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MAGNETIC STRUCTURES

A. Olés *

ABSTRACT

The present state of knowledge about magnetic structures is discussed. Description of progress in magnetic neutron diffraction gives an idea of its contemporary possibilities. The most typical and interesting magnetic structures are presented. Also the problem of magnetic structures symmetry is mentioned.

1 – EXPERIMENTAL ARRANGEMENT

In this article the present state of knowledge about magnetic structure is discussed. To begin with, it is necessary to stress that neutron diffraction is the most straight forward method for magnetic structure determination.

A neutron has a magnetic moment which can interact with atomic moments. The theory of neutron diffraction was developed by Halpern and Johnson[1]. These authors assumed total quenching of the atomic orbital moment. This is frequently observed for the compounds of the 3-d group elements. But for elements of the other groups (4f ...) the orbital moment is significant. Data on orbital scattering are contained in the papers written by Trammel[2], Odiot and St-James[3], Blume[4] and Johnston[5]. Detailed informations about the general theory of neutron scattering by magnetic interactions can be found in the Will's article[6]

Neutron diffractometers are installed only nearby reactors because high neutron fluxes are required. From the full spectrum only thermal neutrons (10 meV) are used (velocities of a few km/s and wavelength of the order of interatomic interval in solids i.e., ~ 1 Å). If the arrangement of magnetic moments appears in the crystal (below the Curie or Néel temperature), the neutron diffraction pattern gives informations on crystallographic as well as on magnetic sittes. The symmetry of both sittes decides about the appearance of new reflections of magnetic origin, or about the overlapping of nuclear and magnetic peaks. The integrated intensity of the neutron Bragg reflection can be written as follows: $I = I_n + I_m$, where I_n is proportional to the nuclear structural factor $|F|^2$ and $I_m \sim |F_m'|^2$. The magnetic part of the neutron diffraction pattern is used to determine the magnetic structure i.e. the values and directions (vs. crystallographic axes) of magnetic atomic moments.

The first magnetic structure was determined in 1949 by Shull and Smart[7] (see figure 1). Since that time great progress took place in reactor engineering as well as in detailed solutions for neutron diffraction methods. Besides the development of very important auxiliary techniques occurred.

Reactor constructors aimed their efforts at increasing neutron fluxes. Now there are three great power reactors installed in the world (10^{15} n/s cm^2 in the core) and a pulsed reactor is being constructed. Increase of neutron fluxes makes possible to decrease the dimensions of the investigated samples. The samples used ordinarily by average reactors ($10^{13} - 10^{14}$ n/s cm^2) present remarkable volume (~ 10cm^3 of powder). The progress of reactor engineering is perceived also in dislocation of horizontal channels of the reactors (see figure 2). The tangential channels are in common use because they assure advantageous ratio of thermal neutrons to fast ones and consequently of the peak-to-background ratio. Moreover, neutron guide tubes increase the physicists experimental possibilities.

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Progress in neutron diffraction methods can be described as follows

For the classical neutron diffractometer (figure 3) the most important improvements were aimed at decreasing measurement time and elimination of $\lambda/2$ contamination, increase in the precision of angular positions of the apparatus, full automatization of diffractometers movements So new monocrystals are used as monochromators-pyrolitic graphite, germanium crystals etc But one must ascertain that metalic monocrystals of copper, zinc, aluminium or lead are still widely employed. Great accuracy was obtained for example after the construction of the so-called "tanzboden" spectrometers in Grenoble The full automatization of all movements of neutron apparatus is now common Very useful in neutron diffraction studies are the programs for raffinement of experimental data [9,10] In the problem of detection, interesting informations on "sandwich" semiconducted neutron detectors were presented by japanese researchers at the IX Congress of I.U.C (Kyoto 1972), but BF_3 detectors are still the most generally used

In some cases the time-of-flight diffractometer is useful[11] Figure 4 is a diagram of such apparatus. The angular 2θ change is here replaced by analysis of the neutron energy The high resolving power for small hkl is one of the main features. The stable sample-detector geometry brings still further advantages (for example when measurements are performed at high pressures)

Application of polarized neutrons opened new horizonts for magnetic studies If the degree of polarization of the neutron beam is near 1, the integrated intensity of the neutron peak is $I \sim (F_n \pm F_m)^2$, where + and − denote respectively parallel and antiparallel polarization in relation to the direction of atomic magnetic moments. Figure 5 gives an idea of the experimental arrangement Luckily, there are crystals for which some reflections fulfill the condition $F_n = \pm F_m$ and polarization of the neutron beam can be obtained by simple Bragg diffraction Polarized neutrons create the possibility of solution of more complicated magnetic structures, enable investigations of spin density distribution in crystals and give accurate data on magnetic form factors.

The reader may find complete and detailed informations about neutron diffraction methods in monographs and some articles[12 to 18].

Also helpfull in the development of magnetic neutron diffraction were the supplementary equipments as crysostats and furnaces, arrangements for high pressures, superconducting electromagnets etc. Specially great progress in discussed field is due to growth of the cryogenic technique. The importance of precise cryostats is connected with the possibility of the existence of different magnetic structures for the same compound in different temperature intervals. Therefore investigation of the thermal dependence of magnetic reflections can give the precious informations not only on the temperatures of magnetic phase transitions but also on their nature (see figure 6). The change of magnetic interactions is studied moreover by use of high pressures[23] Superconducting electromagnets enable investigations of domain effects and of metamagnetic phenomena. High magnetic pulsed fields can change a magnetic structure and are also used in connection with neutron diffraction.

Summarising, from the days of the first neutron diffraction pattern the technical possibilities have been increased, but the idea of the measurements remained the same.

2 – REVIEW OF MAGNETIC STRUCTURES DETERMINED BY NEUTRON DIFFRACTION

The basis for this review are the Tables of Magnetic Structures Determined by Neutron Diffraction edited in Cracow[24,25]. Complete discussion of this rich material requires a detailed monography. One must also limit himself to the most important groups of compounds and to some interesting magnetic structures.

At the beginning of the second half of the century the theory of molecular field demonstrated the possiblity of existence of some antiferromagnetic structures for both, body and face centered cubic

magnetic sittes (figure 7 and 8) Numerous compounds that crystallize in the NaCl, FeS, ZnS, MnAgAs, $AuCu_3$. K_2PbCl_6 etc structure types show the magnetic arrangements illustrated in figure 8. Likewise one often finds compounds in which the magnetic atoms define simple cubic sitte The most common antiferromagnetic structures of this kind are shown in figure 9 For example perovskites ($CaTiO_3$ – type) belong to this kind as also as compounds crystallizing in CsCl structure, and others. However, pseudoperovskites containing both, the ions of rare earth metals and of the iron group shown mostly noncollinear magnetic structures Interesting examples are $ErFeO_3$ *[26] and $HoCrO_3$[27] The first of these compounds has two Neel temperatures Below $T_{N1} = 630$ K magnetic arrangement of the G_x type of the iron appears (see figure 9 and 10) Below $T_t = 80$ k the magnetic moments of iron begin to rotate and at tamperatures lower than of liquid nitrogen a magnetic order of the G_{xy} type was found At $T_{N2} = 4.3$ K the arrangement of magnetic moments of erbium ions arises and belongs to the C_z type.

The investigation of simple ionic compounds contributed to the development of the superexchange theory of magnetic interactions These theoretical models define the magnetic interactions sign rules for 90° and 180° angles[28 to 35] Comparison of theoretical predictions with extensive experimental data indicate very good agreement[36]

Similarly as in the case of mentioned compounds, many informations about magnetic interactions were obtained by neutron diffraction studies of the spinels. The fragment of the spinel sitte is presented in figure 11. The most common ferrimagnetic arrangement of magnetic moments is that predicated by Néel[37], where the thetrahedral sublattice (A) magnetic moments are antiparallel to the moments of the octahedral sublattice (B). Decisive here is the superexchange interaction at ~ 125° Some spinels in which the thetrahedral sublattice is occupied by the magnetic ions and the octahedral by nonmagnetic ions offer only a few examples of the antiferromagnetic structure in sitte A (see figure 12). These are the spinels Co_3O_4[38], $MnAl_2O_4$[39] and $MnGa_2O_4$[40] The magnetic interactions in this case are very weak and they come as follows: cation A – anion – cation B – anion – cation A.

Competitive interactions solely in B sublattice (sublattice A is occupied by nonmagnetic ions) lead often to noncollinear arrangements of magnetic moments. As an example $ZnCr_2O_4$ may be cited (see figure 13). Richness of spinels magnetic structures can confirm evidence about the types of determined magnetic arrangements for example the spiral structure presented by $HgCr_2S_4$[42], Yafet-Kittel structure of $CoMn_2O_4$[43] (see figure 14) and star structure found in $NiMn_2O_4$[44] (see figure 15) etc The garnets can show noncollinear magnetic arrangements, too (the example in figure 16).

