{xBC}\boxed{\frac{1}{T_1}} + \frac{1}{xB}\left(a + \frac{3D^2}{xC}a + \frac{3D}{C}b\right)\boxed{T_1,} \tag{4}$$

$$\alpha_{23} = -\frac{a}{\tilde{x}B}\boxed{T_1,} \tag{10}$$

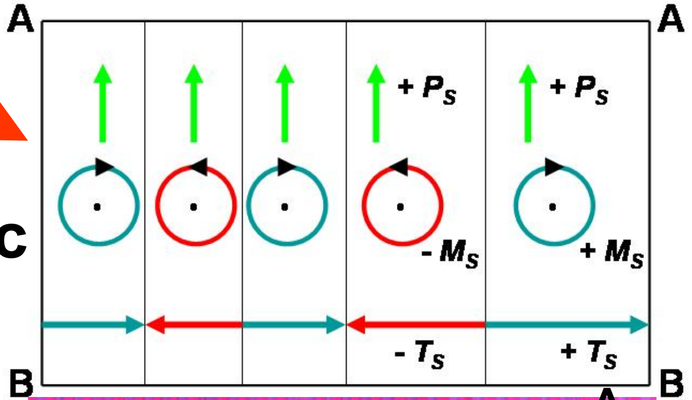
Joint Ferrotoroidic/Ferromagnetic/ Joint Ferroelastic/Ferroelectric Domains



