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*Acta Universitatis Carolinae. Mathematica et Physica*, Vol. 29 (1988), No. 1, 19--31

Persistent URL: <http://dml.cz/dmlcz/142591>

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## Determination of Low-symmetrical Magnetic Structures

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*Received 30 June 1987.*

A description of complex magnetic structures based on Fourier components is used for determination of low-symmetrical structures by powder neutron diffraction.

The application of this concept is explained and exemplified in case of orthorhombic  $\text{RCu}_2$  compounds (R — heavy rare earth).

Pro určování nízkosymetrických struktur z měření neutronové difrakce na práškovém vzorku byl použit popis složitých magnetických struktur založený na Fourierově analýze.

Tento postup je vysvětlen a demonstrován na příkladu ortorombických sloučenin  $\text{RCu}_2$ , kde R představuje těžkou vzácnou zeminu.

Описание сложных магнитных структур основанное на методе Фурье было использовано при определении низкосимметричных структур на основе данных полученных нейтронной дифракцией на порошковых образцах.

Этот подход описан на примере орторомбических соединений типа  $\text{RCu}_2$ , где R—элемент тяжелой редкой земли.

### 1. Introduction

In 1939 Halpern and Johnson [1] published a theoretical work dealing with a problem of neutron scattering on magnetic moments. Only ten years later Shull and Smart [2] carried out the first measurement of neutron diffraction on powder sample of the antiferromagnetic compounds MnO. The neutron diffraction methodology was refined then step by step (single crystal measurements, time-of-flight spectrometers, polarised neutrons etc.), but for example the existence of non-collinear magnetic structures had not been known still before 1959. Only the magnetic structure investigation of rare earth elements being of great importance for magnetism, brought a discovery of helical, modulated and incommensurate magnetic structures.

In this paper we shall describe and exemplify the using of neutron diffraction for investigation of complex magnetic structures. We shall restrict ourselves to intermetallic compounds with a low-symmetry. In the first part we shall determine the

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conception of magnetic structure of low-symmetrical material, in the second we shall pay our attention to Fourier components of a magnetic structure, in the third we shall discuss consequences of this description from the point of view of neutron diffraction. In the last part we shall characterize some typical examples of magnetic structures of rare earth intermetallic compounds.

## **2. A concept of magnetic structure of low-symmetrical material**

The investigation of magnetic structures has been performed in most cases by means of neutron diffraction on polycrystalline samples (mainly on isotropic powder samples). There are reasons for it dealing with both the technology and methodology. It is much easier to obtain a powder specimen than a single crystal of the appropriate size. Even when single crystals are available, a strong argument can often be made for using powder method instead. In a single crystal experiment, diffractometer time is spent in aligning the crystal, checking for twinning, influence of domain structure, extinction effects etc. Of course, information is irretrievably lost in a powder pattern if there is exact coincidence of two or more diffraction peaks and therefore an interpretation of powder data need not be unambiguous.

This disadvantage is practically removed for materials, which we shall call low-symmetrical ones. Generally this conception is related to a symmetry of both crystal-line and magnetic structure.

In case of collinear magnetic structures Shirane [3] introduced so called configurational symmetry (CS) of a magnetic structure. This may be defined as a symmetry of a figure which will arise from a collinear magnetic structure, if we substitute all magnetic moments by appropriate magnetic scattering amplitudes only, which are different not only in magnitude, because of the spin state of the atoms, but also in sign, because of the spin direction. For example the real magnetic symmetry of cubic iron below Curie temperature is tetragonal, but the CS of this magnetic structure is cubic again (all magnetic scattering amplitudes are the same). On the other hand the cubic compound MnO has an antiferromagnetic structure, but the CS is rhombohedral. Shirane showed [3], that a measure of information reduction in powder neutron diffraction was related to a corresponding CS. When this CS is cubic, the spin direction cannot be deduced from the powder data, because any spin direction with respect to the crystallographic axis gives the same magnetic intensities if the domains are oriented randomly. When the CS is tetragonal, rhombohedral or hexagonal, the powder intensities cannot provide more information than the angle between the spin direction and the unique axis of the structure. If the CS is lower, the information contained in powder pattern is not reduced in principle.