In the last few years compunds in which two – or quasi-one-dimensional magnetic structures were possible were intensively investigated In these the dominance of magnetic interactions in some surfaces or some directions appears At present K_2NiF_4[46] is considered as the classical example of the two dimensional structure (figure 17)

The study of alloys of 3d group elements is also an up-to-day matter. It is stimulated by the development of the band model of magnetism Systematic investigations of these diluted alloys give informations about values of localized magnetic moments and about change of magnetic moments with increase of the contents in matrix of an additional element The theory of magnetism of 3d metals and alloys meets serious difficulties Among the numerous models describing the magnetic properties of metals and alloys one can distinguish two general procedures – the model of localized atomic moments and the model of collective electrons. At this point it is interesting to mention a critical collection of experimental data about the origin of ferro and antiferro-magnetism given by Vogt[47]

Three component alloys, for example Heusler type[48,49] are now widely studied. From structural point of view alloys of the 3d group present many types of magnetic arrangements. One must remember that a magnetic structure of the alloy depends also on the degree of atomic order. Example of

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(*) The reader will find more detailed informations about all compounds discussed here in the Tables of Magnetic Structures – references number 24,25

the magnetic noncollinear structure for completely ordered $MnNi_3$[50] is shown in figure 18. Limiting the discussion to such structures which were not mentioned as yet, one can name the traingular structure (see figure 19) and the umbrella structure (figure 20).

Investigations of alloys seem to represent an advantage for the neutron diffraction group in Brazil. Studies of them by means of other methods are conducted here with success. Investigations of the same substances by different methods allow profound physical interpretation.

The magnetic spiral structure was mentioned on the occasion of the discussion about spinels. The first spiral was discovered in 1959 in compound of the 3d-group elements, being a surprise for crystallographers. Presently, however there are well-known crystals, results of the Wolff works[53,54] for which the periodic change of orientation of some atom groups is observed; this period can be incommensurable with lattice constants. The majority of magnetic spiral structures was determined for the compounds of rare earths. The magnetic properties of these elements are caused by localized 4f electrons. The magnetic interactions in these compounds are described by so-called RKKY model[55,56,57]. Rare earth elements offer as it is presented in figure 21 the antiphase domain ordering, the sinusoidally modulated arrangement of magnetic moments, the antiphase cone spiral, the cone spiral, the screw spiral structure or ferromagnetic order. The β – Ce crystal presenting ABAC stacking sequence of close-packed planes reveals also no trivial magnetic structure (see figure 22). Likewise nitrides of rare earth elements have composite magnetic cells (figure 23).

The complicated ordering of the magnetic moments were found in the alloys of rare earths. A beatiful example is illustrated in figure 24 where one perceives the sinusoids determined by the magnetic moments. These sinusoids are coupled in antiparallel succession for NdAl and TbAl and parallel succession for HoAl. For $TbAu_2$, $DyAg_2$, $DyAu_2$ alloys the magnetic order, in a defined range of temperature is represented by a static linear-transverse spin wave propagating along the a-axis (figure 25). The magnetic structure of $ErAg_2$ alloy in different ranges of temperature is shown in figure 26. The cycloidal magnetic ordering is transformed here to linear transverse spin waves. It is also important to mention that the compounds and alloys of rare earth are being now intensively investigated.

Not less attractive are studies of actinides concerning their extraordinary magnetic behaviour. Properties of the magnetic electrons of actinides are more complicated than these of rare earth. For example uranium shows hybrydization of the external electrons. This is connected to the creation of the conducting band. Uranium, neptunium, plutonium as elements are nonmagnetic. Instead when in compounds and alloys localization of the 5f electrons is observed. It is impossible to anticipate now the values of ordered magnetic moments for actinide compounds. Figure 27 presents the change of magnetic arrangement and of the value of magnetic moment for $UAs_{1-x}P_x$[66]. The determination of magnetic phase diagrams made wide interpretation of the results possible. Typical magnetic structure of tetragonal uranium compounds are shown in figure 28.

Adding up the contemporary trends of magnetic neutron diffraction one can expect continuation of the investigations of alloys of both 3d and rare earth elements. Further development of the studies of actinides is a natural consequence of the present stage. Neutron diffraction offers now the possibility of determination of full magnetic phase diagrams, of investigations on the influence of external parameters on magnetic structure (high pressures, high magnetic fields), of phase transition studies. It seems that it should be the attractive field for neutron diffraction methods in the future.

3 – MATHEMATICAL DESCRIPTIONS OF MAGNETIC STRUCTURES

In some cases neutron diffraction studies powder samples do not provide the sclution. In experimental work theoretical indications about the possibility of existence, in the crystal under investigation of defined magnetic structures can be useful. This problem was solved on the basis of both magnetic space group theory and the theory of representations of space groups. One must however

ascertain that most magnetic structures were determined thanks to scientist's intuition. Use of mentioned methods leads to mathematical descriptions of magnetic structures and to the classification of them. Associated with this problem are the names of the following mathematicians and physicists: Haesch, Landau, Lifschitz, Bielov, Opechowski, Bertaut The study of magnetic structure symmetry is a synonym of investigation of its transformatic properties

The first method is the search of the set of all operations under the symmetry of which the magnetic ordering is invariant. This procedure lead us to magnetic space group The magnetic moment is represented here as an axial vector (figure 29) If G denotes the space group of the crystal and τ the time inversion group (τ contains only the unit element e and the time invertion i), the magnetic group can be defined as the subgroup of the $G \otimes \tau$ group This subgroup can not contain the time inversion i as the element. Figure 30 shows the operation of symmetry and antisymmetry elements on magnetic moments. A symmetry operation transforms a magnetic moment as if it were a polar vector An antisymmetry operation reverses the sense of the vector. The magnetic group (M) contains the elements $A_m e = A_m$ and $B_n i = b_n$, where A_m and B_n are the elements of the G group Group G fulfills also these conditions and it is thus called the trivial magnetic group. There are 230 trivial magnetic groups (uncolored groups), 230 gray groups (they describe paramagnetic crystals) and 1191 black-and-white magnetic groups (ferro – and antiferromagnets). The full specification of so-called 1651 Shubnikov groups was given by Bielov et al[70]. Opechowski[71,72] showed the manner by which magnetic groups are constructed The great merit of Opechowski is the determination of the conditions, which the magnetic group must perform to grant existence of the magnetic structure which is invariant under the action of this group.

The second procedure comprises the study on transformations of the magnetic structure under the action of the G space group elements. This leads to attribute a space group matrix representation of the magnetic structure Bertaut[73] was the first to utilize such representations for the description of symmetry of magnetic structures. He also showed that this description can be useful for the discussion of the effective spin hamiltonian of the magnetic arrangements. All experimental material obtained in the world so far concerning magnetic structures was described both on the basis of the theory of magnetic groups[74] and representation of space groups[75]. The new edition of the Tables of Magnetic Structures[25] contains besides the experimental data and the mentioned descriptions Discussion of the conclusions resulting from these descriptions exceeds the scope of this paper.

Edition of this review is connected with the International Atomic Energy Agency program for the development of magnetic neutron diffraction in Brazil

RESUMO

O atual estado de conhecimento sobre estruturas magnéticas é discutido A descrição do progresso em difração magnética de nêutrons dá uma ideia de suas possibilidades contemporâneas As estruturas magnéticas mais típicas e interessantes são mostradas O problema da simetria das estruturas magnéticas é também mencionado.

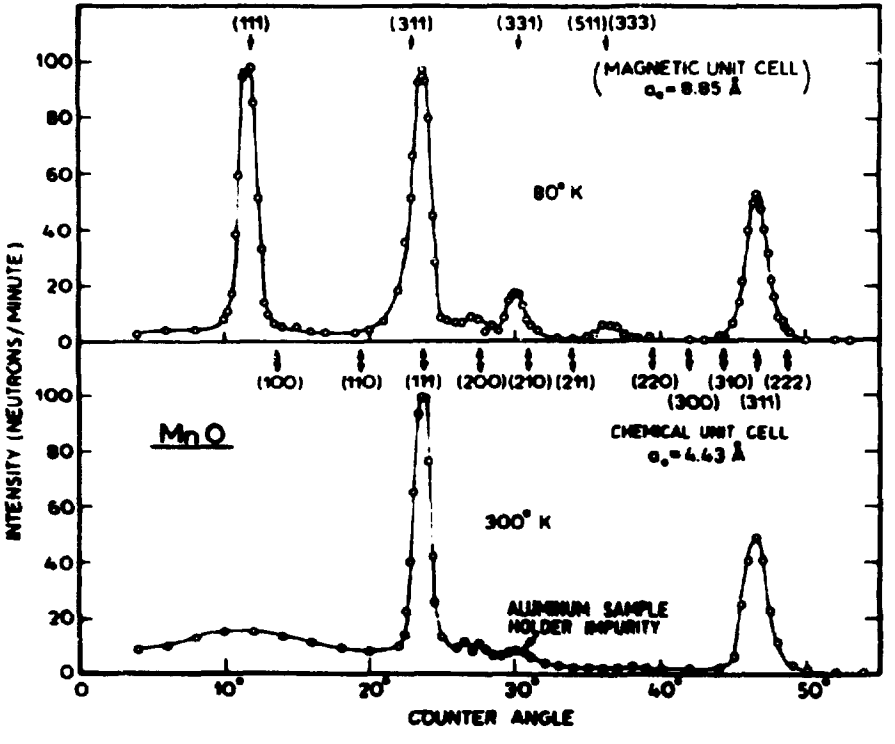


Figure 1 – Neutron diffraction pattern of MnO[7].