Co-I-boracite $Co_3B_7O_{13}I$

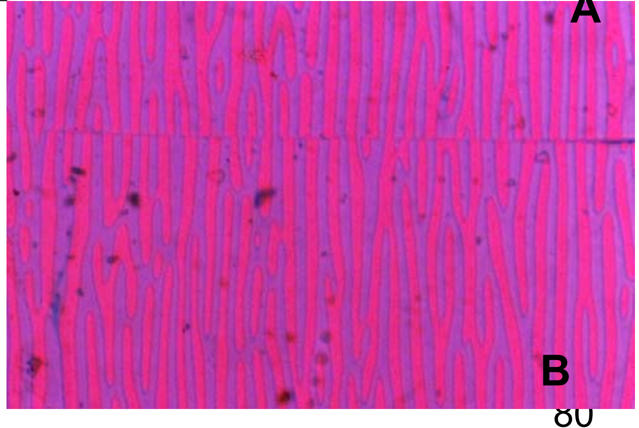
Species $\bar{4}3m1'Fm'm2'$

schematic

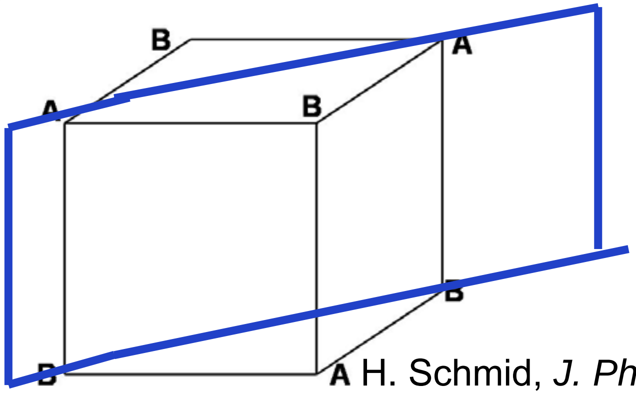


observed

A



B



H. Schmid, *J. Phys.:Cond. Matt.* **20** (2008) 434201

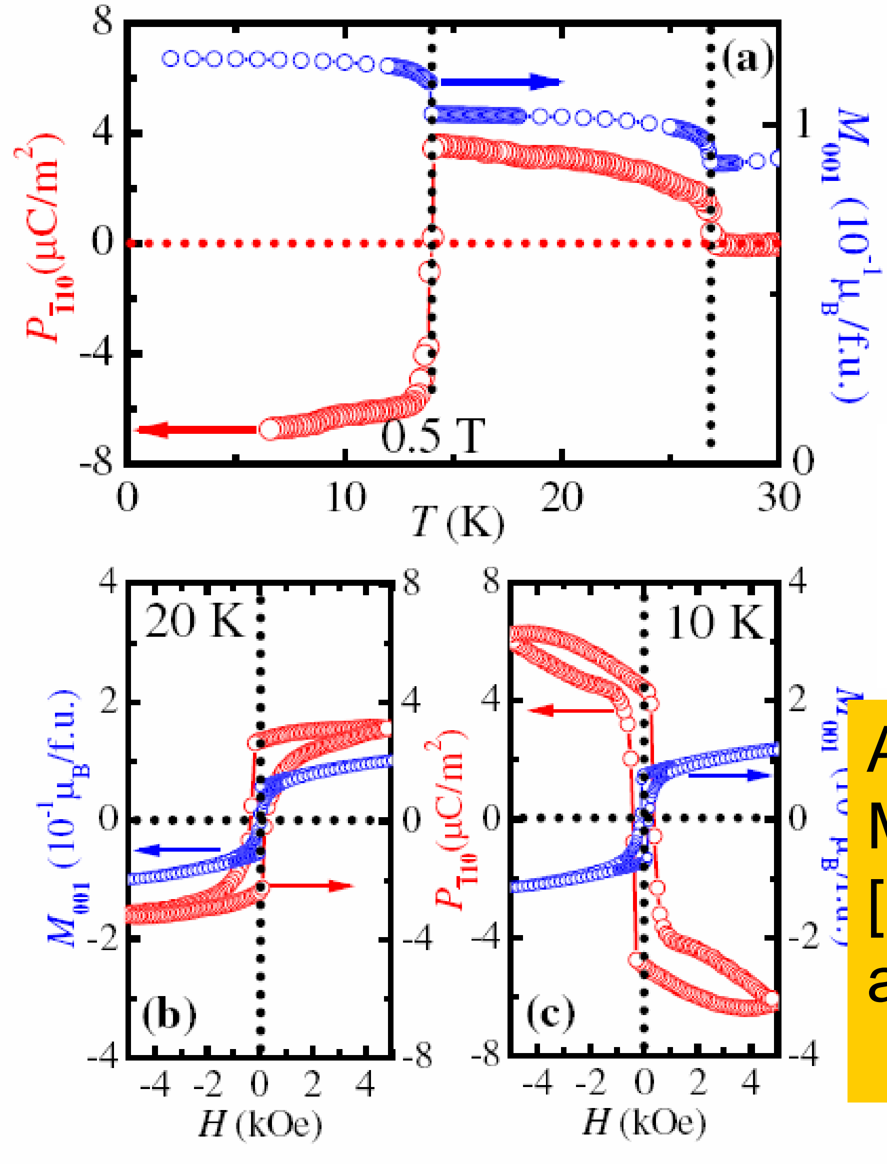
For details of toroidal moments see:

- Claude Ederer and Nicola A. Spaldin, Phys. Rev. B **76**, 214404 (2007)
- N.A. Spaldin, M. Fiebig and M. Mostovoy, J. Phys. Condens. Matter, **20**, 434203 (2008)

Example of Type-II multiferroic:

the conical spin spiral-based, joint order-parameter ferroelectric ferrimagnet, the spinel $CoCr_2O_4$

Y.J. Coi et al.,PRL **102**, 067601 (2009)

