Alternative Approaches to Magnetic Structures

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Outline:

1. Historical introduction to magnetic structures
2. Early Magnetic Crystallography. Shubnikov Groups and Representations
3. Future of Magnetic Crystallography. Superspace groups and Representations. New computing tools

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1. **Historical introduction to magnetic structures**
2. Early Magnetic Crystallography. Shubnikov Groups and Representations
3. Future of Magnetic Crystallography. Superspace groups and Representations. New computing tools

History: Magnetic neutron scattering

Historical overview:

Chadwick (1932): Discovery of the neutron (Proc Roy Soc **A136** 692)

Bloch (1936): interaction between magnetic atoms and neutrons

Schwinger (1937): QM treatment (Phys Rev **51** 544)

Alvarez and Bloch (1940): n-magnetic moment (Phys Rev **57** 111)

Halpern et al. (1937-1941): First comprehensive theory of magnetic neutron scattering (Phys Rev **51** 992; **52** 52; **55** 898; **59** 960)

History: Magnetic neutron scattering

Polarized neutrons milestones:

Shull et al. (1951)
Neutron Scattering and polarisation by ferromagnetic materials. Phys. Rev. **84** (1951) 912

Blume and Maleyev et al. (1963)
Polarisation effects in the magnetic elastic scattering of slow neutrons. Phys. Rev. **130** (1963) 1670
Sov. Phys. Solid State **4**, 3461

Moon et al. (1969)
Polarisation Analysis of Thermal Neutron scattering
Phys. Rev. **181** (1969) 920

History: Magnetic neutron scattering

Letters to the Editor

[*The Editor does not hold himself responsible for opinions expressed by his correspondents. Neither can he undertake to return, nor to correspond with the writers of, rejected manuscripts intended for this or any other part of* NATURE. *No notice is taken of anonymous communications.*]

Possible Existence of a Neutron

IT has been shown by Bothe and others that beryllium when bombarded by α-particles of polonium emits a radiation of great penetrating power, which has an absorption coefficient in lead of about 0·3 (cm.)$^{-1}$. Recently Mme. Curie-Joliot and M. Joliot found, when measuring the ionisation produced by this beryllium radiation in a vessel with a thin window, that the ionisation increased when matter containing hydrogen was placed in front of the window. The effect appeared to be due to the ejection of protons with velocities up to a maximum of nearly 3×10^9 cm. per sec. They suggested that the transference of energy to the proton was by a process similar to the Compton effect, and estimated that the beryllium radiation had a quantum energy of 50×10^6 electron volts.

I have made some experiments using the valve counter to examine the properties of this radiation excited in beryllium. The valve counter consists of a small ionisation chamber connected to an amplifier, and the sudden production of ions by the entry of a particle, such as a proton or α-particle, is recorded by the deflexion of an oscillograph. These experiments have shown that the radiation ejects particles from hydrogen, helium, lithium, beryllium, carbon, air, and argon. The particles ejected from hydrogen behave, as regards range and ionising power, like protons with speeds up to about $3{\cdot}2 \times 10^9$ cm. per sec. The particles from the other elements have a large ionising power, and appear to be in each case recoil atoms of the elements.

If we ascribe the ejection of the proton to a Compton recoil from a quantum of 52×10^6 electron volts, then the nitrogen recoil atom arising by a similar process should have an energy not greater than about 400,000 volts, should produce not more than about 10,000 ions, and have a range in air at N.T.P. of about 1·3 mm. Actually, some of the recoil atoms in nitrogen produce at least 30,000 ions. In collaboration with Dr. Feather, I have observed the recoil atoms in an expansion chamber, and their range, estimated visually, was sometimes as much as 3 mm. at N.T.P.

These results, and others I have obtained in the course of the work, are very difficult to explain on the assumption that the radiation from beryllium is a quantum radiation, if energy and momentum are to be conserved in the collisions. The difficulties disappear, however, if it be assumed that the radiation consists of particles of mass 1 and charge 0, or neutrons. The capture of the α-particle by the Be^9 nucleus may be supposed to result in the formation of a C^{12} nucleus and the emission of the neutron. From the energy relations of this process the velocity of the neutron emitted in the forward direction may well be about 3×10^9 cm. per sec. The collisions of this neutron with the atoms through which it passes give rise to the recoil atoms, and the observed energies of the recoil atoms are in fair agreement with this view. Moreover, I have observed that the protons ejected from hydrogen by the radiation emitted in the opposite direction to that of the exciting α-particle appear to have a much smaller range than those ejected by the forward radiation. This again receives a simple explanation on the neutron hypothesis.

If it be supposed that the radiation consists of quanta, then the capture of the α-particle by the Be^9 nucleus will form a C^{13} nucleus. The mass defect of C^{13} is known with sufficient accuracy to show that the energy of the quantum emitted in this process cannot be greater than about 14×10^6 volts. It is difficult to make such a quantum responsible for the effects observed.

It is to be expected that many of the effects of a neutron in passing through matter should resemble those of a quantum of high energy, and it is not easy to reach the final decision between the two hypotheses. Up to the present, all the evidence is in favour of the neutron, while the quantum hypothesis can only be upheld if the conservation of energy and momentum be relinquished at some point.

J. CHADWICK.

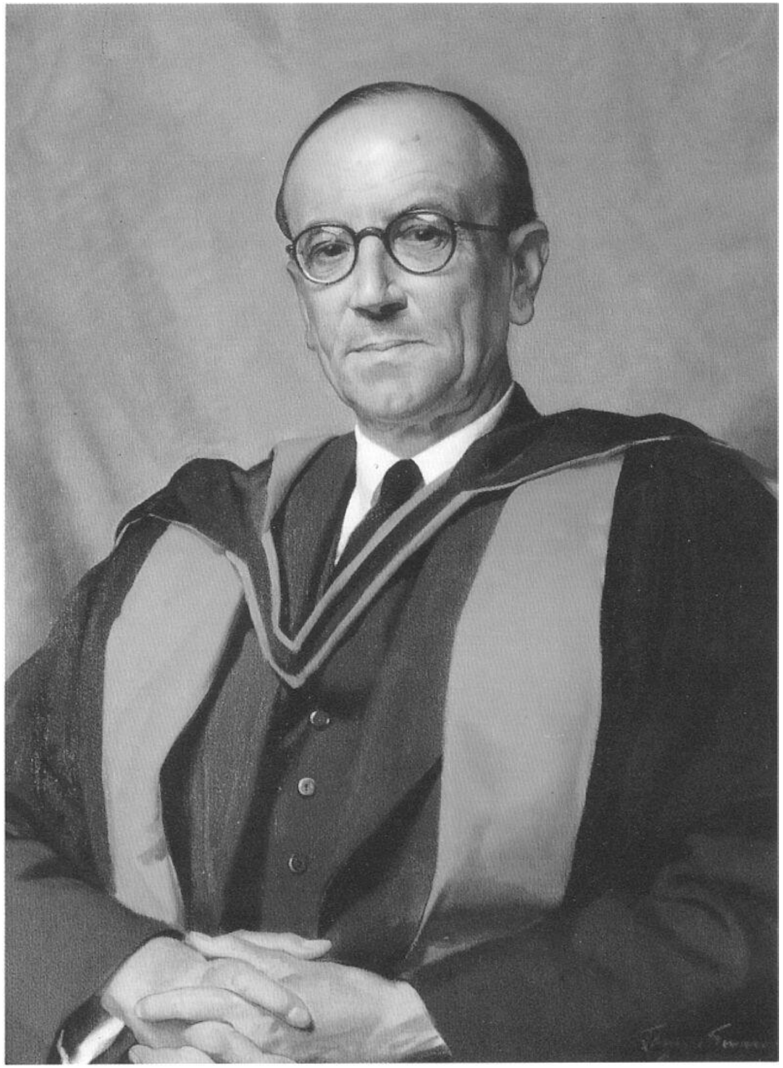
Cavendish Laboratory,
Cambridge, Feb. 17.

The Oldoway Human Skeleton

A LETTER appeared in NATURE of Oct. 24, 1931, signed by Messrs. Leakey, Hopwood, and Reck, in which, among other conclusions, it is stated that "there is no possible doubt that the human skeleton came from Bed No. 2 and not from Bed No. 4". This must be taken to mean that the skeleton is to be considered as a natural deposit in Bed No. 2, which is overlaid by the later beds Nos. 3 and 4, and that all consideration of human interment is ruled out.

If this be true, it is a most unusual occurrence. The skeleton, which is of modern type, with filed teeth, was found completely articulated down even to the phalanges, and in a position of extraordinary contraction. Complete mammalian skeletons of any age are, as field palæontologists know, of great rarity. When they occur, their perfection can usually be explained as the result of sudden death and immediate covering by volcanic dust. Many of the more or less perfect skeletons which may be seen in museums have been rearticulated from bones found somewhat scattered as the result of death from floods, or in the neighbourhood of drying water-holes. We know of no case of a perfect articulated skeleton being found in company with such broken and scattered remains as appear to be abundant at Oldoway. Either the skeletons are all complete, as in the *Stenomylus* quarry at Sioux City, Nebraska, or are all scattered and broken in various degrees, as in ordinary bone beds. The probability, therefore, that the Oldoway skeleton represents an artificial burial is thus one that will occur to palæontologists.

The skeleton was exhumed in 1913, and published photographs show that the excavation made for its disinterment was extensive. It is, therefore, very difficult to believe that in 1931 there can be reliable evidence left at the site as to the conditions under which it was deposited. If naturally deposited in Bed No. 2, the skeleton is of the highest possible importance, because it would be of pre-Mousterian age, and would be in the company of *Pithecanthropus* and the Piltdown, Heidelberg, and Peking men, all of whose remains are fragmentary to the last degree. Of the few other human remains for which such antiquity is claimed, the Galley Hill skeleton and the Ipswich skeleton are, or apparently were, complete. The first of these was never seen *in situ* by any trained observer, and the latter has, we believe, been withdrawn by its discoverer. The other fragments, found long ago, are entirely without satisfactory evidence as to their mode of occurrence.