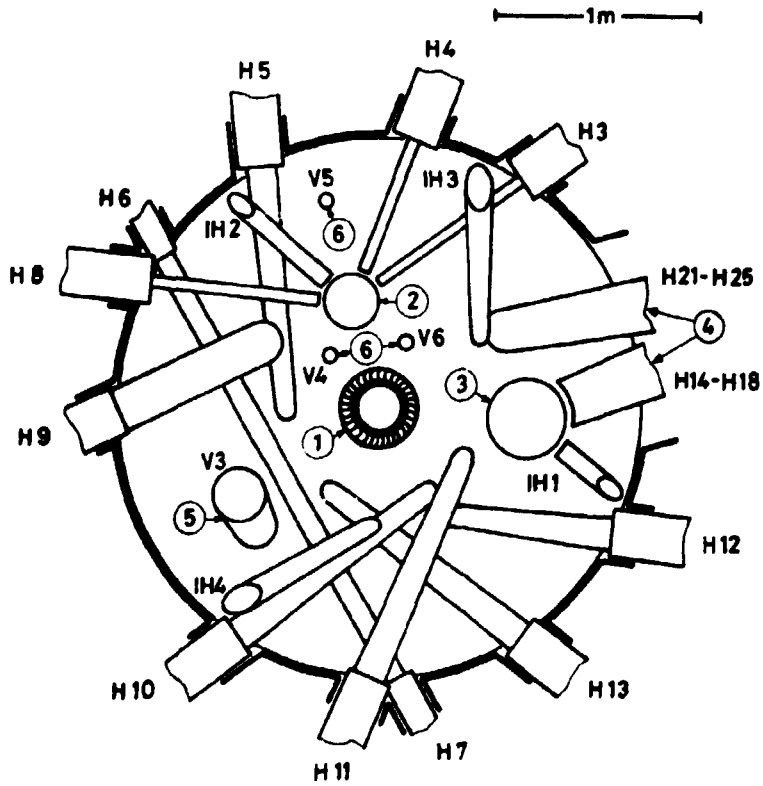


Figure 2 – Arrangement of the beam tubes at the HFR – Grenoble reactor[8].

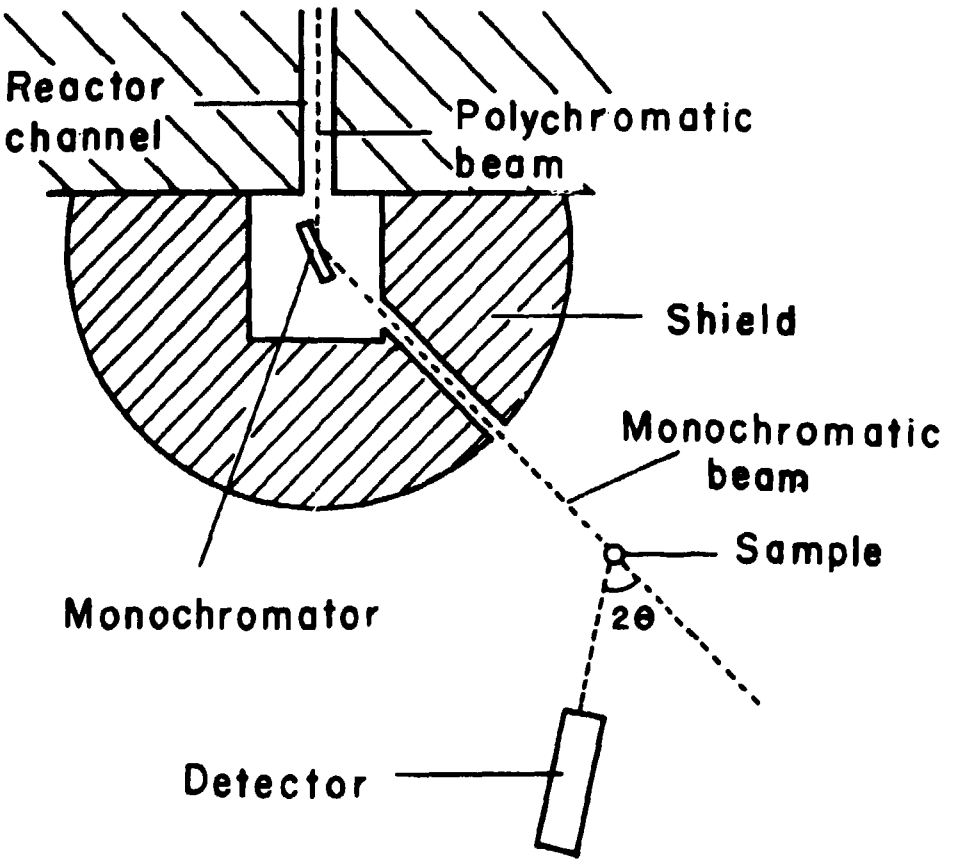


Figure 3 – Outline of the classical neutron diffractometer.

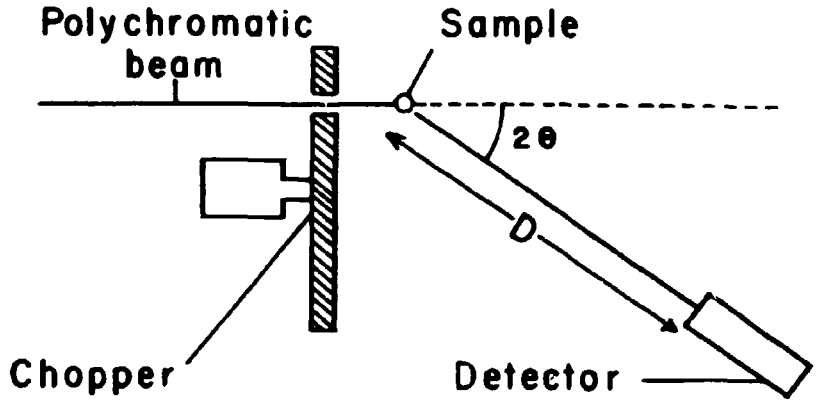


Figure 4 – Time of-flight neutron diffractometer.

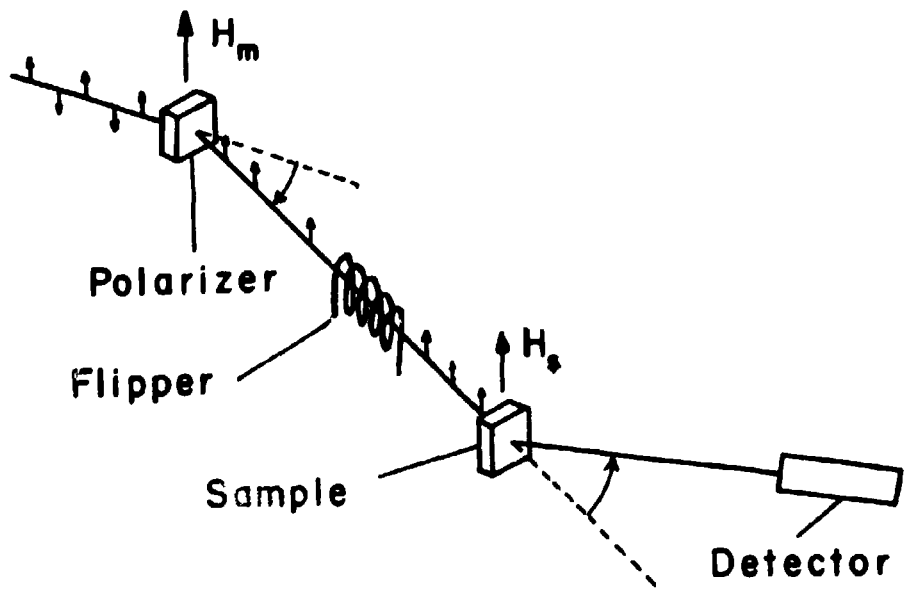
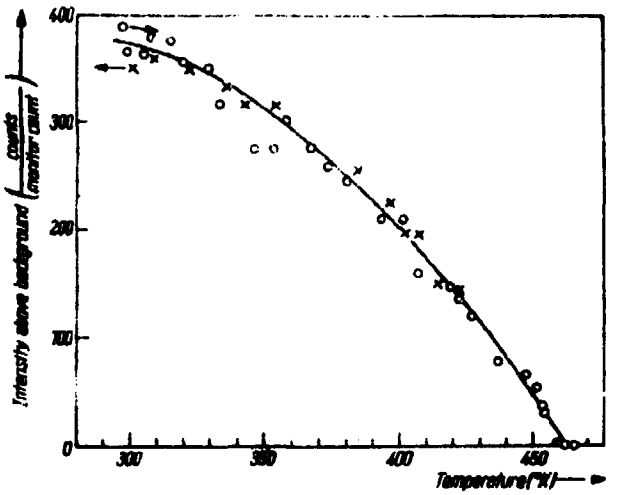
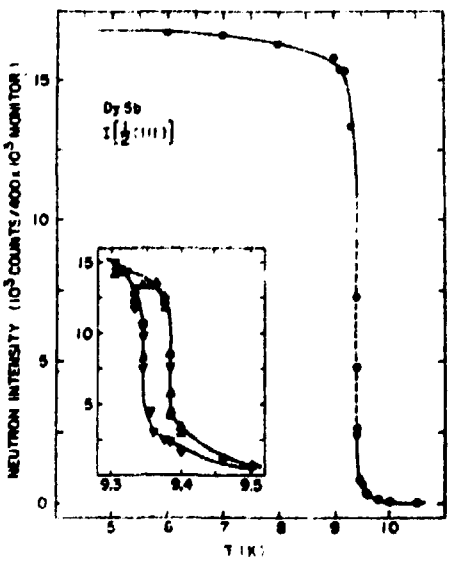
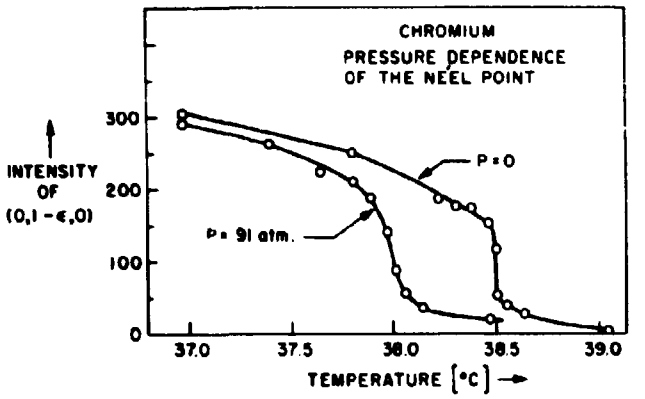