This classification cannot be generally used in case of non-collinear structures. Nevertheless, it can be concluded that the magnetic structure can be fully determined from neutron powder pattern for materials with orthorhombic and lower crystallographic symmetries.

It is clear, that the low-symmetrical materials are interesting with respect of magnetic properties too (e.g. low symmetrical Brillouin zone, magnetocrystalline anisotropy with unique easy direction, single ground-state of non-Kramers ion in crystal field, etc.).

In case of rare earth intermetallic compounds, where the magnetic ordering is a result of long range exchange via conduction electrons, the low-symmetrical structures provide a good opportunity to investigate complex modulated structures (very often with a propagation vector incommensurate with the crystal structure) directly by powder neutron diffraction.

### 3. Description of magnetic structure in terms of Fourier components

Let us consider a crystal structure being determined by translational vectors  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$  and particular magnetic sites  $\mathbf{q}_j$  within a unit cell,  $j = 1, \dots, P$ . Then any location of magnetic moments in crystal can be expressed as

$$\begin{aligned} \mathbf{r}_{j,n} &= \mathbf{q}_j + n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}, & n_i \text{ integers} \\ \mathbf{r}_{j,n} &= \mathbf{q}_j + \mathbf{R}_n \end{aligned}$$

The magnetic structure can be defined as a static space ordering of magnetic moments  $\mathbf{M}_{j,n}$  (corresponding to  $\mathbf{r}_{j,n}$ ) conforming to certain symmetry elements. We assume localized magnetic moments only, a space distribution of the magnetic moment around the position  $\mathbf{r}_{j,n}$  is involved in the appropriate magnetic form factor. Any arbitrary magnetic structure can be written in terms of its Fourier components,

$$(1) \quad \mathbf{M}_{j,n} = \sum_{\mathbf{q}} \mathbf{Q}_j(\mathbf{q}) \exp(i\mathbf{q}\mathbf{r}_{j,n})$$

Here the summation is over wave vectors  $\mathbf{q}$  associated with nonvanishing components (i.e.  $\mathbf{Q}_j(\mathbf{q}) \neq \mathbf{0}$  for some  $j$ ). So a magnetic structure can be fully characterised only by a few parameters  $\mathbf{q}$ ,  $\mathbf{Q}_j(\mathbf{q})$ , corresponding to  $\mathbf{q}_j$  sites in the chemical unit cell.

Vectors  $\mathbf{q}$  are so called propagation vectors (or wave vectors) of the magnetic structure. In most cases  $\mathbf{q}$  belong to the first Brillouin zone, but there are structures, where we observe also higher harmonics of  $\mathbf{q}$ -wave (e.g. non-sinusoidal modulation, anti-phase domain etc.).

### 4. Neutron diffraction

Neutrons are scattered both by nuclear and magnetic forces. However, Halpern and Johnson [1] have shown that the resulting intensities are purely additive when the neutrons are unpolarised. It follows from the above treatment, that the magnetic

contribution to the intensity of unpolarized neutrons elastically scattered from a single crystal is proportional to

$$(2) \quad \sigma(\boldsymbol{\kappa}) = |\mathbf{P}(\boldsymbol{\kappa})|^2 - \left| \frac{\boldsymbol{\kappa}}{\kappa} \cdot \mathbf{P}(\boldsymbol{\kappa}) \right|^2$$

where  $\boldsymbol{\kappa}$  is the neutron scattering vector (difference between the scattered ( $\mathbf{k}$ ) and incident ( $\mathbf{k}_0$ ) wave vectors), and

$$(3) \quad \mathbf{P}(\boldsymbol{\kappa}) = \sum_{j,n} f_j(\boldsymbol{\kappa}) M_{j,n} \exp(i\boldsymbol{\kappa} r_{j,n})$$

$f_j(\boldsymbol{\kappa})$  being the form factor.

By substituting Fourier components from Eq. (1) we obtain

$$\mathbf{P}(\boldsymbol{\kappa}) = \sum_{q,j} \{f_j(\boldsymbol{\kappa}) \mathcal{Q}_j(\mathbf{q}) \exp[i(\mathbf{q} + \boldsymbol{\kappa}) \cdot \mathbf{e}_j] \cdot \sum_n \exp[i(\mathbf{q} + \boldsymbol{\kappa}) \cdot \mathbf{R}_n]\}$$

Here the summation over  $n$  is the interference function proportional to a sum of delta-functions  $\sum_{\mathbf{K}} \delta_{\mathbf{q}+\boldsymbol{\kappa},\mathbf{K}}$ ,  $\mathbf{K}$  being any reciprocal-lattice vector.