History: Magnetic neutron scattering

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Letters to the Editor

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History: Magnetic neutron scattering

NEUTRONS FOR SCIENCE®

On the Theory of Neutron Scattering by Magnetic Substances

In a note submitted for publication to the *Physical Review* we have suggested a new method for detecting magnetic scattering of neutrons which is based on a comparative study of paramagnetic substances with identical nuclei but varying magnetic moments. As a theoretical basis we used a letter by Bloch[1] who was the first to point out and quantitatively describe the magnetic scattering of neutrons. His results were later rederived in a quantum-theoretical treatment by Schwinger.[2]

Both authors have essentially treated the magnetic atom as an external field which is uninfluenced by the collision process. A complete quantum-mechanical treatment leads to the following results which for clarity, we state for different special cases.

(A) Unmagnetized paramagnetic bodies (with the magnetic ion in an *S* state)

The magnetic cross section is

$$\sigma=(8\pi e^4/3m^2c^4)\gamma_n^2 j(j+1). \qquad (1)$$

Wherein γ_n denotes the magnetic moment of the neutron in nuclear Bohr magnetons and the other symbols are self-explanatory. The result is independent of the spin-state of the incident neutron beam. It raises all values of the magnetic cross sections given in our previous note in the ratio $(j+1)/j$.

(B) Ferromagnetic bodies

Here the result depends on the energetic possibility of

transitions to neighboring spectroscopic levels, the presence of isotopes and the existence of spin-dependent nuclear forces. The magnetic cross section on the other hand, is increased by transitions of the atoms to neighboring energy states.

In the above considerations we have refrained from including form factors which can considerably influence the results, even for thermal neutrons, but which are taken into account in our detailed calculations.

O. Halpern
M. H. Johnson, Jr.

New York University,
University Heights,
May 13, 1937.

[1] F. Bloch, Phys. Rev. **50**, 259 (1936).
[2] J. Schwinger, Phys. Rev. **51**, 544 (1937). Bloch's formula seems to be distorted by misprint; we could not verify the interpretive correction given by Schwinger.

The Ionosphere and Magnetic Storms*

It has been recognized for many years that there was some relation between magnetic storms and poor radio transmission conditions at high frequencies. It was believed that disturbances of the ionosphere produced both the magnetic storms and poor radio transmission conditions. The ideas concerning this relation were somewhat nebulous because of a lack of specific information concerning either normal or abnormal conditions of the ionosphere.

In two previous Letters to the Editor[1,2] we have described in detail many of the specific effects which we have observed to occur in the ionosphere during and following magnetic disturbances. Our observations and conclusions have been confirmed by many other observations at the

History: Magnetic neutron scattering

NEUTRONS FOR SCIENCE®

On the Theory of Neutron Scattering by Magnetic Substances

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MAY 15, 1939 PHYSICAL REVIEW VOLUME 55

On the Magnetic Scattering of Neutrons

O. HALPERN AND M. H. JOHNSON
New York University, University Heights, New York, New York

(Received December 3, 1938)

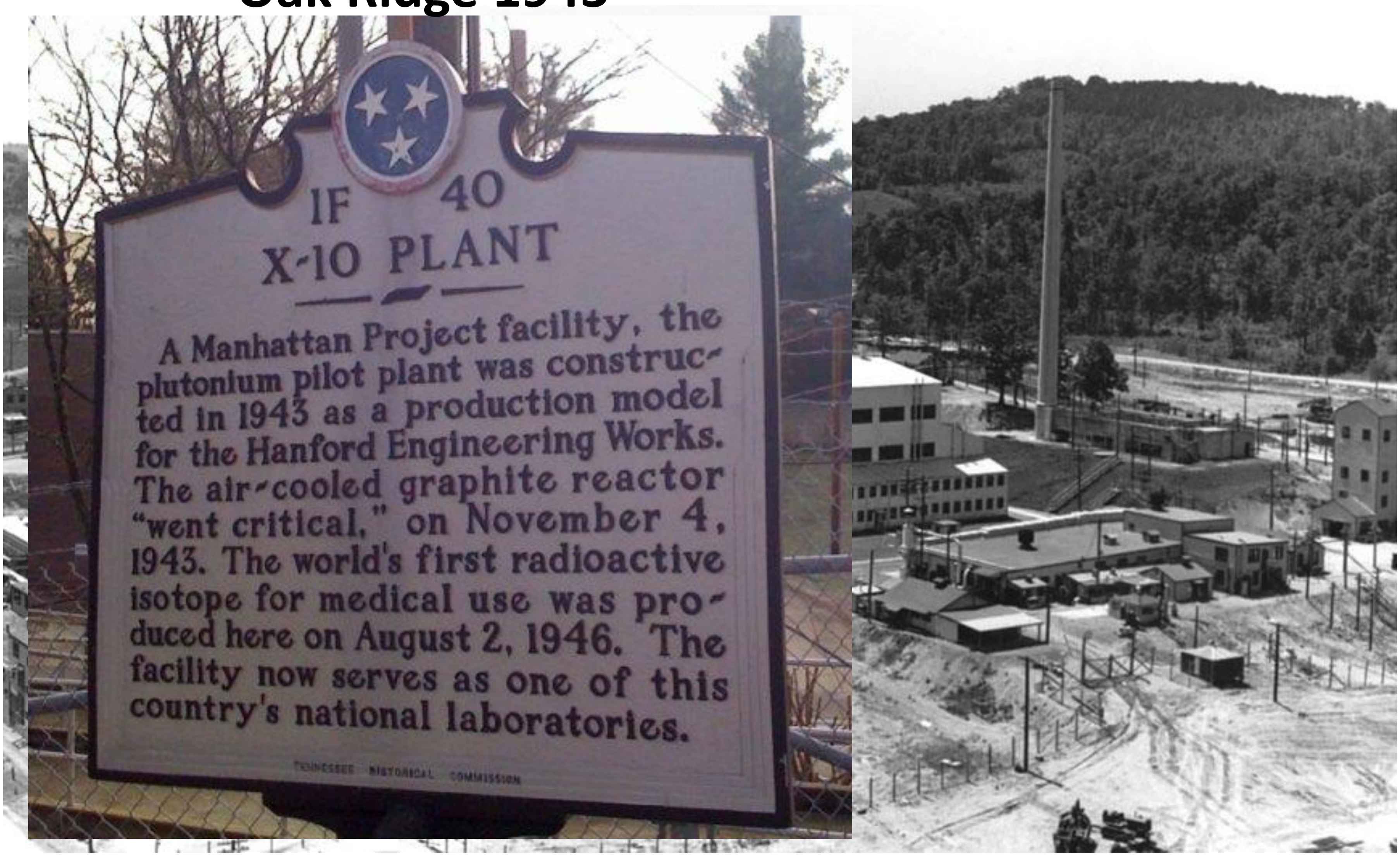
In this paper there is contained a full elaboration of two previously published short notes on the subject of magnetic scattering of neutrons together with a comprehensive treatment of certain sides of this problem which have already received some attention from other authors. After presenting the state of the problem in the introduction and discussing in detail our reasons for the choice of an interaction function between neutrons and electrons, and the nonmagnetic interaction between neutrons and nuclei, the various possible cases of coherent and incoherent scattering and depolarization phenomena are treated. Later applications to the theory of ferromagnetic scattering are kept in mind. The general expression for the cross section due to magnetic interaction is obtained and applied to various classes of phenomena (scattering by free, rigidly aligned, and coupled magnetic ions). The influence of the elastic form-factor is treated quantitatively with the aid of a simple model for the current distribution in the ion. Finally a series of performed or suggested experiments is discussed mainly from the point of view whether they will permit theoretical interpretation. Arrangements are described which will allow one to obtain a reliable value for the neutron's magnetic moment and also give insight into the magnetic constitution of the scatterer (ion or crystal) which will exceed the knowledge obtainable from macroscopic magnetic experiments.

Here the result depends on the energetic possibility of

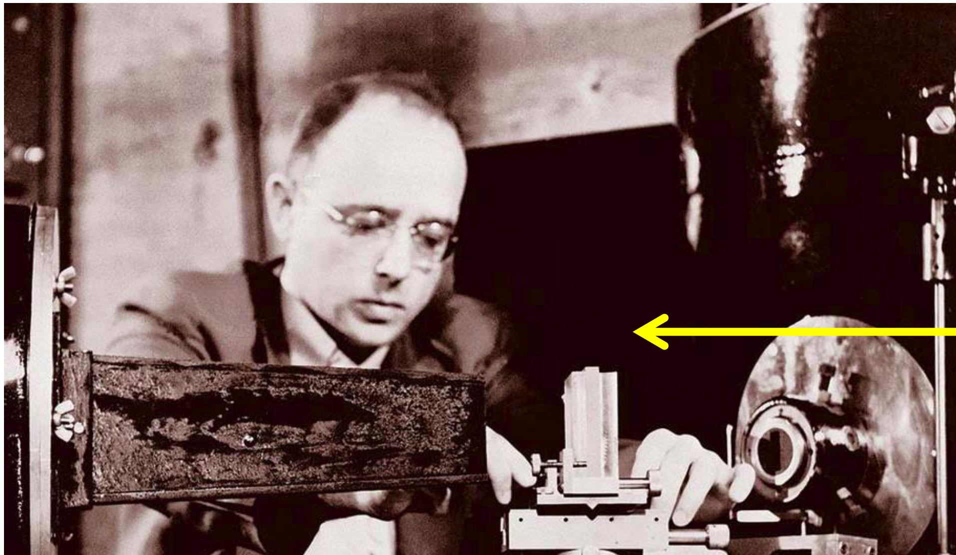
magnetic disturbances. Our observations and conclusions have been confirmed by many other observations at the