Figure 5 – Polarized neutron diffractometer.


Intensity above background (counts / monitor count)
400
300
200
100
0
300
350
400
450
Temperature(°K)


NEUTRON INTENSITY (10³ COUNTS / 400 x 10³ MONITOR)
15
10
5
0
5
6
7
8
9
10
T (K)
DySb
I(½,½,1)
15
10
5
9.3
9.4
9.5



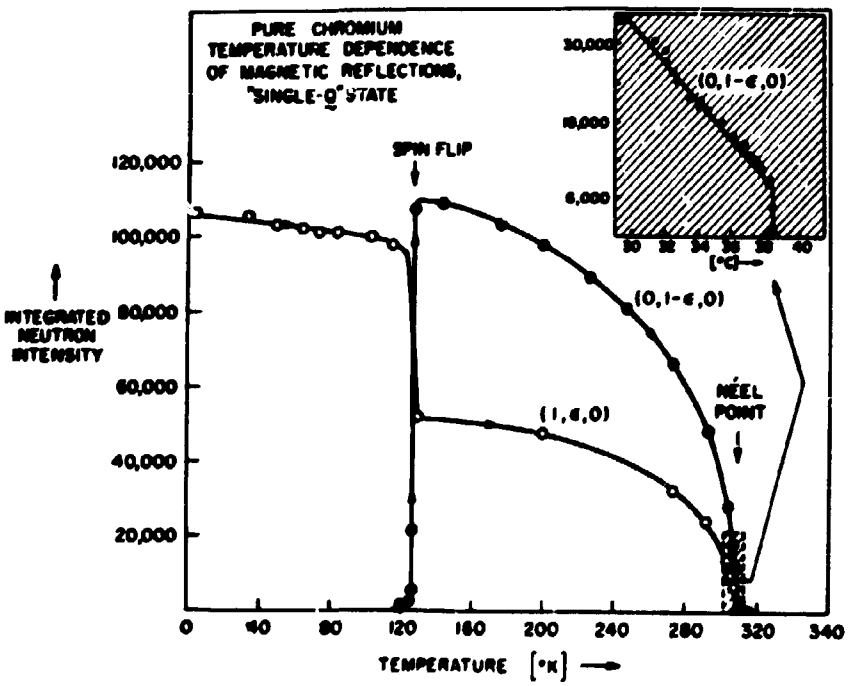


Figure 6 — Examples of the thermal dependence of magnetic reflections:

a) second order transformation[19];
b) first order transformation with hysteresis[20];
c) change of the temperature dependence of the magnetic intensity with pressure[21];
d) temperature dependence of the neutron intensity from a Cr crystal[22]

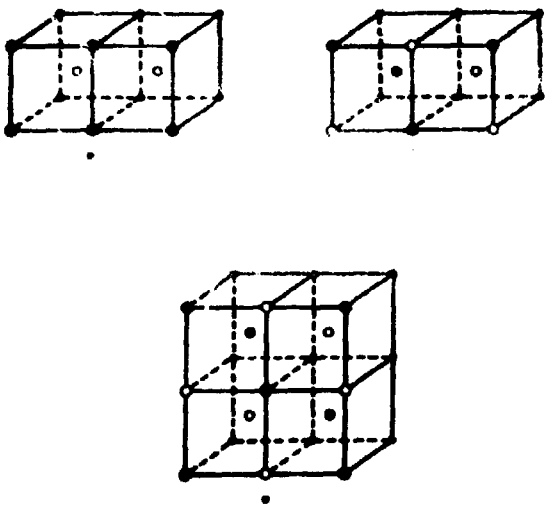


Figure 7 – Some magnetic structures for bcc sitte.

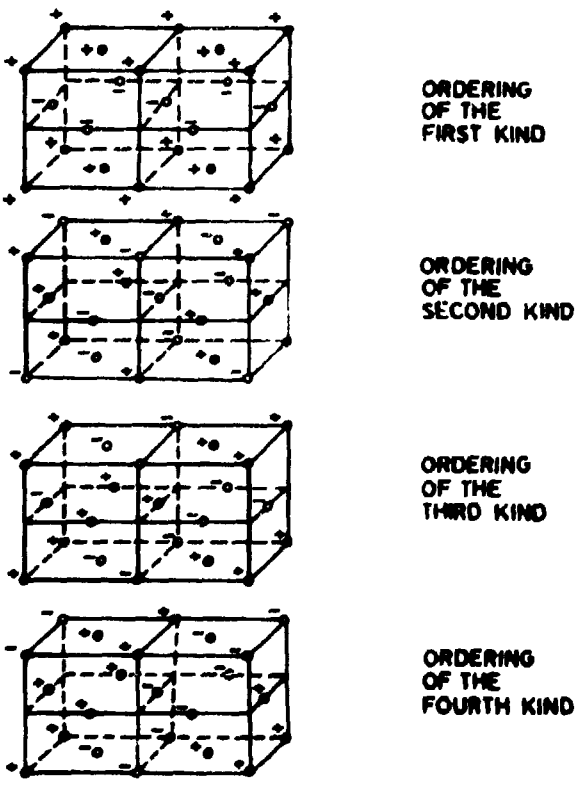


Figure 8 – The most common orders for fcc sitte.

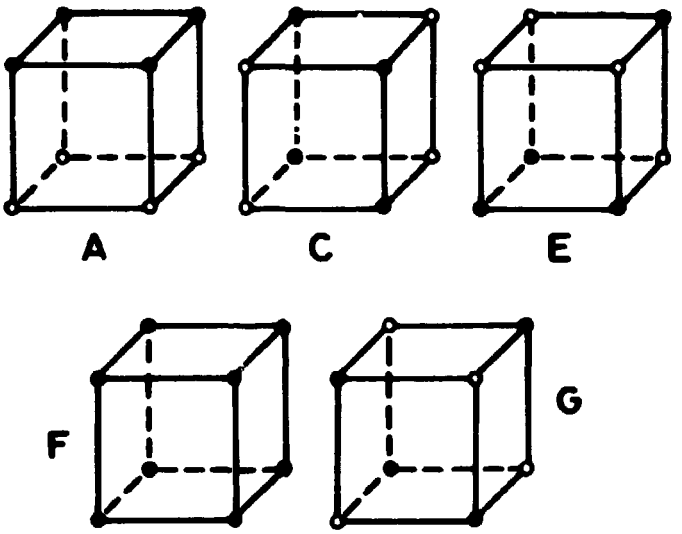


Figure 9 – The most common magnetic arrangements for scc sitte.