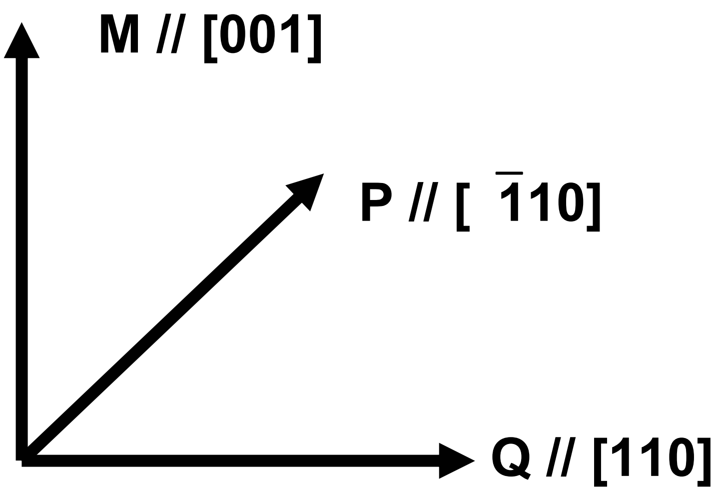


Spinel $CoCr_2O_4$

FIG. 2 (color online). (a) *T* dependence of electric polarization, **P**, along the [$\bar{1}$10] direction, and **M** along the [001] direction below 30 K. **P** suddenly switches sign when cooling across 14 K without changing the signs of **M** and **Q**. (b) and (c) *H* dependence of **M** and **P** at 20 K and 10 K, respectively. The reversal of all of **M**, **P**, and **Q** is achieved by *H* reversal.

A. Scaramucci, T.A. Kaplan and M.Mostovoy , arXiv: 0906.5298v1 [cond-mat.str-e1] 29 Jun 2009 are claiming P_S/M_S coupling due to domain wall clamping

Y.J. Choi et al., PRL 102, 067601 (2009)

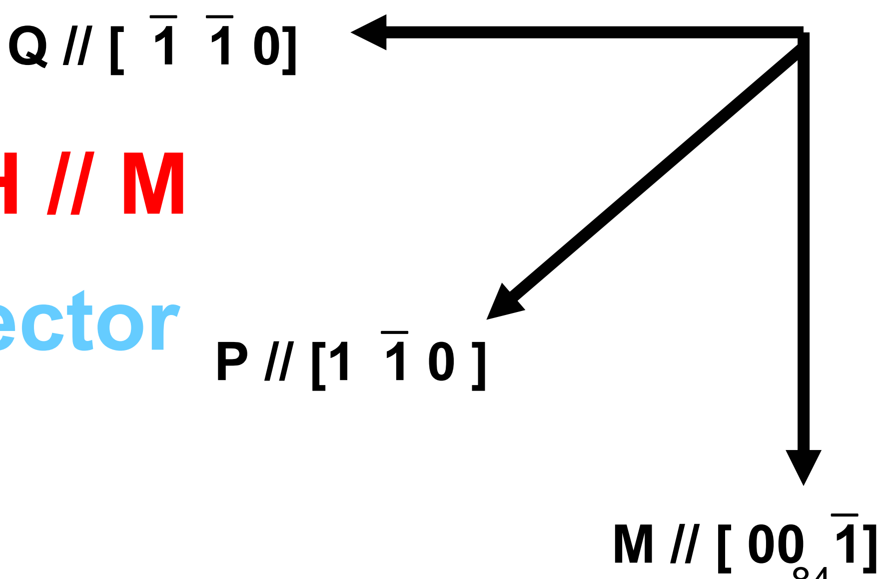


M // [001]

P // [$\bar{1}$10]

Q // [110]

$CoCr_2O_4$ at 10K



Q // [$\bar{1}$ $\bar{1}$ 0]

P // [1 $\bar{1}$ 0]