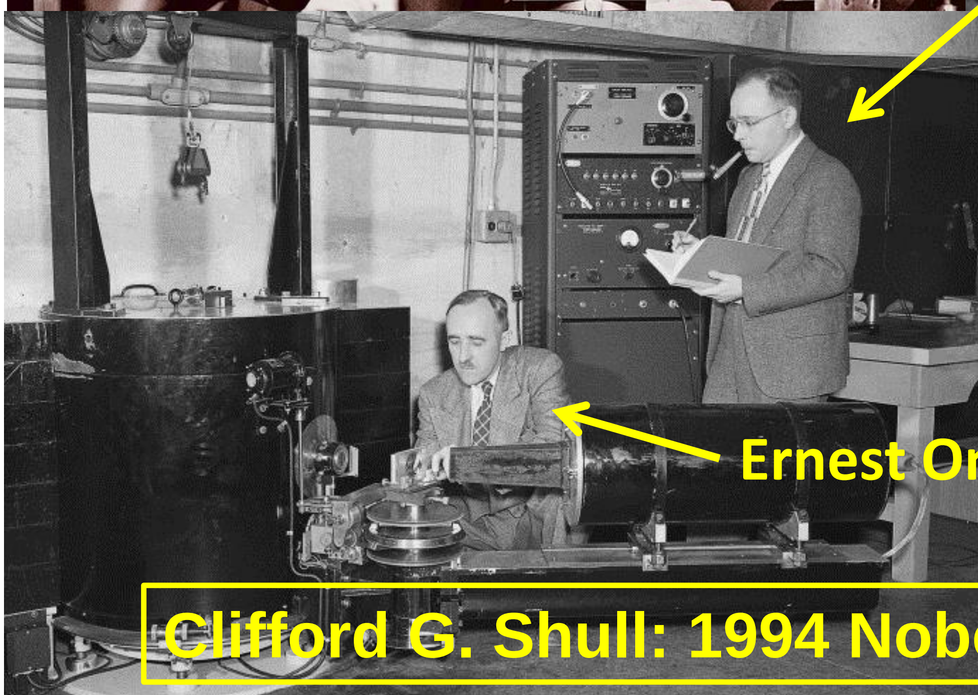
History: Magnetic neutron scattering

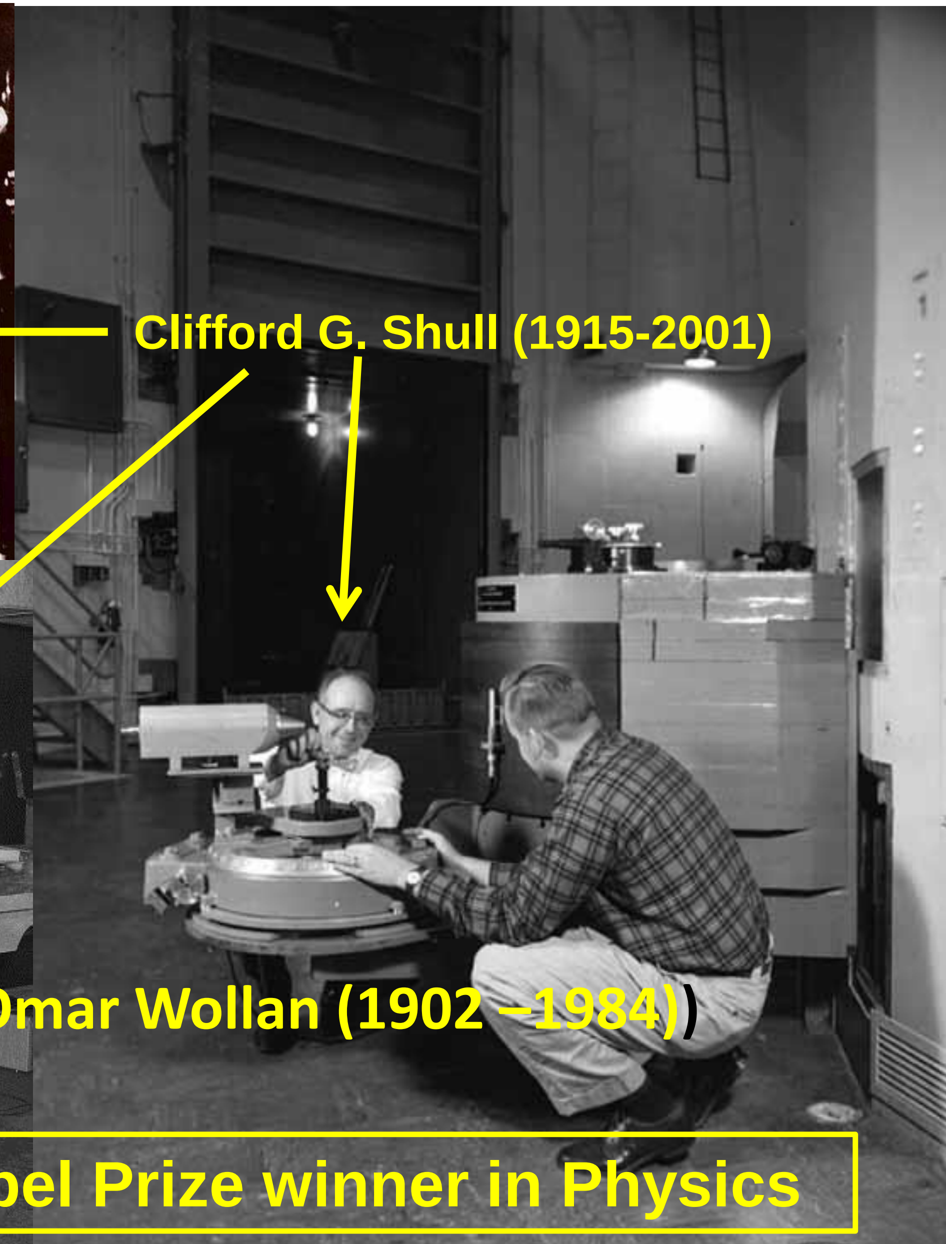
Oak Ridge 1943



First magnetic neutron diffraction experiments







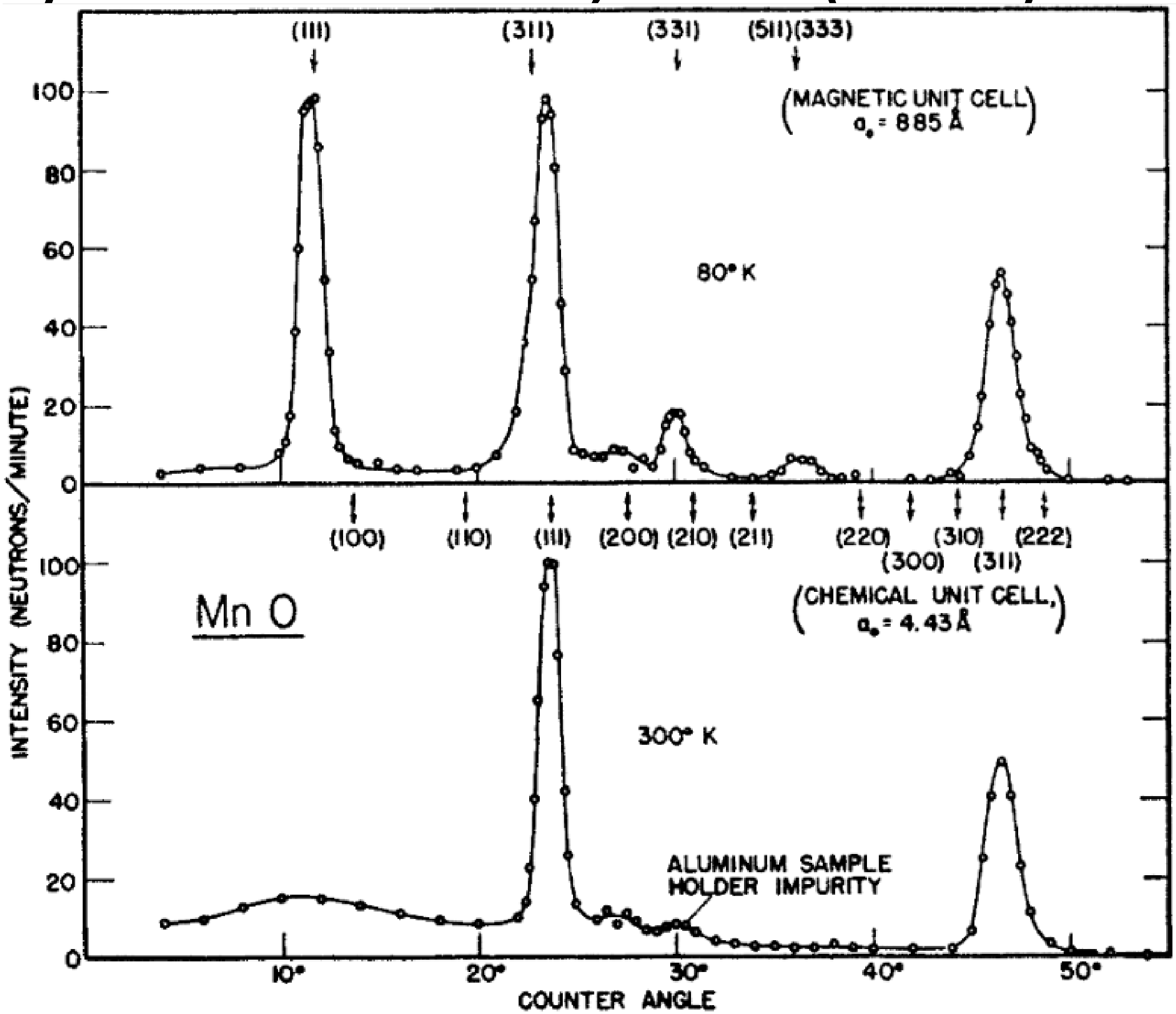
Clifford G. Shull (1915-2001)

Ernest Omar Wollan (1902 –1984))

Clifford G. Shull: 1994 Nobel Prize winner in Physics

First magnetic neutron diffraction experiments

Physical Review **76**, 1256 (1949)