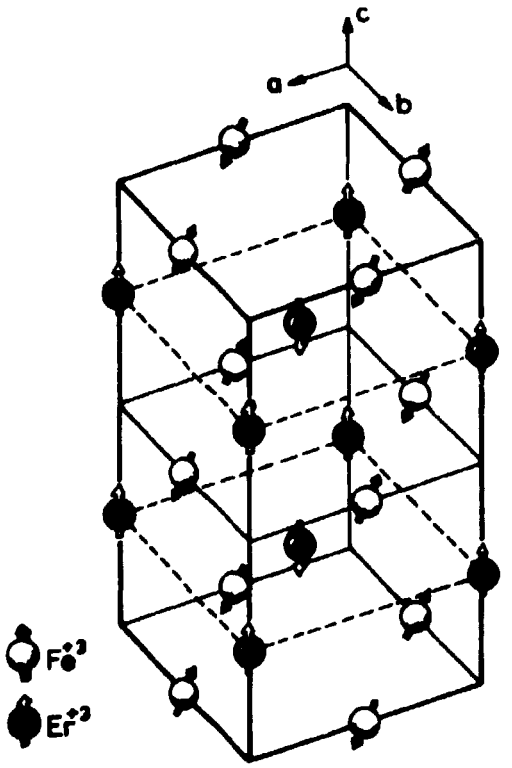


Figure 10 – Low temperature magnetic structure of $ErFeO_3$ [26]

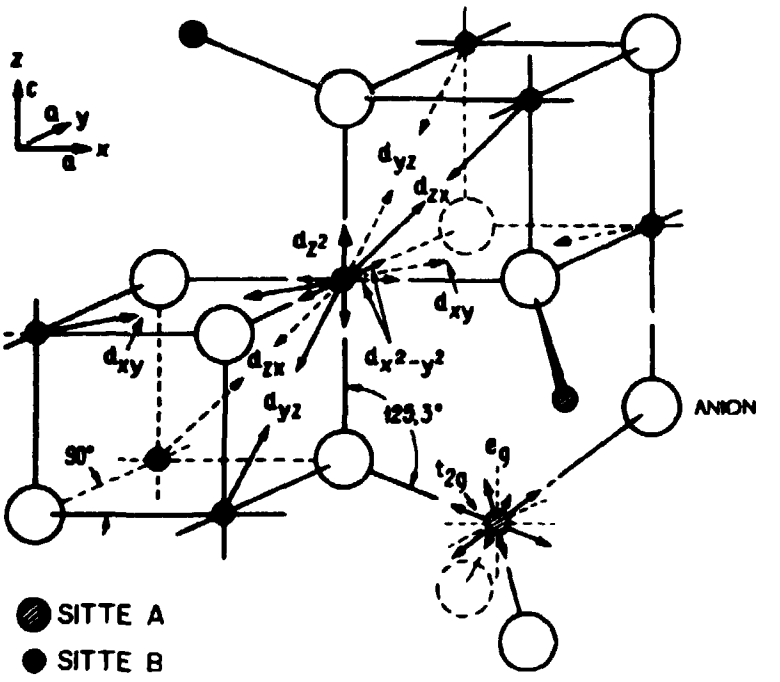


Figure 11 — Fragment of the spinel sitte[28].

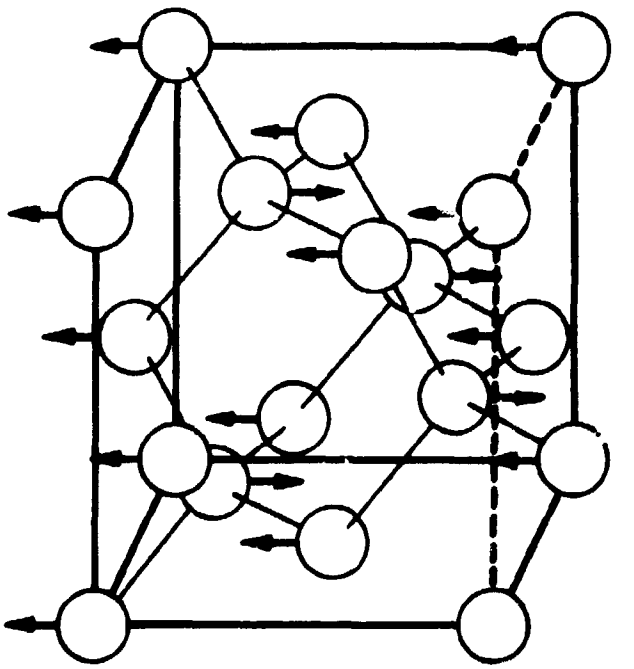


Figure 12 — Magnetic structure of the spinel -- A-A type.

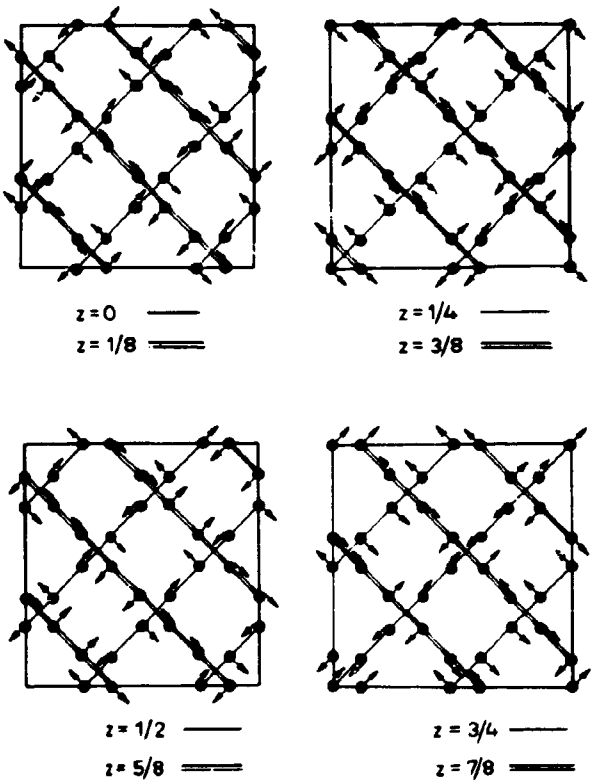


Figure 13 – Magnetic structure of the spinel – example of the B-B type[41]

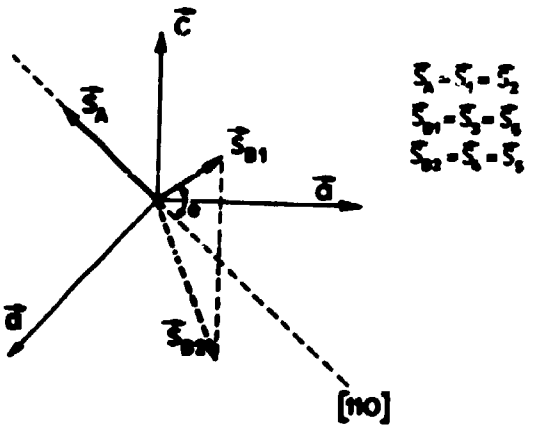


Figure 14 – The structure of Yafet-Kittel type

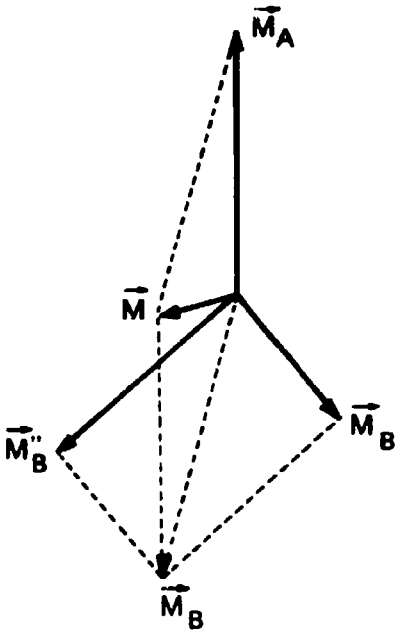


Figure 15 – The star structure in $NiMn_2O_4$[44].

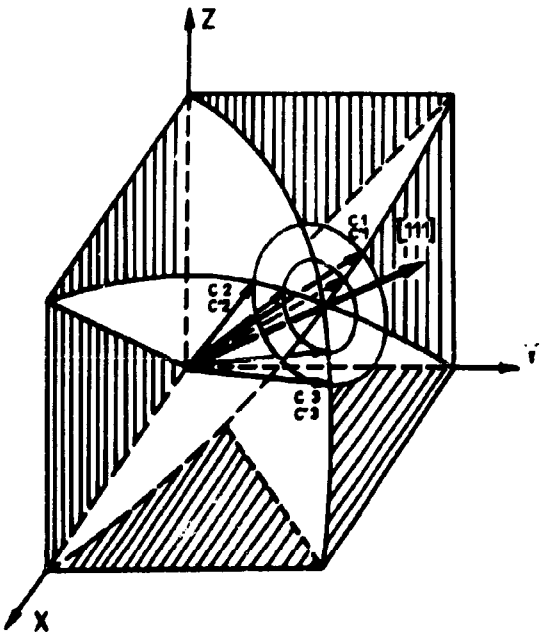


Figure 16 – Rare earth sublattice spin arrangement of $Yb_3Fe_5O_{12}$ at 1.4 K[45].