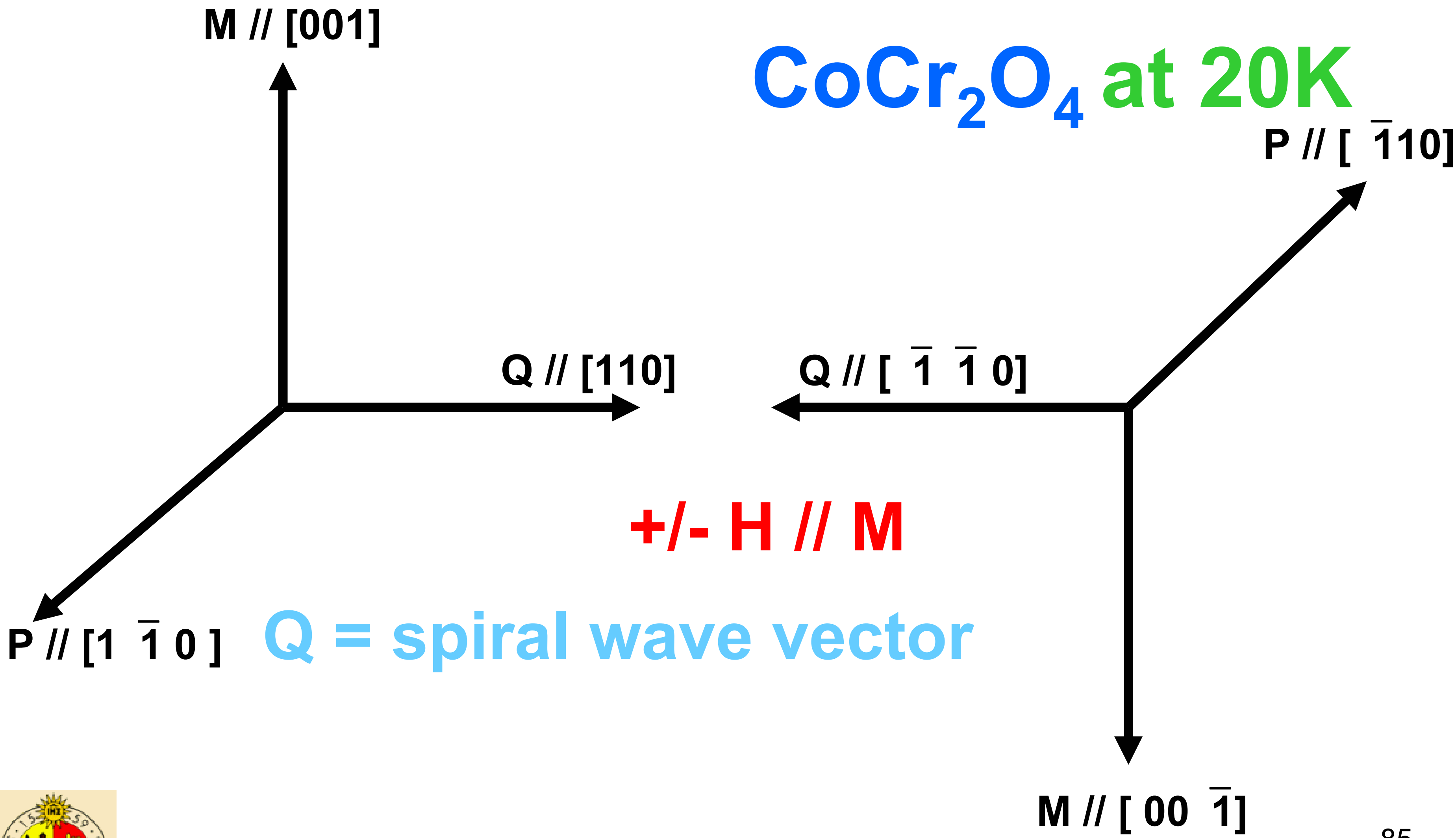
M // [00 $\bar{1}$]

+/- H // M

Q = spiral wave vector

Y.J. Choi et al., PRL 102, 067601 (2009)

$CoCr_2O_4$ at 20K



M // [001]

Q // [110]

P // [1 $\bar{1}$ 0]