First magnetic neutron diffraction experiments

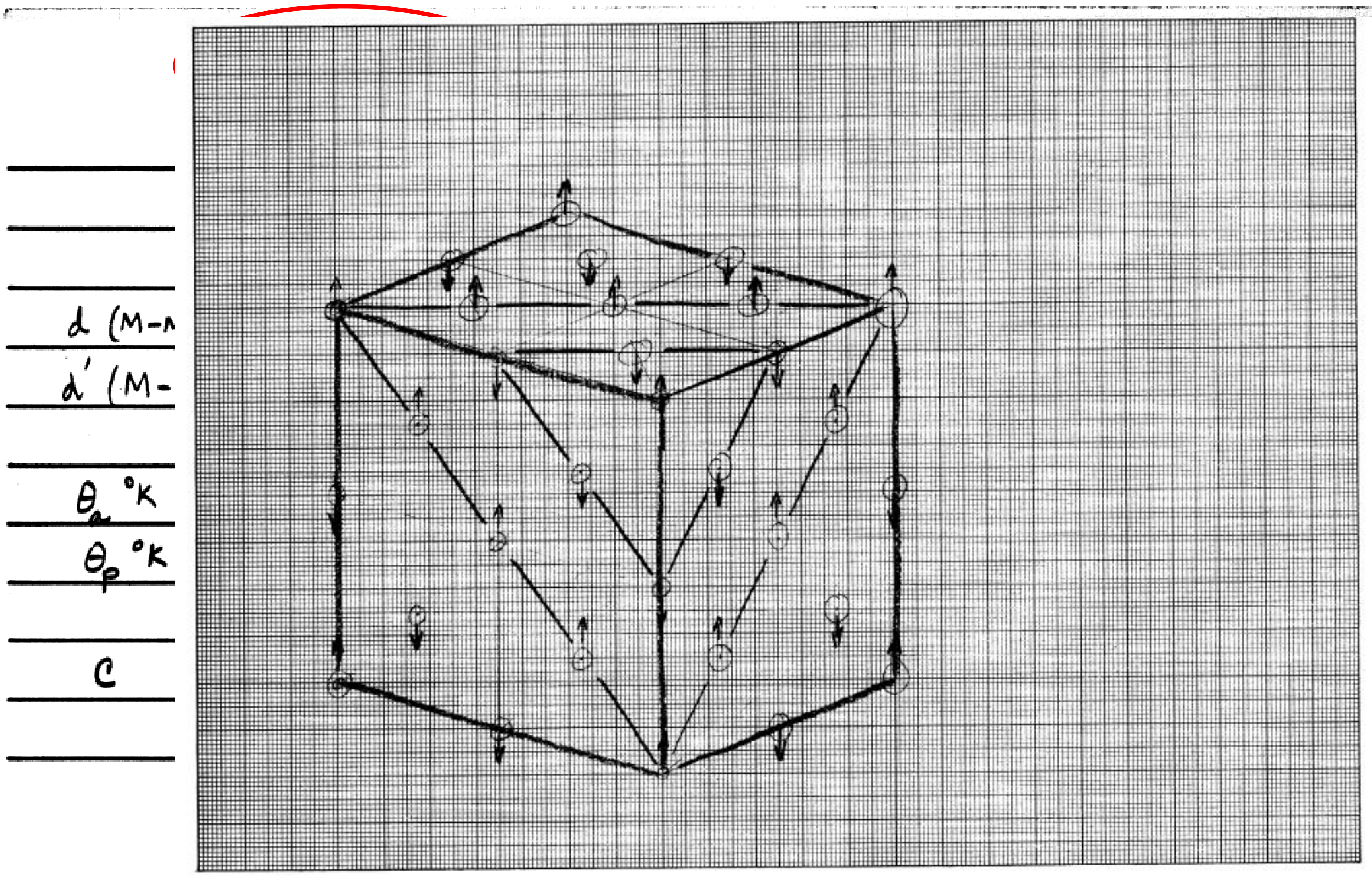
L. Neel

Ann. de Physique, 3 p. 137 (1948)
C.R. Acad Sci Paris 228 64-6 (1949)

	MnO	MnS	FeO	FeF_2	MnF_2	$\alpha\ Fe_2O_3$
d (M-M)	3.12	3,68	3.03	3,36	3.30	2,91 {2.88, 2.94}
d′ (M-O)	2,21	2,61	2,14	2,12	2,11	2,03
θ_a °K	-610	-528	-570	-117	-113	-2000
θ_p °K	122	165	198	79	72	950
C	4,4	4,3	6,24	3,88	4,08	4,4

Clifford G. Shull: 1994 Nobel Prize winner in Physics

First magnetic neutron diffraction experiments



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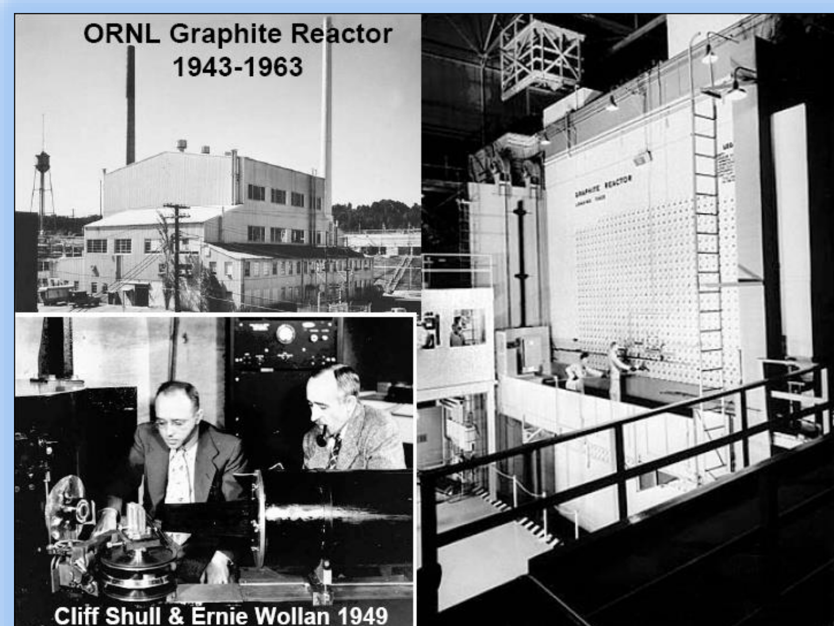
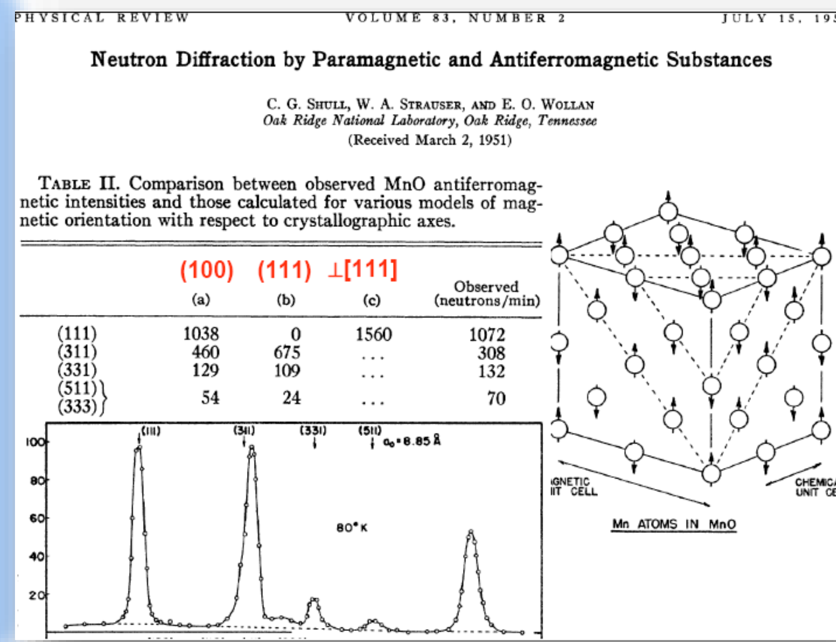
First magnetic neutron diffraction experiments





PHYSICAL REVIEW VOLUME 83, NUMBER 2 JULY 15, 1951

Neutron Diffraction by Paramagnetic and Antiferromagnetic Substances

C. G. Shull, W. A. Strauser, and E. O. Wollan
Oak Ridge National Laboratory, Oak Ridge, Tennessee
(Received March 2, 1951)

Table II. Comparison between observed MnO antiferromagnetic intensities and those calculated for various models of magnetic orientation with respect to crystallographic axes.

	(100) (a)	(111) (b)	⊥[111] (c)	Observed (neutrons/min)
(111)	1038	0	1560	1072
(311)	460	675	...	308
(331)	129	109	...	132
(511) (333)	54	24	...	70

- ✓ The first direct evidence of antiferromagnetism was produced in determining the magnetic structure of MnO
- ✓ the Néel model of ferrimagnetism was confirmed for Fe_3O_4,
- ✓ the first magnetic form-factor data were obtained by measuring the paramagnetic scattering by Mn compounds,
- ✓ the production of polarized neutrons by Bragg reflection from ferromagnets was demonstrated

Thanks to Clarina de la Cruz

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1. Historical introduction to magnetic structures
2. **Early Magnetic Crystallography. Shubnikov Groups and Representations**
3. Future of Magnetic Crystallography. Superspace groups and Representations. New computing tools

A crucial person in the field of magnetic structure determination was:

Felix Bertaut (1913- 2003)
Original name: Erwin Lewy,
He signed his papers as
E. F. Bertaut

"Felix Bertaut is a mathematician who does crystallography". Andre Guinier

Magnetic Structure Description and Determination

Two (Three?) principal methods ("classifications schemes") were developed for magnetic structure determination up to the middle of the seventies.

In terms of W. Opechowski in *Acta Cryst.* **A27**, 470 (1971):

C1: Des … **ikov groups**
W. Ope… Vol. 2A,
Ed. G.T.…

C1': De… **c groups** .
W. Ope…
See also… 974)
W. Ope… North
Holland…

I'm using C1 in a different sense as that used by Opechowski (for him C1' includes C1 in the sense used here).
C1 in the sense used by Opechowski is concerned with groups leaving invariant scalar functions f(**r**), and C1' is concerned with groups leaving invariant vector functions **B**(**r**)

C2: Description of magnetic structures based on representation analysis.
See E.F. Bertaut, Acta Cryst **A24**, 217 (1968), Y.A. Izyumov et al., JMMM (1979-1980)

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In terms of W. Opechowski in *Acta Cryst.* **A27**, 470 (1971):

C1: Description of magnetic structures based on conventional Shubnikov groups

W. Opechowski and R. Guccione. Magnetic Symmetry, in Magnetism, Vol. 2A, Ed. G.T. Rado and H. Suhl, Academic Press, 1965

C1': Description of magnetic structures based on non-crystallographic groups .