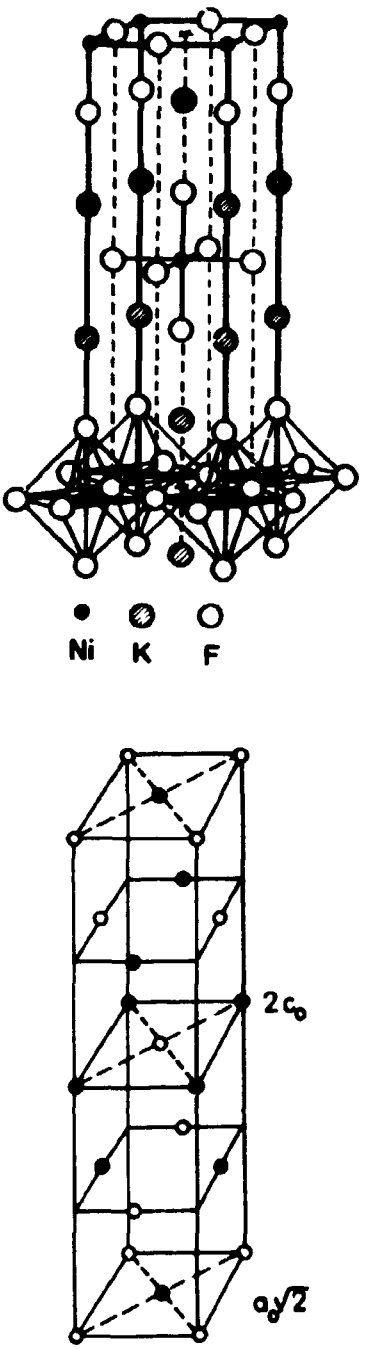


Figure 17 – Crystallographic and magnetic structure of K_2NiF_4 [48].

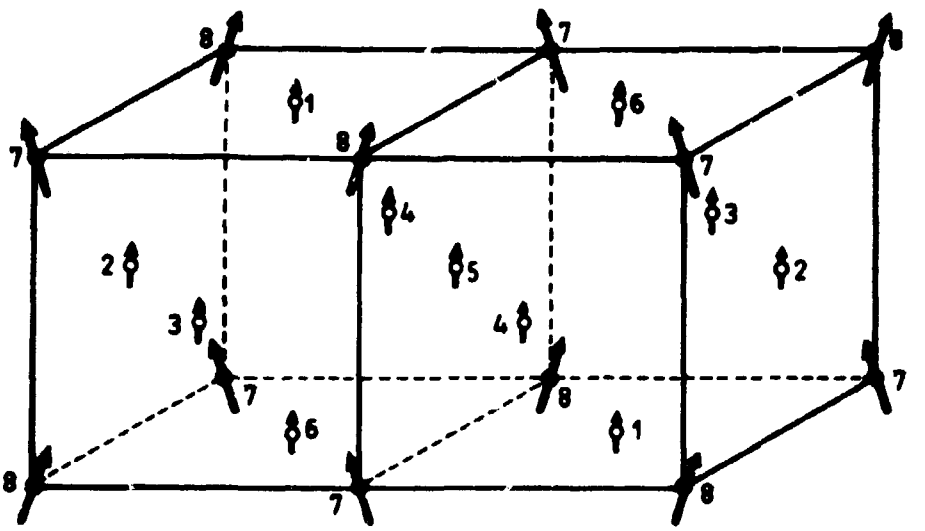


Figure 18 – Magnetic structure of ordered $MnNi_3$[50].

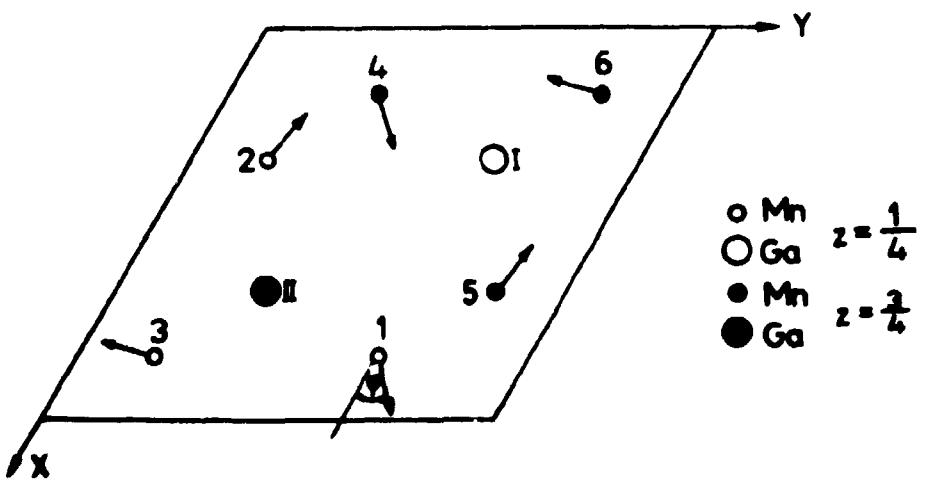


Figure 19 – Triangular magnetic structure of $Mn_{4.83}Ga_{1.16}$[51].

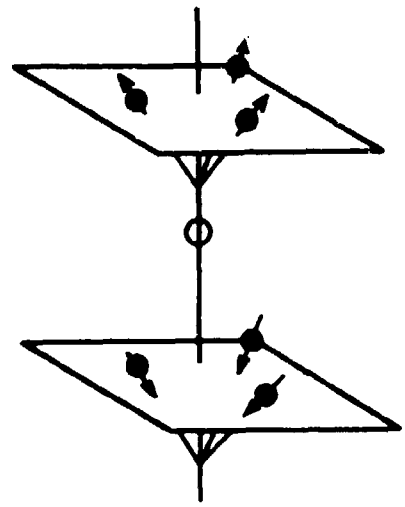


Figure 20 – Umbrella magnetic order in CrSe alloy[52].

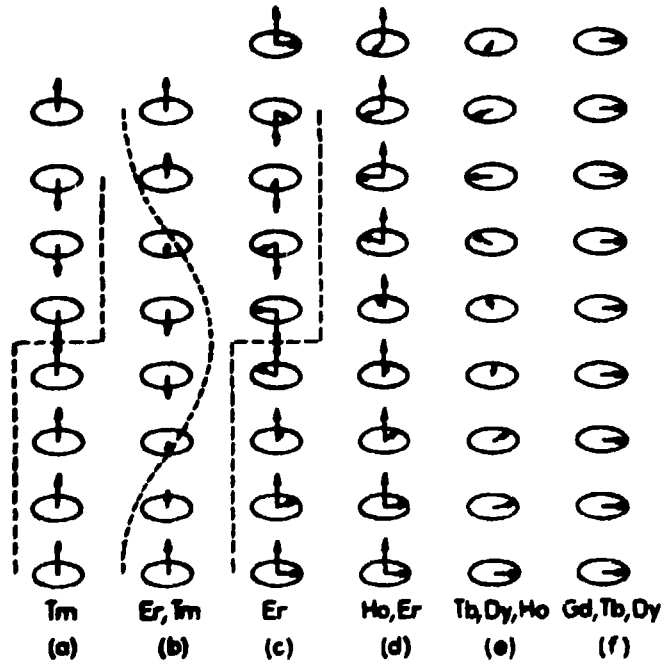


Figure 21 – Magnetic order of some rare earth elements[58,59,60].

a) Tm at very low temperature;
b) Tm between 56 K and 40 K, Er between 84 K and 53,5 K;
c) Er below 53,5 K;
d) Ho below 20 K, Er at 4.2 K;
e) Tb, Dy, Ho between T_N and T_C;
f) transition to classical ferromagnetic in Tb and Dy at T_c, magnetic structure of Gd.

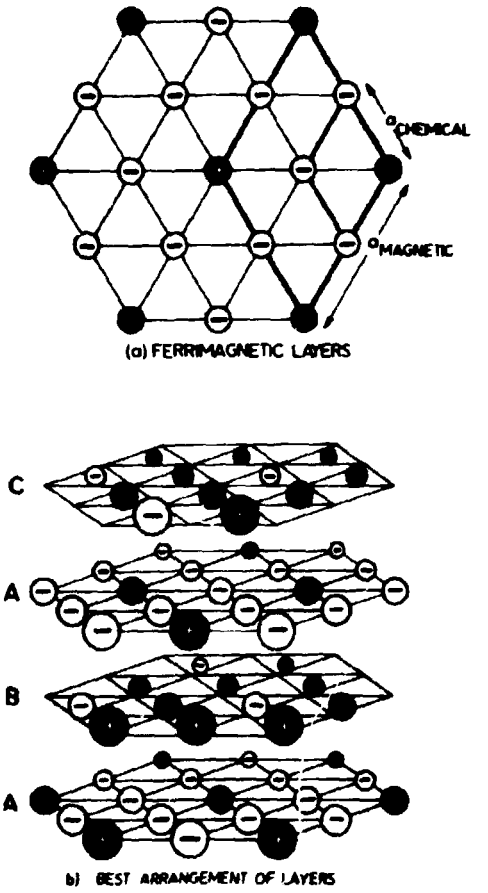


Figure 22 – Arrangement of magnetic moments in β – Ce[61].