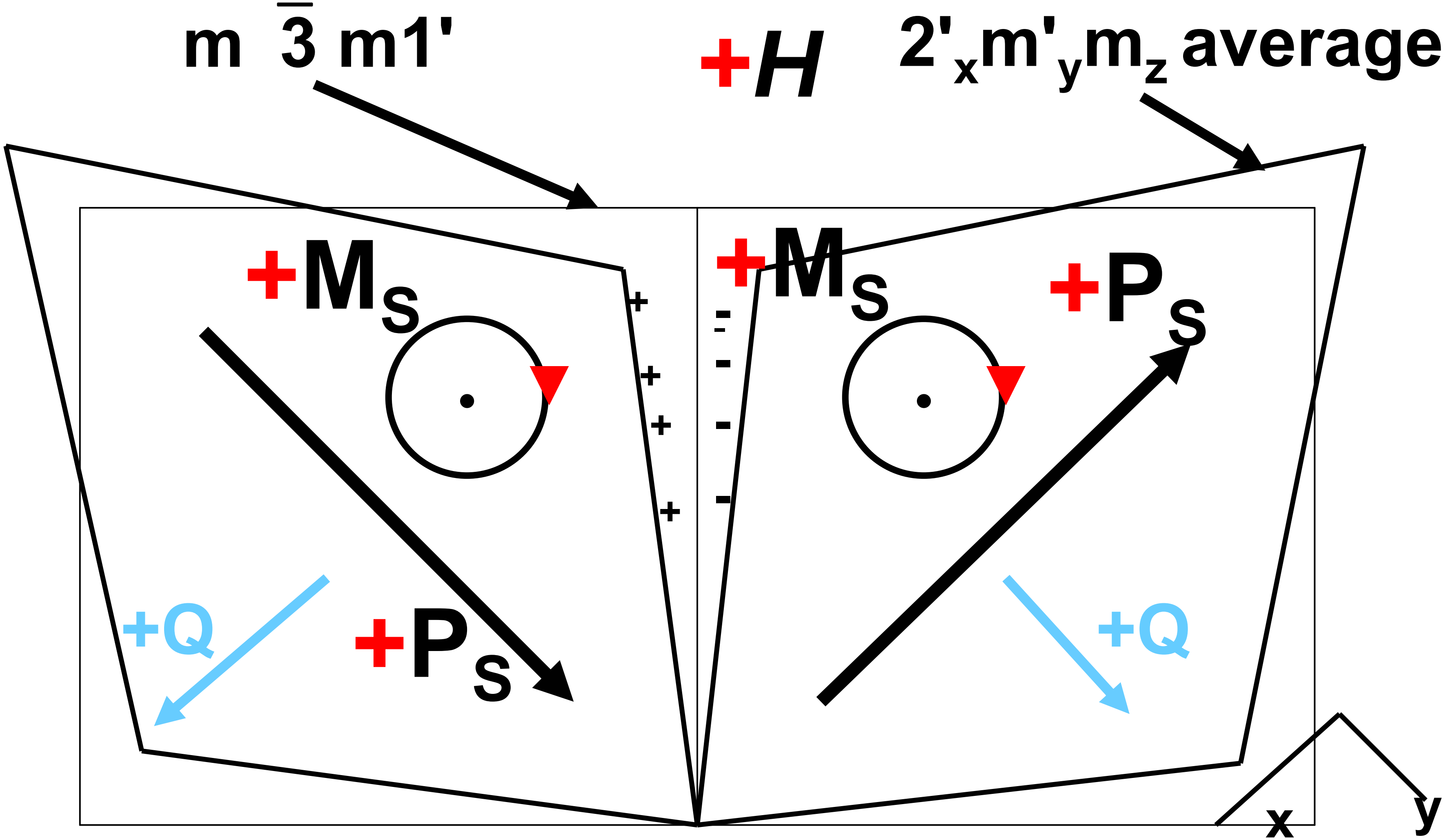
P // [$\bar{1}$10]

Q // [$\bar{1}$ $\bar{1}$ 0]