W. Opechowski and T. Dreyfus, Acta Cryst **A27**, 470 (1971).

See also: D.B. Litvin & W. Opechowski, *Spin Groups*, Physica **76**, 538 (1974)

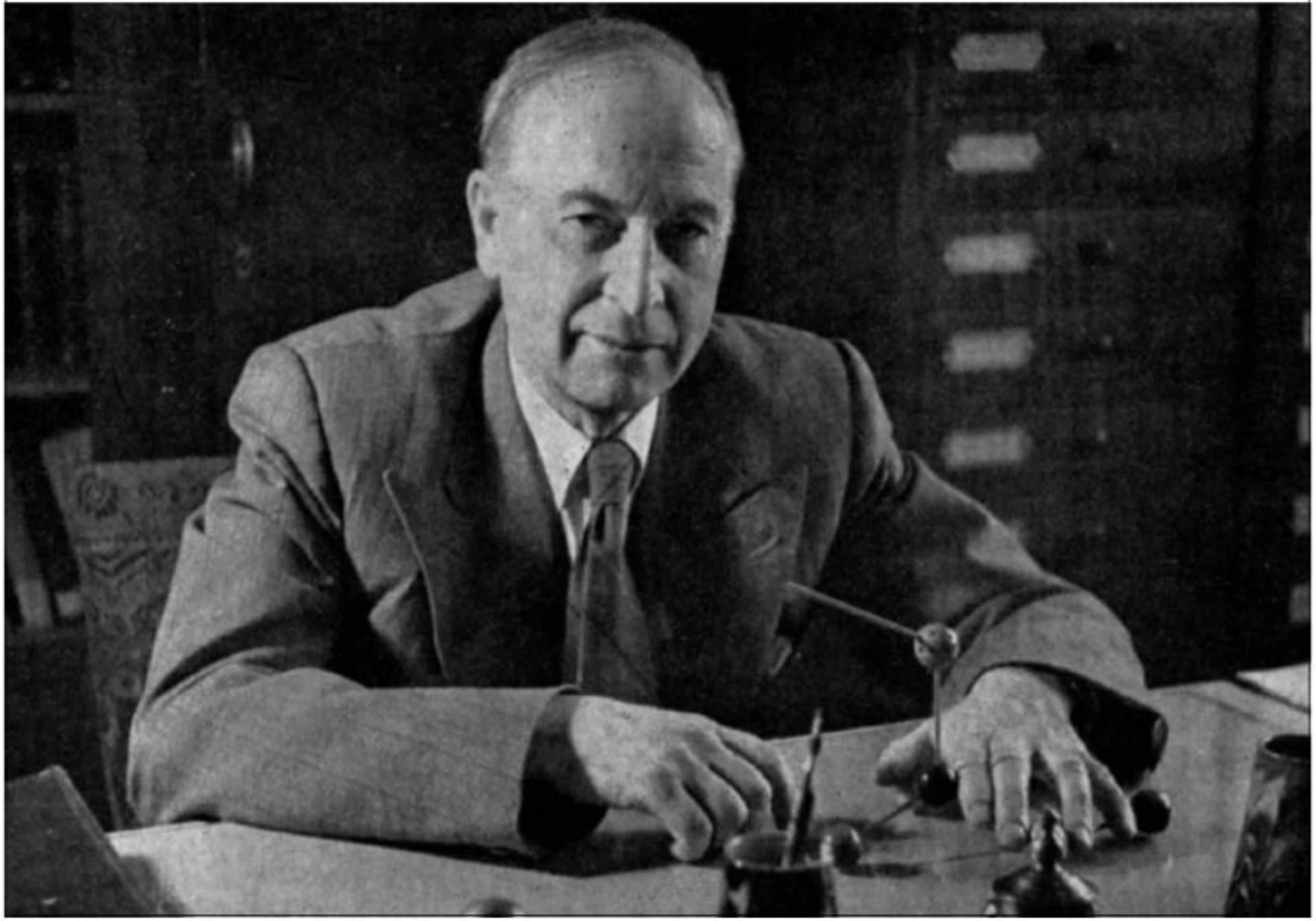
W. Opechowski in *Crystallographic and Meta-crystallographic Groups*, North Holland, 1986

C2: Description of magnetic structures based on representation analysis.

See E.F. Bertaut, Acta Cryst **A24**, 217 (1968), Y.A. Izyumov et al., JMMM (1979-1980)

Magnetic Structure Description and Determination

Alexey Vasilyevich Shubnikov 1887-1970



Magnetic Structure Description and Determination

1945: Shubnikov re-introduces the time reversal group {1,1'} first described by **Heesch in 1929**, Z. Krist. **71**, 95.

1951: Shubnikov describes the bi-colour point groups

1955: Belov, **Neronova** & **Smirnova** provide for the first time the full list of 1651 Shubnikov space groups. Sov. Phys. Crystallogr. **1**, 487-488

1957: Zamorzaev derives, using group theory, the Shubnikov groups. Kristallografiya **2**, 15 (Sov. Phys. Cryst., **3**, 401)

1965: Opechowski and **Guccione** derive and enumerate the full list of magnetic space groups (Shubnikov groups)

Magnetic Structure Description and Determination

NEUTRONS FOR SCIENCE®

1968: Describing 3-dimensional Periodic Magnetic Structures by Shubnikov Groups
Koptsik, V.A.
Soviet Physics Crystallography, **12** (5) , 723 (1968)

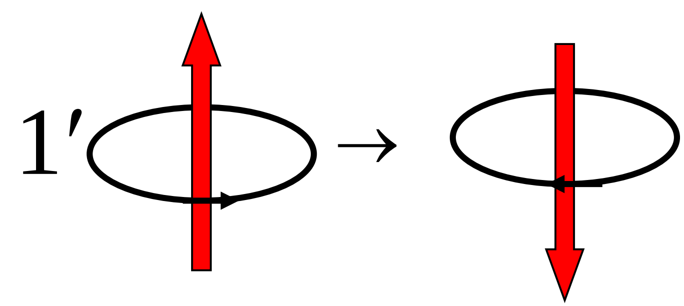
2001: **Daniel B. Litvin** provides for the first time the full description of all Shubnikov (Magnetic Space) Groups.
Acta Cryst. **A57**, 729-730

Magnetic moments as axial vectors

The magnetic moment (shortly called “spin”) of an atom can be considered as an “axial vector”. It may be associated to a “current loop”. The behaviour of elementary current loops under symmetry operators can be deduced from the behaviour of the “velocity” vector that is a “polar” vector.

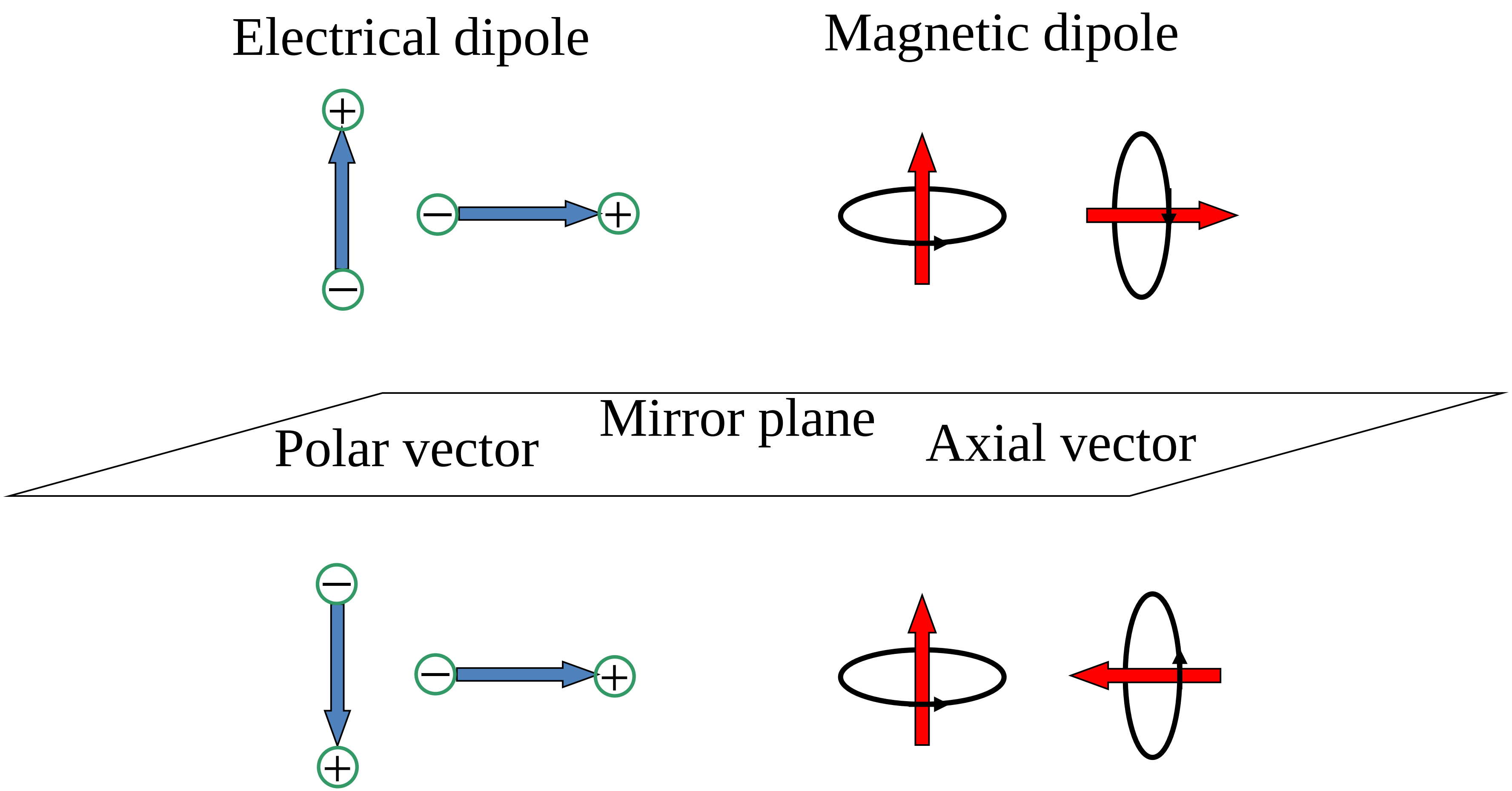
Time reversal = spin reversal

(change the sense of the current)