Hence we write

$$(4) \quad \mathbf{P}(\boldsymbol{\kappa}) \sim \sum_{\mathbf{K},\mathbf{q}} \delta_{\mathbf{q}+\boldsymbol{\kappa},\mathbf{K}} \cdot \mathbf{F}(\mathbf{K}, \mathbf{q})$$

where the structure factor is given by

$$(5) \quad \mathbf{F}(\mathbf{K}, \mathbf{q}) = \sum_j f_j(\mathbf{K} - \mathbf{q}) \mathcal{Q}_j(\mathbf{q}) \exp(i\mathbf{K} \cdot \mathbf{e}_j)$$

The expressions (4) and (2) show that the scattered neutron intensity can give peaks only when  $\boldsymbol{\kappa} = \mathbf{K} - \mathbf{q}$  and simultaneously  $\boldsymbol{\kappa}$  must not be parallel to  $\mathbf{F}(\mathbf{K}, \mathbf{q})$  (therefore peaks  $(0, 0, 0)^{+q}$  do not exist for longitudinally modulated structures, because of  $\mathbf{q} \parallel \mathcal{Q}_j(\mathbf{q})$ ). The reality of the vectors  $M_{j,n}$  requires that

$$(6) \quad \mathcal{Q}_j^*(\mathbf{q}) = \mathcal{Q}_j(-\mathbf{q})$$

In other words, using Eq. (2)–(5) one can show, that for any magnetic peak represented in reciprocal space by  $\boldsymbol{\kappa}_1 = \mathbf{K} - \mathbf{q}$ , there is also a peak represented by the neutron scattering vector  $\boldsymbol{\kappa}_2 = \mathbf{K} + \mathbf{q}$ . Thus, associated with each point  $\mathbf{K}$  in reciprocal space there is a number of scattering points,  $\mathbf{K} \pm \mathbf{q}$ , equal to the number of different  $\mathbf{q}$  vectors for which there are nonzero Fourier components in Eq. (1). The  $\mathbf{q} = \mathbf{0}$  Fourier component produces magnetic peaks only at the nuclear peak locations ( $\boldsymbol{\kappa} = \mathbf{K}$ ). All others are so called “satellites”. If holds  $|\boldsymbol{\kappa}_1| = |\boldsymbol{\kappa}_2|$ , then a pair of satellites,  $\mathbf{K} \pm \mathbf{q}$ , is reduced in a single magnetic satellite peak in neutron powder pattern. From Eqs. (5), (6) follows also an important test for right indexing of magnetic reflections – intensities of both individual peaks in all satellite pairs should be practically the same (after systematic corrections for powder magnetic diffraction).

The foregoing expressions show that the intensity of reflections  $\kappa = \mathbf{K} \pm \mathbf{q}$  is determined by Fourier components  $\mathcal{Q}_j(\mathbf{q})$  only – it means, that if magnitude and orientation of magnetic moment in an arbitrary crystal position are changed without a change of  $\mathcal{Q}_j(\mathbf{q})$ , the intensities of all reflections  $\kappa = \mathbf{K} \pm \mathbf{q}$  remain unchanged.

The description being shown above assumes single crystal neutron diffraction. If we consider neutron diffraction on a powder specimen of low-symmetrical matter, it is clear, that the total intensity of every measured reflection contains all peaks with the same  $|\kappa|$ , i.e. it is necessary to take all appropriate combinations  $\mathbf{K} \pm \mathbf{q}$  into account and evaluate their intensity contributions according Eqs. (2)–(6). It is substantial, that the information dealing with the magnetic structure is not lost in principle in this case.