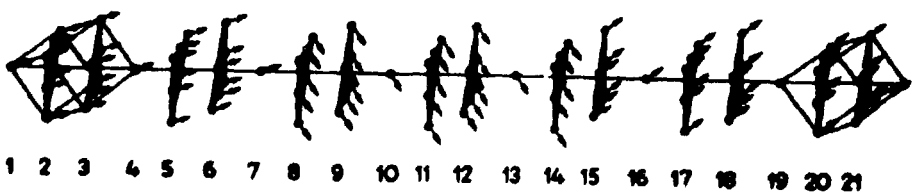


Figure 23 – Stacking of ferromagnetic planes in DyN magnetic cell[62].

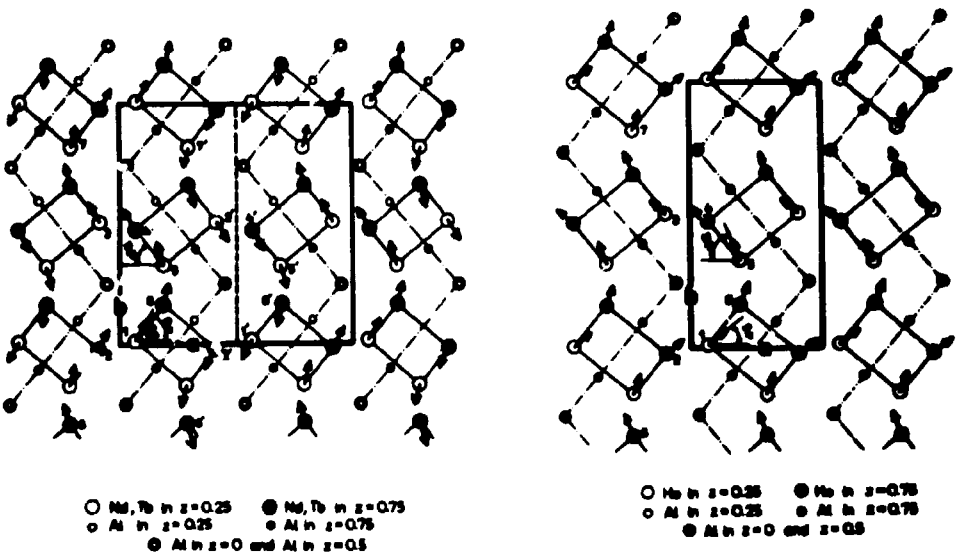


Figure 24 – Magnetic structure of NdAl, TbAl and HoAl[63]

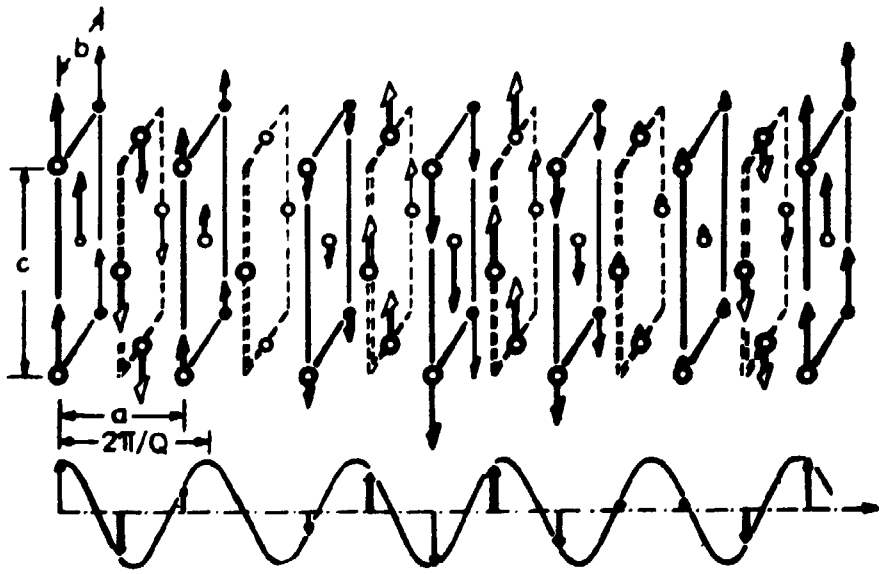


Figure 25 – α – phase magnetic structure of $TbAu_2$ – a linear transverse wave polarized along c direction and propagating along a axis[64]

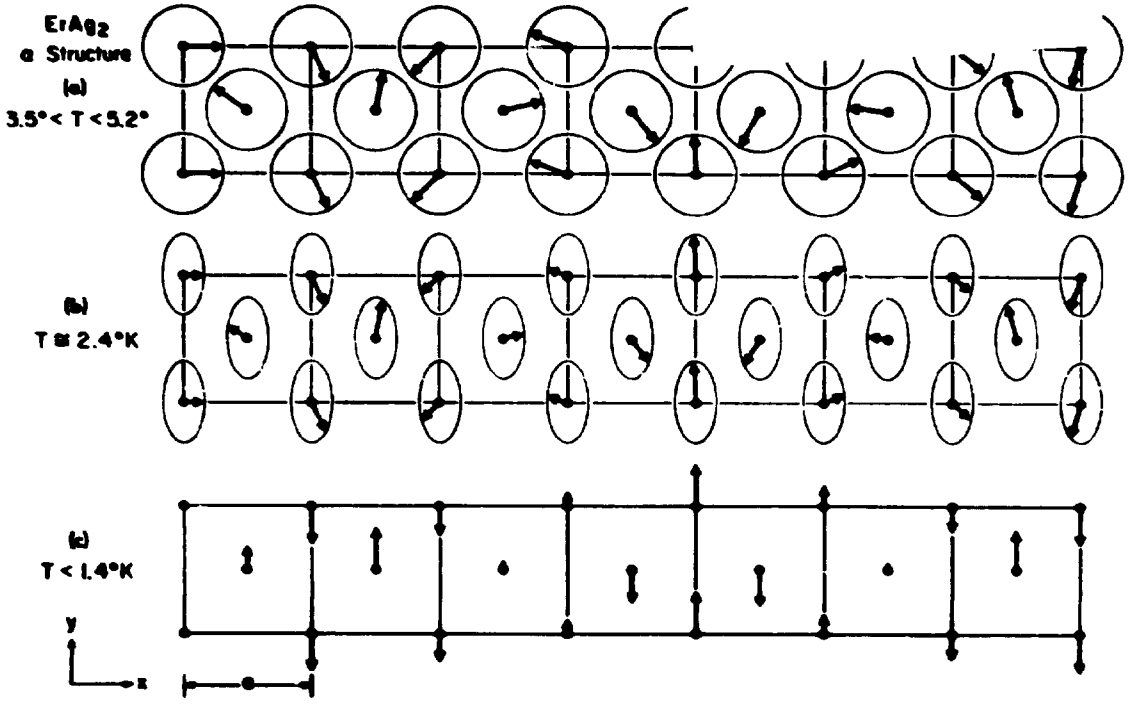


Figure 26 – Magnetic structures of $ErAg_2$ alloy in different ranges of temperature[65].