A new operator can be introduced and noted as $1'$, it flips the magnetic moment. This operator is called “spin reversal” operator or classical “time reversal” operator

Magnetic moments as axial vectors



$$\mathbf{m}_j{}' = g\,\mathbf{m}_j = \det(h)\,\delta\,h\,\mathbf{m}_j$$

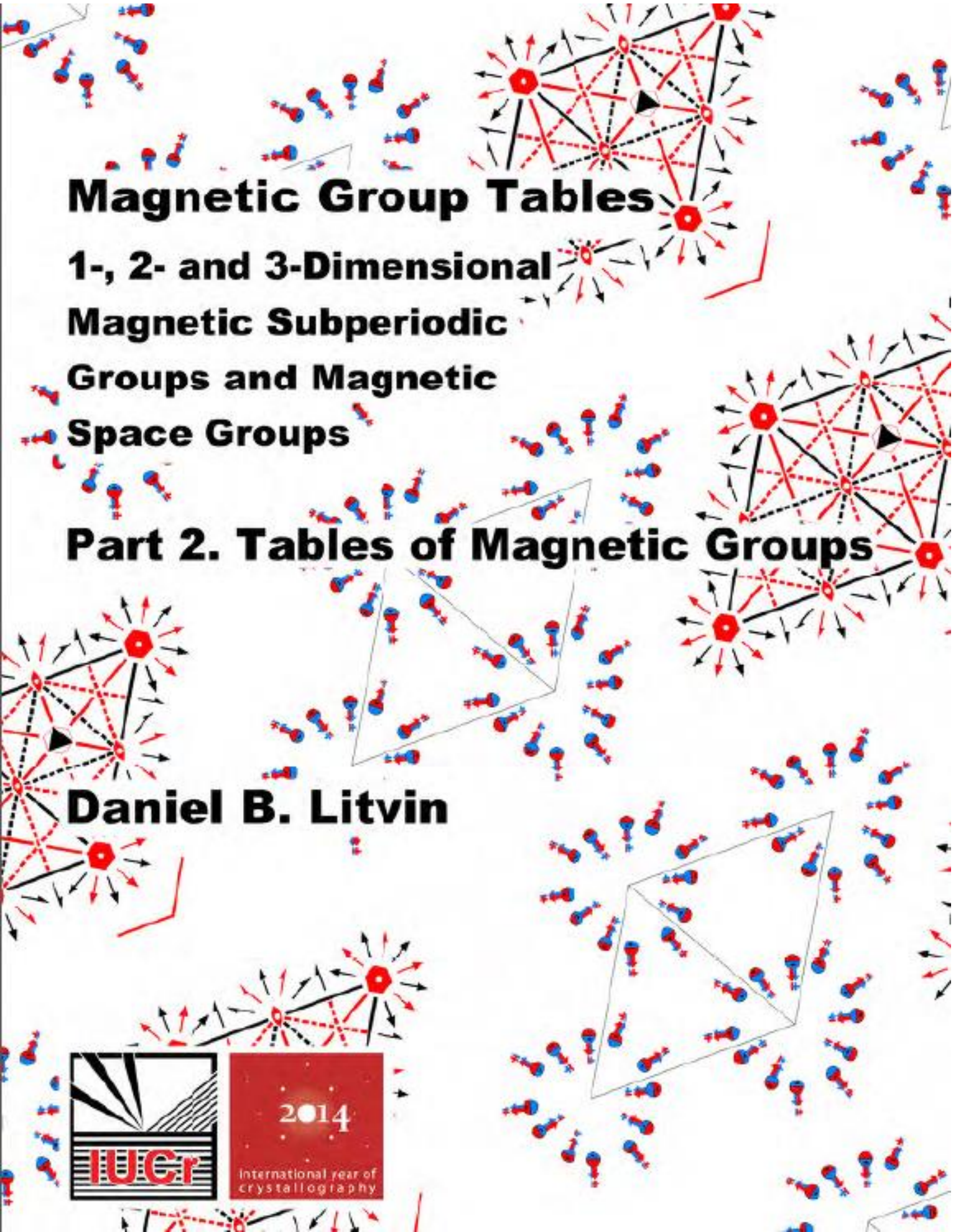
Magnetic Structure Description and Determination

2001: Daniel B. Litvin provides for the first time the full description of all Shubnikov (Magnetic Space) Groups. Acta Cryst. **A57**, 729-730

http://www.bk.psu.edu/faculty/litvin/home.html

Magnetic Structure Description and Determination

NEUTRONS FOR SCIENCE®



We are concerned here with the tables of Magnetic Groups, but many other papers from D.B. Litvin can be downloaded from its personal page at

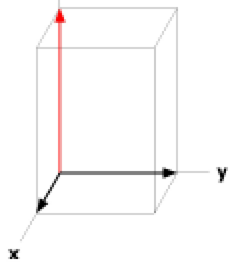
http://www.bk.psu.edu/faculty/litvin/

The first part is a comprehensive introduction to the tables and the second part contain each individual Magnetic Space Group item with Wyckoff positions and diagrams

Group Ordering Number (BNS): 548, BNS: 62.450, OG: 59.9.486

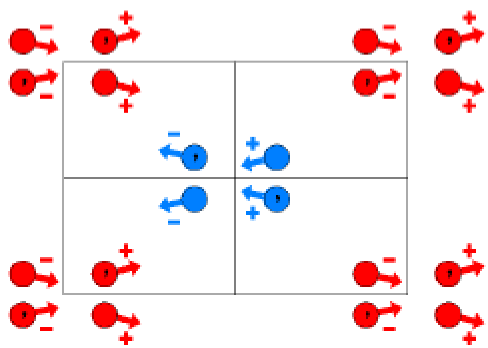
OG: $P_{2c}m'mm$

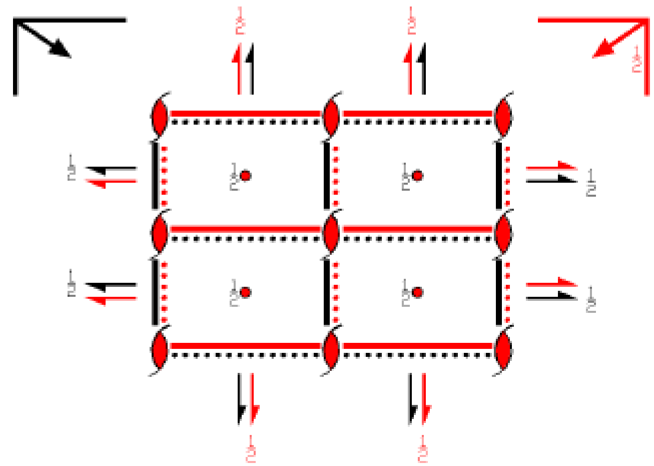
BNS: $P_{a}nma$



$P_{2c}m'mn$	mmm1'	Orthorhombic
59.9.486	$P_{2c}2_1/m'2_1'/m2'/n$	

OG-BNS transformation: (1/2,1/2,1/2; c,-b,2a)





Origin at m'm2'/n at 1/4,1/4,0 from $\bar{1}$'

Asymmetric unit $0 \le x \le 1/2$; $0 \le y \le 1/2$; $0 \le z \le 1/2$

Symmetry Operations

For (0,0,0) + set

(1) 1 (1|0,0,0)	(2) 2' 0,0,z (2_z|0,0,0)'	(3) 2' (0,1/2,0) 1/4,y,0 (2_y|1/2,1/2,0)'	(4) 2 (1/2,0,0) x,1/4,0 (2_x|1/2,1/2,0)
(5) $\bar{1}$' 1/4,1/4,0 ($\bar{1}$|1/2,1/2,0)'	(6) n (1/2,1/2,0) x,y,0 (m_z|1/2,1/2,0)	(7) m x,0,z (m_y|0,0,0)	(8) m' 0,y,z (m_x|0,0,0)'

For (0,0,1)' + set

(1) t' (0,0,1) (1|0,0,1)'	(2) 2 (0,0,1) 0,0,z (2_z|0,0,1)	(3) 2 (0,1/2,0) 1/4,y,1/2 (2_y|1/2,1/2,1)	(4) 2' (1/2,0,0) x,1/4,1/2 (2_x|1/2,1/2,1)'
(5) $\bar{1}$ 1/4,1/4,1/2 ($\bar{1}$|1/2,1/2,1)	(6) n' (1/2,1/2,0) x,y,1/2 (m_z|1/2,1/2,1)'	(7) c' (0,0,1) x,0,z (m_y|0,0,1)'	(8) c (0,0,1) 0,y,z (m_x|0,0,1)

Continued	59.9.486	$P_{2c}m'mn$

Generators selected (1); t(1,0,0); t(0,1,0); t'(0,0,1); (2); (3); (5).

Positions

Multiplicity,
Wyckoff letter,
Site Symmetry.