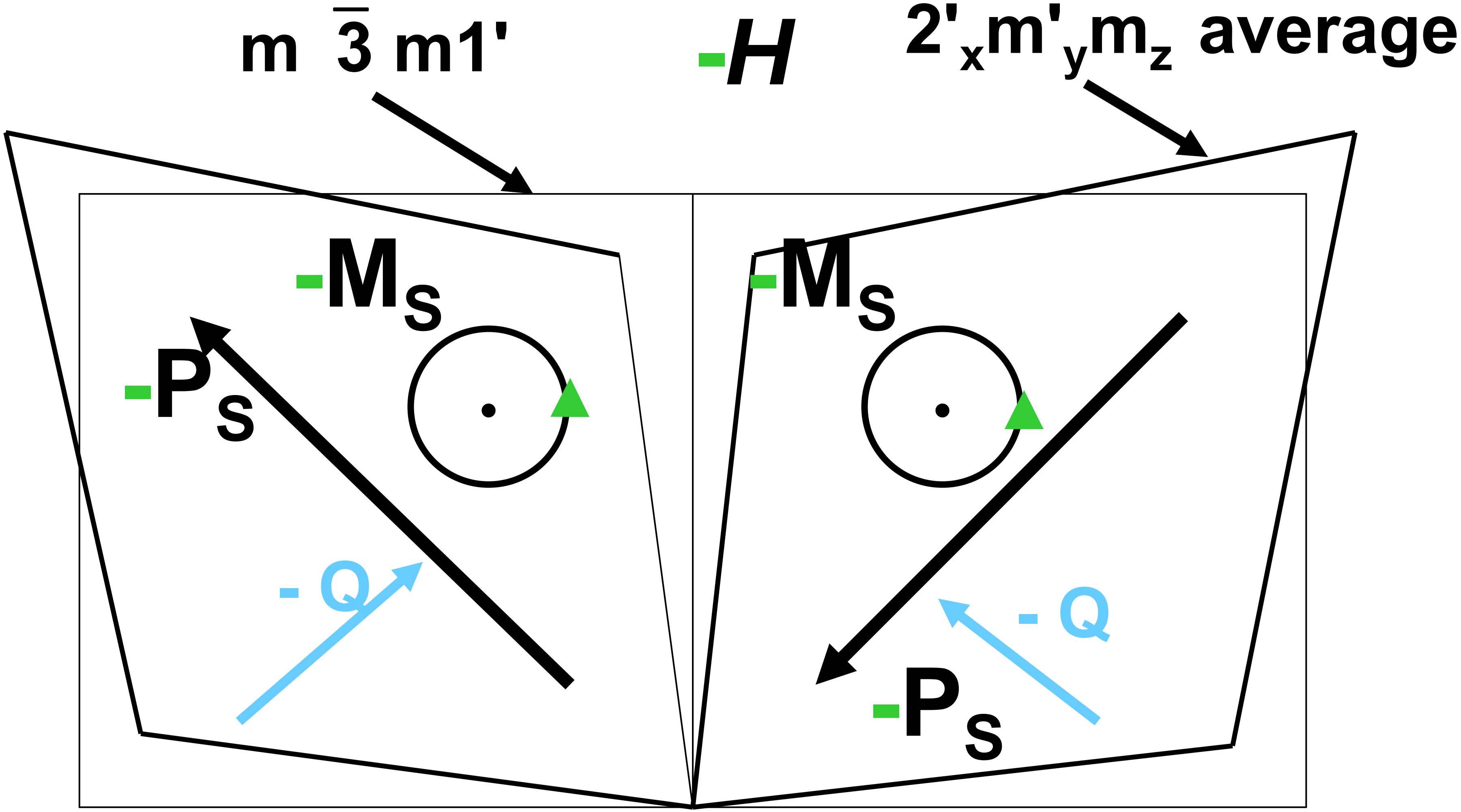
M // [00 $\bar{1}$]

+/- H // M

Q = spiral wave vector



CoCr$_2$O$_4$ below 14K, 12 domain states
Full ferroelectric, Partial ferromagnetic, Partial ferroelastic. According to Aizu (1970) and Litvin (2008) 12x2 states!!



$m\bar{3}m1'$

$-H$

$2'_x m'_y m_z$ average

$-M_S$

$-P_S$

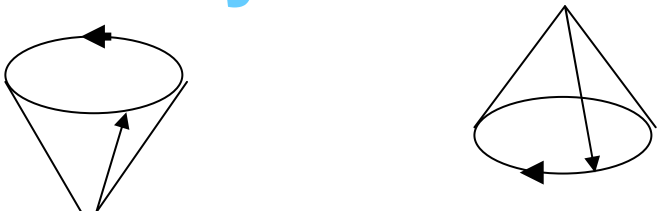
$-Q$

$-M_S$

$-Q$

$-P_S$

Change of sign of Q corresponds to a change of chirality. Conical spiral spins:



Conclusions

- In Type-I-multiferroics coupling between spontaneous polarization and magnetic order is partial and "split", and ruled by ferroelastic "reorientation switching"
- In Type-II-multiferroics there is strong coupling between magnetic order and ferroelectricity,but so far limited to low temperatures. The antiferromagnetic / ferroelectric CuO (210 to 220K) gives some hope for finding other "High T_c" Type-II compounds
- In the meantime probably man-made hetero-phase structures with clever extrinsic coupling mechanisms may have a chance to lead faster to applications

Acknowledgments

Impossible to cite all scientists and technicians, of Battelle-Geneva and the University of Geneva, the living and the dead. They merit deep-felt gratitude

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