### 5. Fourier analysis of some rare earth intermetallics

Application of Fourier analysis for low-symmetrical materials can be well exemplified in case of the orthorhombic  $\text{RCu}_2$  compounds ( $\text{R} = \text{rare earth except for La}$ ). The magnetic  $\text{R}^{3+}$  ions are responsible for magnetic properties of these intermetallics and it is the long range oscillatory indirect exchange interactions between the  $\text{R}^{3+}$  ions combined with the crystalline anisotropy that lead to a long range antiferro-

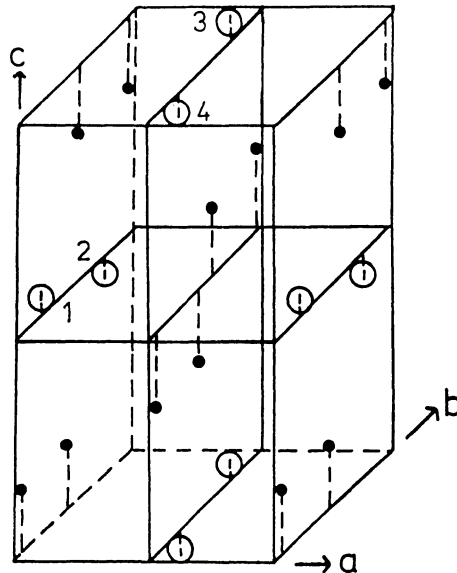


Fig. 1. The chemical unit cell of the orthorhombic  $\text{CeCu}_2$ -type structure, which consists of four rare earth atoms at  $4e$  sites and eight copper atoms at  $8h$  sites marked with open and closed circles, respectively.

magnetic order at low temperatures ( $\sim 10^1$  K). The influence of the magnetocrystalline anisotropy can be estimated by a study of a series of isostructural  $\text{RCu}_2$  compounds, i.e. compounds with different orbital moments. The impact of the exchange interactions can be considered by varying the electron concentration. In particular, substitution of Ni (with full 3d-states) for Cu leads to a lowering of the conduction electron concentration and an increasing tendency towards ferromagnetic alignment.

These compounds crystallize in the orthorhombic body centered  $\text{CeCu}_2$  structure, which can be described as a stacking of alternating layers of R and Cu atoms along the  $c$  or  $b$ -axis. In the paramagnetic region the observed diffraction patterns of all compounds are consistent with the space group  $\text{Imma}$  – i.e. there are only peaks  $(h, k, l)$  where  $h + k + l$  is even, the R atoms are in (4e) positions  $\mathbf{q}_1 = (0, \frac{1}{4}, z)$ ,  $\mathbf{q}_2 = (0, -\frac{1}{4}, -z)$ ,  $\mathbf{q}_3 = (\frac{1}{2}, \frac{3}{4}, \frac{1}{2} + z)$  and  $\mathbf{q}_4 = (\frac{1}{2}, \frac{1}{4}, \frac{1}{2} - z)$ , the Cu atoms are in appropriate (8h) positions – see Fig. 1. Below the ordering temperature the structure factor  $F(\mathbf{K}, \mathbf{q})$  (Eq. (5)) can be expressed for  $\text{RCu}_2$  in the form

$$(7) \quad F(\mathbf{K}, \mathbf{q}) = f(\mathbf{K} - \mathbf{q}) \sum_{j=1}^4 Q_j(\mathbf{q}) \exp(i\mathbf{K}\mathbf{q}_j)$$

$$F(\mathbf{K}, \mathbf{q}) = f(\mathbf{K} - \mathbf{q}) \{ (Q_1(\mathbf{q}) \pm Q_3(\mathbf{q})) \exp[i\mathbf{K}\mathbf{q}_1] + (Q_2(\mathbf{q}) \pm Q_4(\mathbf{q})) \exp[-i\mathbf{K}\mathbf{q}_1] \}$$

where the upper sign holds when  $h + k + l$  is even, the lower when  $h + k + l$  is odd. From here it follows that if there are for given  $\mathbf{q}$  only satellites of reciprocal lattice points  $\mathbf{K}$  with  $h + k + l$  even in the powder pattern, then must be

$$(8) \quad \begin{aligned} Q_1(\mathbf{q}) &= Q_3(\mathbf{q}) \\ Q_2(\mathbf{q}) &= Q_4(\mathbf{q}) \end{aligned}$$

If there are only satellites of  $\mathbf{K}$  with  $h + k + l$  odd, then

$$(8') \quad \begin{aligned} Q_1(\mathbf{q}) &= -Q_3(\mathbf{q}) \\ Q_2(\mathbf{q}) &= -Q_4(\mathbf{q}) \end{aligned}$$