Coordinates

(0,0,0) + (0,0,1)' +

16 g 1

(1) x,y,z [u,v,w]	(2) $\bar{x},\bar{y}$,z [u,v,$\bar{w}$]	(3) $\bar{x}$+1/2,y+1/2,$\bar{z}$ [u,$\bar{v}$,w]	(4) x+1/2,$\bar{y}$+1/2,$\bar{z}$ [u,$\bar{v}$,$\bar{w}$]
(5) $\bar{x}$+1/2,$\bar{y}$+1/2,$\bar{z}$ [$\bar{u}$,$\bar{v}$,$\bar{w}$]	(6) x+1/2,y+1/2,$\bar{z}$ [$\bar{u}$,$\bar{v}$,w]	(7) x,$\bar{y}$,z [$\bar{u}$,v,$\bar{w}$]	(8) $\bar{x}$,y,z [$\bar{u}$,v,w]

8	f	.m.	x,0,z [0,v,0]	$\bar{x}$,0,z [0,v,0]	$\bar{x}$+1/2,1/2,$\bar{z}$ [0,$\bar{v}$,0]	x+1/2,1/2,$\bar{z}$ [0,$\bar{v}$,0]
8	e	m'.	0,y,z [0,v,w]	0,$\bar{y}$,z [0,v,$\bar{w}$]	1/2,y+1/2,$\bar{z}$ [0,$\bar{v}$,w]	1/2,$\bar{y}$+1/2,$\bar{z}$ [0,$\bar{v}$,$\bar{w}$]
8	d	$\bar{1}$	1/4,1/4,1/2 [u,v,w]	3/4,3/4,1/2 [u,v,$\bar{w}$]	1/4,3/4,1/2 [$\bar{u}$,v,$\bar{w}$]	3/4,1/4,1/2 [$\bar{u}$,v,w]
8	c	$\bar{1}$'	1/4,1/4,0 [0,0,0]	3/4,3/4,0 [0,0,0]	1/4,3/4,0 [0,0,0]	3/4,1/4,0 [0,0,0]
4	b	m'm2'	0,1/2,z [0,v,0]	1/2,0,$\bar{z}$ [0,$\bar{v}$,0]		
4	a	m'm2'	0,0,z [0,v,0]	1/2,1/2,$\bar{z}$ [0,$\bar{v}$,0]		

Symmetry of Special Projections

Along [0,0,1] c2mm1'	Along [1,0,0] p2mg	Along [0,1,0] p2mg1'
a* = a b* = b	a* = b b* = c	a* = -a b* = c
Origin at 0,0,z	Origin at x,1/4,0	Origin at 1/4,y,0

Magnetic Structure Description and Determination

Continued 59.9.486 P_{2c} m'mn

Only recently the magnetic space groups are available in a computer database

Magnetic Space Groups
Compiled by Harold T. Stokes and Branton J. Campbell
Brigham Young University, Provo, Utah, USA
June 2010

These data are based on data from:
Daniel Litvin, **Magnetic Space Group Types**,
Acta Cryst. **A57** (2001) 729-730.
http://www.bk.psu.edu/faculty/litvin/Download.html

Symmetry of Special Projections

Along [0,0,1] c2mm1'	Along [1,0,0] p2mg	Along [0,1,0] p2mg1'
a* = a b* = b	a* = b b* = c	a* = -a b* = c
Origin at 0,0,z	Origin at x,1/4,0	Origin at 1/4,y,0

Magnetic Structure Description and Determination

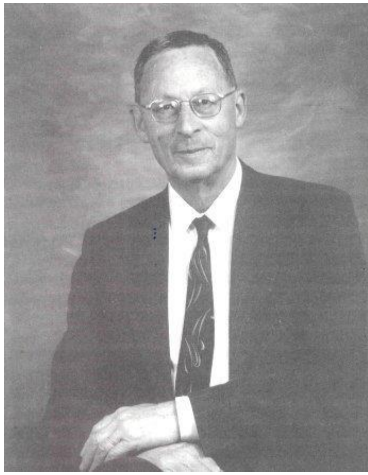
Acta Cryst. (1968). A**24**, 217

Representation Analysis of Magnetic Structures

By E. F. Bertaut

Laboratoire d'Électrostatique et de Physique du Métal, C.N.R.S., B.P. 319 *et*
Laboratoire de Diffraction Neutronique, C.E.N.G., B.P. 269, *Grenoble* 38, *France*

(*Received* 20 *July* 1967)



In the analysis of spin structures a 'natural' point of view looks for the set of symmetry operations which leave the magnetic structure invariant and has led to the development of magnetic or Shubnikov groups. A second point of view presented here simply asks for the transformation properties of a magnetic structure under the classical symmetry operations of the 230 conventional space groups and allows one to assign irreducible representations of the actual space group to all known magnetic structures. The superiority of representation theory over symmetry invariance under Shubnikov groups is already demonstrated by the fact proven here that the only invariant magnetic structures describable by magnetic groups belong to real one-dimensional representations of the 230 space groups. Representation theory on the other hand is richer because the number of representations is infinite, *i.e.* it can deal not only with magnetic structures belonging to one-dimensional real representations, but also with those belonging to one-dimensional complex and even to two-dimensional and three-dimensional representations associated with any $\mathbf{k}$ vector in or on the first Brillouin zone.

We generate from the transformation matrices of the spins a representation Γ of the space group which is reducible. We find the basis vectors of the irreducible representations contained in Γ.

The basis vectors are linear combinations of the spins and describe the structure. The method is first applied to the $\mathbf{k}=0$ case where magnetic and chemical cells are identical and then extended to the case where magnetic and chemical cells are different ($\mathbf{k}\neq 0$) with special emphasis on $\mathbf{k}$ vectors lying on the surface of the first Brillouin zone in non-symmorphic space groups. As a specific example we consider several methods of finding the two-dimensional irreducible representations and its basis vectors associated with $\mathbf{k}=\frac{1}{2}\,\mathbf{b}_2=[0\frac{1}{2}0]$ in space group *Pbnm* (D_{2h}^{16}).

Magnetic Structure Description and Determination

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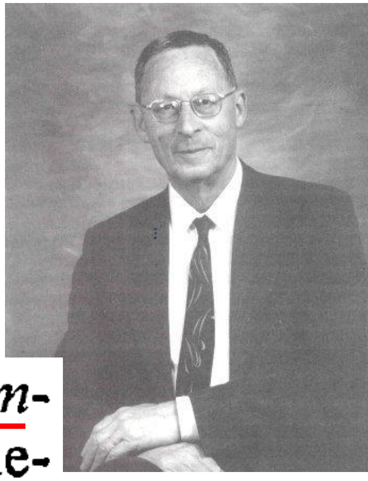


Acta Cryst. (1968). A**24**, 217

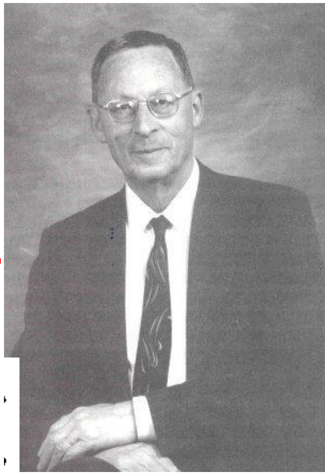
Representation Analysis of Magnetic Structures

BY E. F. BERTAUT

Laboratoire d'Électrostatique et de Physique du Métal, C.N.R.S., B.P. 319 *et*
Laboratoire de Diffraction Neutronique, C.E.N.G., B.P. 269, *Grenoble* 38, *France*

In opposition to the (widely accepted) view of *symmetry invariance* under the Shubnikov groups we develop in § 2 a new point of view which investigates the *transformation properties of magnetic structures* under the operations of the 'trivial' 230 space groups. Moreover this new point of view will prove to be more general. We show indeed that all the magnetic groups can be generated from the knowledge of the ensemble of one-dimensional real representations of the 230 space groups; in other words the 'magnetic' groups can only describe those magnetic structures which belong to one-dimensional representations, having characters $+1$ or -1, of the classical space groups.

7. Magnetoelectricity



The reader may get the impression that the author is hostile to the use of magnetic groups. In fact the author is only defending representation theory. The main objection of the reader might be that in the abstract sense magnetic and space groups are isomorphous* so that a structure belonging to a representation of a space group G (even when the representation is not one-dimensional real) also belongs to a representation of the isomorphous Shubnikov group G'. This is perfectly correct, but still means that we would abandon symmetry invariance in favour of representation theory.

Can we ignore magnetic groups entirely? The answer is no, not only in microscopic, say atomic systems† (Dimmock & Wheeler, 1962) but also macroscopically when a magnetic system is coupled with other forms of energy.

Acta Cryst. (1971). A**27**, 470

Classifications of Magnetic Structures

BY W. OPECHOWSKI AND TOMMY DREYFUS*

Department of Physics, University of British Columbia, Vancouver, Canada

(*Received* 17 *August* 1970)

Two different classification schemes have been used for concise characterization of magnetic structures: one (called here $C1'$) making use of magnetic groups, and another, more recent (called here $C2$), in which representations of space groups play an essential part. While the mathematical principles of $C1'$ have already been formulated in all their generality, this is not so in the case of $C2$ (although many magnetic structures have been discussed from the point of view of $C2$). In this paper the principles of $C2$ are formulated in a mathematically general way, a link between $C1'$ and $C2$ is established, and a few illustrative examples of magnetic structures are discussed. It turns out that $C1'$ and $C2$ are equivalent in a precise mathematical sense, provided cyclic boundary conditions are imposed on the crystal; each magnetic structure has then its appropriate label in both classifications. If, however, one is not willing to impose such conditions, $C2$ may in some cases (as for example helical structures) meet with mathematical difficulties while $C1'$ never does. Claims made by Bertaut (*Acta Cryst.* (1968). A**24**, 217) that $C2$ is 'more general' than $C1'$ are thus unjustified.

Discussion of C1, C1' and C2 approaches for magnetic structures

Point of view of W. Opechowski => C1' is the good approach

Full discussion of C1, C1’ and C2 approaches for magnetic structures

Journal de Physique, Coll. C1, 32 (sup. 2-3) (1971), c1-462-460

JOURNAL DE PHYSIQUE *Colloque C 1, supplément au nº 2-3, Tome 32, Février-Mars 1971, page* C 1 - 462

MAGNETIC STRUCTURE ANALYSIS AND GROUP THEORY

E. F. BERTAUT
C. N. R. S. and C. E. N.-G., rue des Martyrs, Grenoble

Résumé. — L’analyse de structures magnétiques par la théorie des groupes (analyse de représentations) est basée sur la transformation de vecteurs spins, situés dans une position cristallographique donnée, sous les opérations de symétrie d’un groupe d’espace **G** ou sous-groupe $\mathbf{G_k}$ du cristal dans lequel se trouve la structure magnétique. Le vecteur d’onde **k** caractérisant le groupe de translation est déduit de l’expérience de diffraction neutronique. Les équations de transformation linéaires induisent une représentation Γ de **G** ou de $\mathbf{G_k}$. On réduit Γ en représentations irréductibles (r. i.). Les vecteurs de base, sous-tendant les r. i. décrivent des structures magnétiques possibles de sorte que l’on n’a à comparer qu’un faible nombre de modèles avec l’expérience. La symétrie de l’hamiltonien (de la représentation irréductible) est généralement plus élevée que la symétrie de Shubnikov de la structure magnétique. Quant au schéma de classification d’Opechowski, notre schéma (C2) utilise d’une manière cohérente et exclusive les *groupes d’espace*, même pour des spins sinusoïdaux et hélicoïdaux alors que dans le schéma C1′ on doit ajouter des groupes *non cristallographiques* pour une description de ces cas.