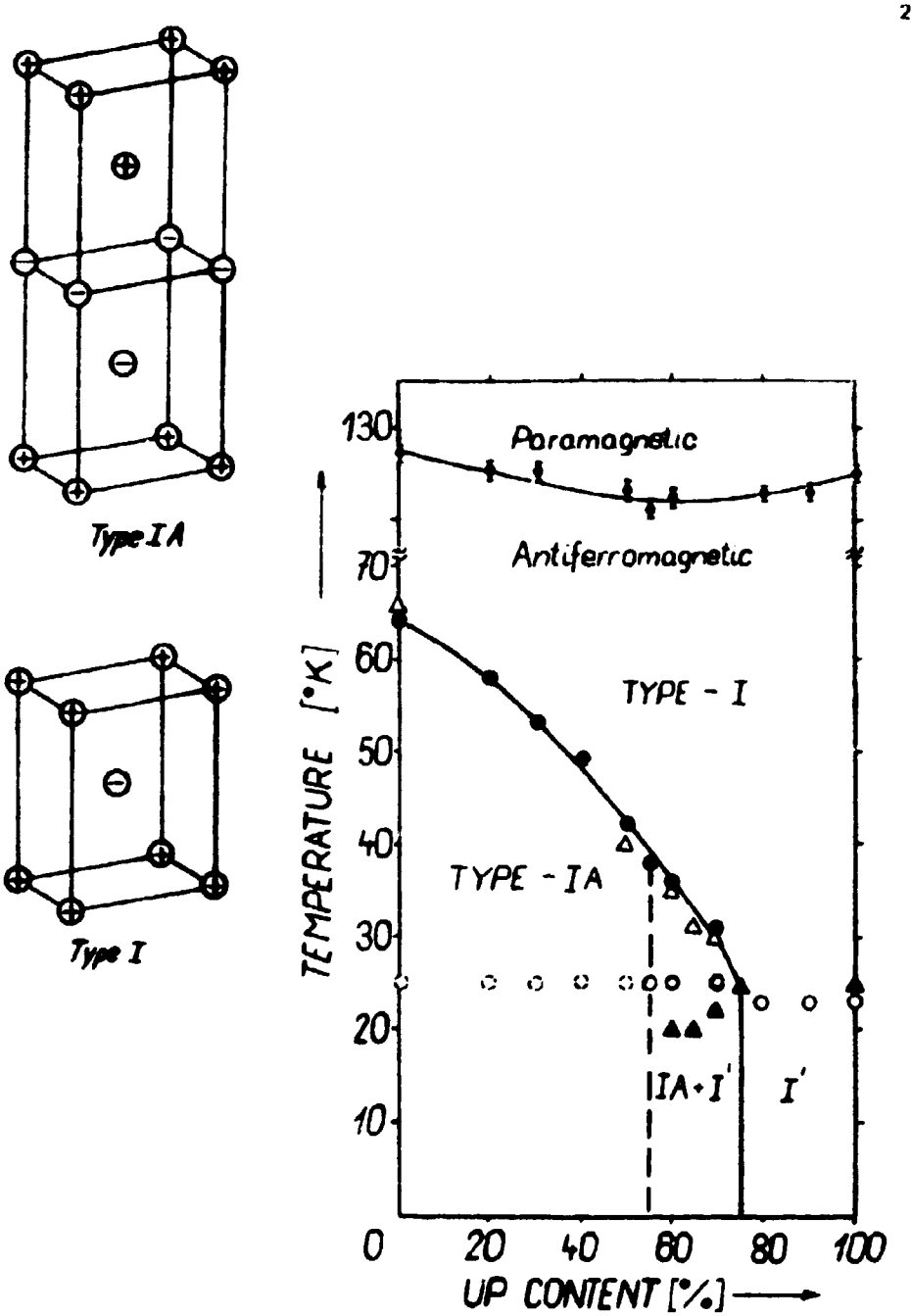


Figure 27 – a) Magnetic structures I and IA type;
b) Magnetic phase diagram of $UAs_{1-x}P_x$. White circles denote value of the magnetic moment[66]

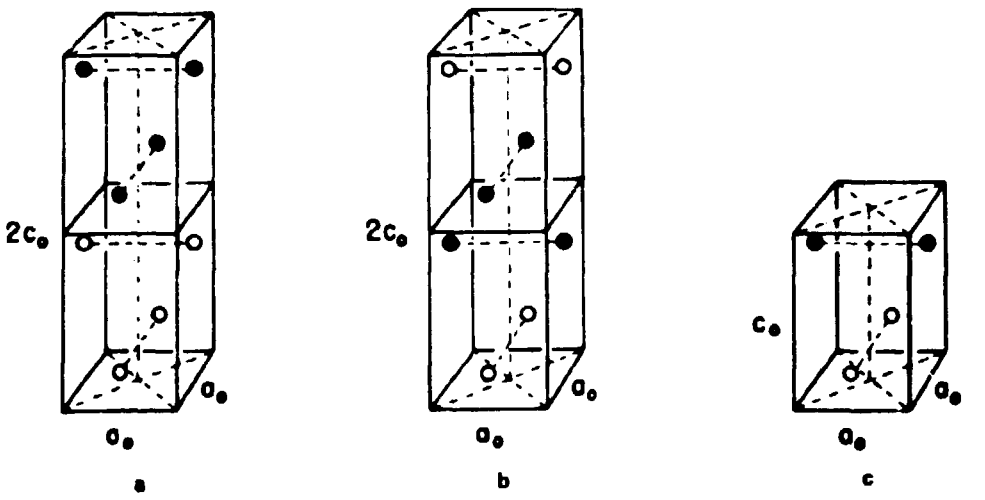


Figure 28 – Magnetic structure of t ; agonal uranium compounds;
a) $UOTe$[67];
b) UAs_2[68];
c) $UOSe$[69]

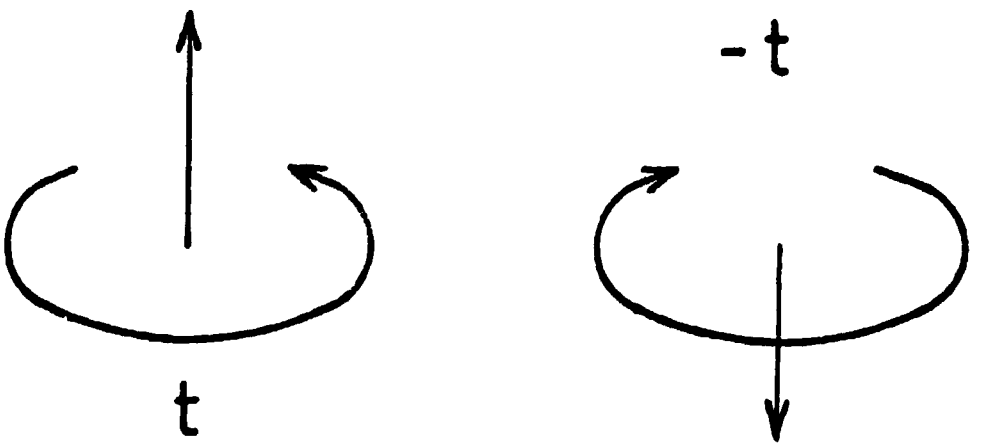


Figure 29 – Magnetic axial vector.

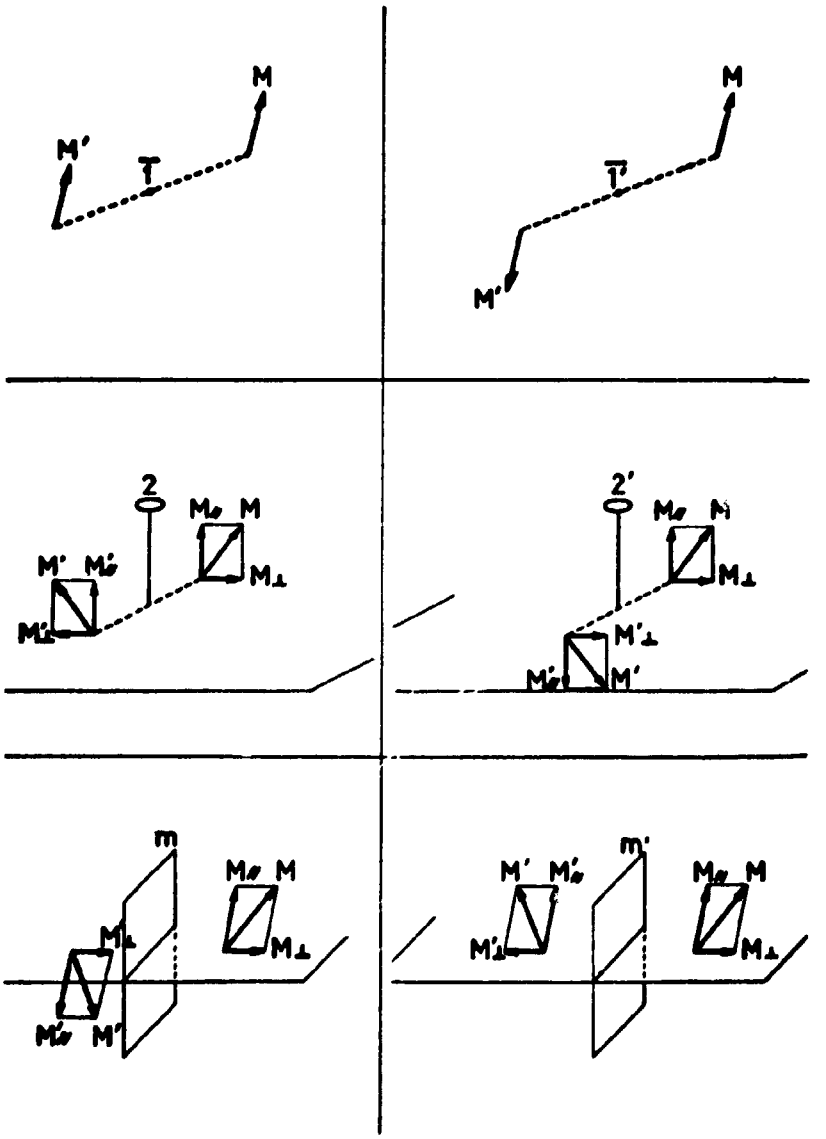


Figure 30 – Operation of symmetry and antisymmetry elements

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