#### $\text{TbCu}_2$

The magnetic structure of  $\text{TbCu}_2$  [4] was found to be collinear antiferromagnetic and the magnetic unit cell is tripled in the  $a$ -direction. The magnetic moments are aligned along the  $a$ -axis. There are two types of magnetic reflections in the neutron diffraction powder pattern; one type of reflections  $(h, k, l)$  with  $h + k + l$  odd and another type of reflections  $(h \pm \frac{1}{3}, k, l)$  with  $h + k + l$  even. The two types of reflections have different temperature dependencies of their intensities. The intensities of the reflections belonging to the first type, which is connected with  $\mathbf{q} = \mathbf{0}$ , decrease most rapidly with temperature. The second type of reflections is characterized by the propagation vector  $\mathbf{q} = \frac{1}{3}\mathbf{a}^*$  and their intensities disappear at  $T_N$ . From this follows that the first and second type intensities reflect the temperature dependence of  $Q_j(\mathbf{0})$  and  $Q_j(\frac{1}{3}\mathbf{a}^*)$  components in Eq. (1), respectively.

Using Eq. (1) and conditions (8), (8'), we can expect the magnetic structure of  $\text{TbCu}_2$  in the form

$$(9) \quad \begin{aligned} M_{1,n} &= -\alpha(T) + \beta(T) \cos(\tfrac{1}{3}\mathbf{a}^* \cdot \mathbf{R}_n) \\ M_{2,n} &= \alpha(T) - \beta(T) \cos(\tfrac{1}{3}\mathbf{a}^* \cdot \mathbf{R}_n) \\ M_{3,n} &= \alpha(T) + \beta(T) \cos(\pi/3 + \tfrac{1}{3}\mathbf{a}^* \cdot \mathbf{R}_n) \\ M_{4,n} &= -\alpha(T) - \beta(T) \cos(\pi/3 + \tfrac{1}{3}\mathbf{a}^* \cdot \mathbf{R}_n) \end{aligned}$$

This is in full agreement with experiment [5]. The vectors  $\alpha(T)$  and  $\beta(T)$  are parallel to the  $\mathbf{a}$ -axis and correspond to an absolute and a harmonic term in the Fourier series, respectively. The observed neutron intensities fulfil the relations

$$\begin{aligned} I(h, k, l; T) &\sim \alpha^2(T) & (h + k + l \text{ odd}) \\ I(h \pm \tfrac{1}{3}, k, l; T) &\sim \beta^2(T) & (h + k + l \text{ even}) \end{aligned}$$

Three regions of temperature with different ordered moments on  $\text{Tb}^{3+}$  ions are observed:

Region I: ( $47\text{K} < T < 55\text{K}$ , see Fig. 2 and Fig. 3b) with sublattice magnetisations  $M$  and  $m = M/2$  ( $\alpha(T) = 0$ )

Region II: ( $16\text{K} < T < 47\text{K}$ ) with sublattice magnetisations  $M$  and  $m$   
 $\tfrac{1}{2}M < m < M$  ( $0 < \alpha(T) < \tfrac{1}{4}\beta(T)$ )

Region III: ( $T < 16\text{K}$ , see Fig. 3a) with sublattice magnetisations  
 $M$  and  $m$ ,  $M = m$  ( $\alpha(T) = \tfrac{1}{4}\beta(T)$ ).