Abstract. — The analysis of magnetic structures by group theory (representation analysis) is based on the transformation of spins on a given lattice site under the symmetry operations of a crystallographic space group **G** or a subgroup $\mathbf{G_k}$ of the crystal in which the magnetic structure is imbedded. The wave vector **k** labelling the translation group is taken from the neutron diffraction experiment. The linear transformation equations induce a representation Γ of **G** or $\mathbf{G_k}$. Γ is reduced to irreducible representations. Basis vectors, constructed from them, describe possible magnetic structures so that only a small number of models have to be compared with experiment. The symmetry of the hamiltonian (of the irreducible representation) is generally higher than the Shubnikov symmetry of the magnetic structure. As far as Opechowski’s classification scheme is concerned our scheme (C2) uses *space* groups consistently, even for sinusoidal and helical spins whereas in the scheme C1′ one must add *non crystallographic* groups for a full description of the latter case.

Magnetic Structure Description and Determination

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Full discussion of C1, C1' and C2 approaches for magnetic structures

Journal de Physique, Coll. C1, 32 (sup. 2-3) (1971), c1-462-460

JOURNAL DE PHYSIQUE *Colloque C 1, supplément au n° 2-3, Tome 32, Février-Mars 1971, page* C 1 - 462

MAGNETIC STRUCTURE ANALYSIS AND GROUP THEORY

E. F. BERTAUT
C. N. R. S. and C. E. N.-G., rue des Martyrs, Grenoble

Introduction. — Representation analysis of a magnetic structure is not only *a*) labelling or classifying a structure, but consists mainly of *b*) the search for the structure before it is known and of *c*) the discussion of the interactions which might explain the final structure model. Professor Opechowski has not evaluated the merits of representation analysis for *b*) and *c*). Thus I shall answer his criticism at the end of my lecture.

Discussion of C1, C1' and C2 approaches for magnetic structures

Journal de Physique, Coll. C1, 32 (sup. 2-3) (1971), c1-462-460

C1: Description of magnetic structures based on conventional Shubnikov groups

C1': Description of magnetic structures based on non-crystallographic groups.

C2: Description of magnetic structures based on representation analysis.

I have claimed the superiority of classification C 2 over that by Shubnikov groups, and *not* over the classification C 1', as defined by Professor Opechowski.

Magnetic Structure Description and Determination

The option **C1'** developed by W. Opechowski was extended by D.B. Litvin and W. Opechowski with the concept of "spin groups" in which continuous rotation groups (Lie groups) may be used for describing helical structures {the symmetry operators are g=($\mathcal{R}$ || $\boldsymbol{R}$ | $\mathbf{t}$), for a helical structure $\mathbf{S}(\mathbf{r}+\mathbf{t}) = \mathcal{R}\,\mathbf{S}(\mathbf{r})$}

- V.E. Naish, Izv. Acad. Nauk, SSSR Ser. Fiz. **27**, 1496 (1963).
- W. Opechowski and T. Dreyfus, *Classification of Magnetic Structures*, Acta Cryst **A27**, 470 (1971).
- D.B. Litvin, *Spin Translation Groups*, Acta Cryst **A29**, 651 (1973)
- D.B. Litvin & W. Opechowski, *Spin Groups*, Physica **76**, 538 (1974)
- W. Opechowski, *Crystallographic and Meta-crystallographic Groups*, North Holland (1986)
- R. Lifshitz and S. E. Mandel, *Magnetically ordered quasicrystals: enumeration of spin groups and calculation of magnetic selection rules*, Acta Cryst **A60**, 167 (2004)

The option **C1’** developed by W. Opechowski was extended by D.B.

C1’

No practical expression for magnetic structure factor were provided for the general case .

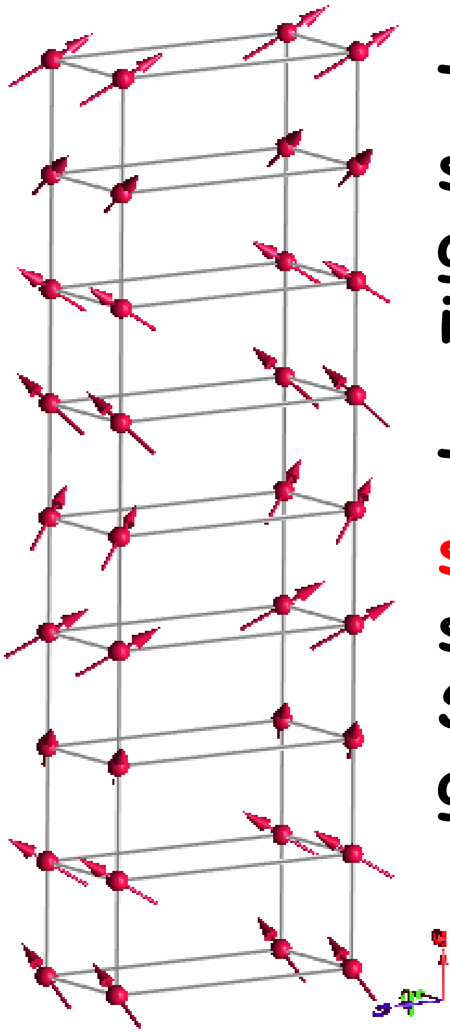
A search in the Web of Science with topic “spin groups” or “spin translation groups” or “spin rotation groups” gives only 82 items of which only 3 are related to magnetic structures.

- R. Lifshitz and S. E. Mandel, *Magnetically ordered quasicrystals: enumeration of spin groups and calculation of magnetic selection rules*, Acta Cryst **A60**, 167 (2004)

Outline:

1. Historical introduction to magnetic structures
2. Early Magnetic Crystallography. Shubnikov Groups and Representations
3. **Future of Magnetic Crystallography. Superspace groups and Representations. New computing tools**

Types of magnetic structures



The (magnetic) structure of crystalline solids possess always a series of geometrical transformations that leave invariant the atomic (spin) arrangement.

These transformations constitute a symmetry group in the mathematical sense: point groups, space groups, Shubnikov groups, spin groups, superspace groups, …

Superspace Symmetry

Pim de Wolff (1919–1998),
Delft Institute of Technology,
The Nederland

The introduction of superspace approach was a breakthrough that allowed to treat “aperiodic crystals” diffraction data

Superspace Symmetry

Seminal papers on superspace approach

Wolff, P. M. de (1974). *Acta Cryst.* A**30**, 777-785.

Wolff, P. M. de (1977). *Acta Cryst.* A**33**, 493-497.

Wolff, P. M. de, Janssen, T. & Janner, A. (1981). *Acta Cryst.* A**37**, 625-636.

Superspace Symmetry

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research perspectives

Acta Crystallographica Section B
Structural Science, Crystal Engineering and Materials

ISSN 2052-5206

Aperiodic crystals and superspace concepts

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Received 12 June 2014
Accepted 24 June 2014

For several decades the lattice periodicity of crystals, as shown by Laue, was considered to be their essential property. In the early sixties of the last century compounds were found which for many reasons should be called crystals, but were not lattice periodic. This opened the field of aperiodic crystals. An overview of this development is given. Many materials of this kind were found, sometimes with very interesting properties. In the beginning the development was slow, but the number of structures of this type increased enormously. In the meantime hundreds of scientists have contributed to this field using a multi-disciplinary approach.

Awarded with the tenth Ewald Prize for "the development of superspace crystallography and its application to the analysis of aperiodic crystals" (Montreal 2014)

Superspace and Representations

PHYSICAL REVIEW B VOLUME 30, NUMBER 3 1 AUGUST 1984

Superspace groups and Landau theory.
A physical approach to superspace symmetry in incommensurate structures

J. M. Pérez-Mato, G. Madariaga, and M. J. Tello
Departamento de Física, Facultad de Ciencias, Universidad del Pais Vasco, Apartado 644, Bilbao, Spain
(Received 19 December 1983)

Physica 126A (1984) 163–176
North-Holland, Amsterdam

SUPERSPACE GROUPS AND REPRESENTATIONS OF ORDINARY SPACE GROUPS: ALTERNATIVE APPROACHES TO THE SYMMETRY OF INCOMMENSURATE CRYSTAL PHASES*

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Institute for Theoretical Physics, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Superspace and Representations

PHYSICAL REVIEW B VOLUME 30, NUMBER 3 1 AUGUST 1984

Superspace groups and Landau theory. A physical approach to superspace symmetry in incommensurate structures

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(Received 19 December 1983)

Magnetic space and superspace groups, representation analysis: competing or friendly concepts?

Acta Cryst **A66**, 649 (2010)

Václav Petříček,* Jiří Fuksa and Michal Dušek

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Magnetic superspace groups

Journal of Physics: Condensed Matter **24**, 163201 (2012)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **24** (2012) 163201 (20pp) doi:10.1088/0953-8984/24/16/163201

TOPICAL REVIEW

Magnetic superspace groups and symmetry constraints in incommensurate magnetic phases

J M Perez-Mato[1], J L Ribeiro[2], V Petricek[3] and M I Aroyo[1]

The future of Magnetic Crystallography is clearly an unified approach of symmetry invariance and representations:

C3 > C1 + C2

The End!

Some references for symmetry analysis

The mathematical theory of symmetry in solids
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2nd Edition, O.V. Kovalev,
Ed. by Harold T. Stokes and Dorian M. Hatch, Gordon and Breach Science Publishers, 1993.

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Y.A. Izyumov, V.E. Naish and R.P. Ozerov
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Y.A. Izyumov, V.E. Naish, J Magn.Magn.Mat. **12**,239 (1979); Y.A. Izyumov, V.E. Naish and V.N. Syromiatnikov J Magn.Magn.Mat. **12**, 249 (1979); Y.A. Izyumov, V.E. Naish and S.B. Petrov, J Magn.Magn.Mat. **13**, 267 (1979); Y.A. Izyumov, V.E. Naish and S.B. Petrov, J Magn.Magn.Mat. **13**, 275 (1979); Y.A. Izyumov, J Magn.Magn.Mat. **21**, 33 (1980).

Bilbao Crystallographic Server: http://www.cryst.ehu.es/

ISOTROPY Software Suite : http://stokes.byu.edu/iso/isotropy.php

FullProf Suite : http://www.ill.eu/sites/fullprof/