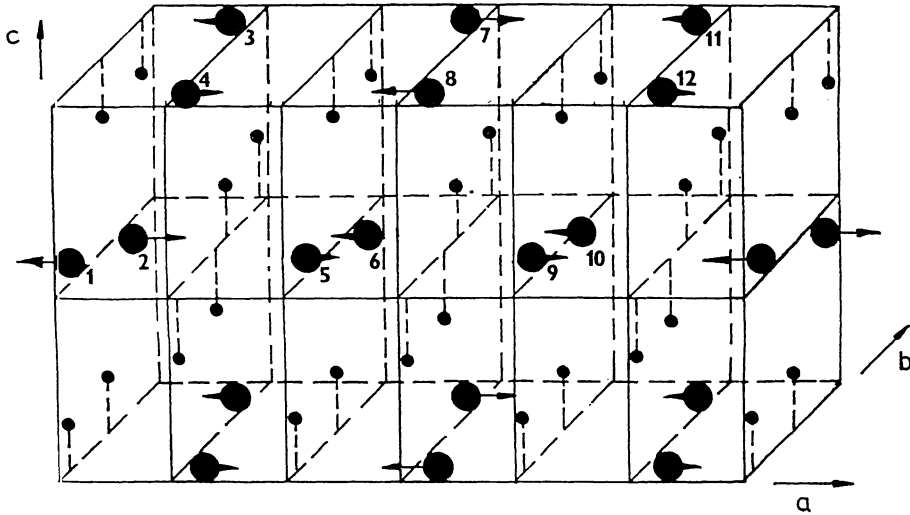


Fig. 2. The high temperature ( $47\text{K} < T < 55\text{K}$ ) magnetic structure of  $\text{TbCu}_2$ . The magnetic moments referred to in Eq. (9) for  $\mathbf{R}_n = \mathbf{0}$  are shown by 1, 2, 3 and 4.



We can see that the magnetic structure of  $\text{TbCu}_2$  is a pure longitudinally modulated structure in region I and this component is preserved also at lower temperatures – therefore the reflection  $(\pm\frac{1}{3}, 0, 0)$  does not arise.

Qualitatively similar results have been found for powdered  $\text{Tb}(\text{Cu}_{0.95}\text{Ni}_{0.05})_2$  [5]. For this alloy,  $T_N = 59$  K and  $\alpha(T)$  vanishes already at  $\approx 38$  K. The pure longitudinally modulated structure was found also for  $\text{Tb}_{0.6}\text{Y}_{0.4}\text{Cu}_2$  [6] at  $T = 4.2$  K and for  $\text{HoCu}_2$  at  $7 \text{ K} < T < T_N = 10 \text{ K}$  [7].

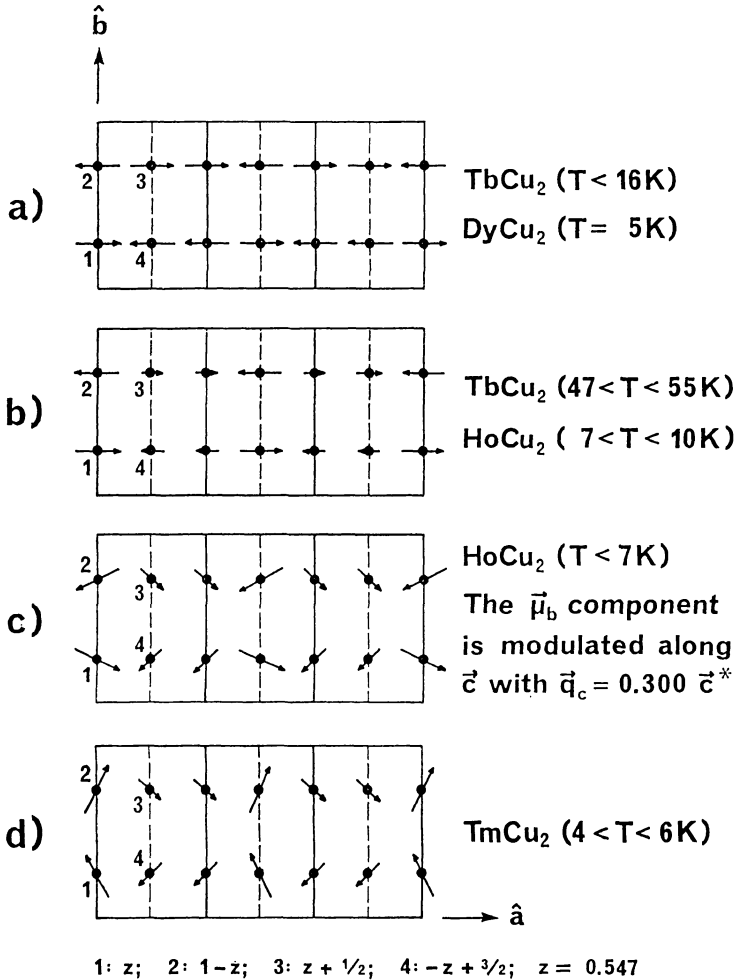


Fig. 3. Projection of the magnetic structures in the  $(a, b)$  plane for some of the  $\text{RCu}_2$  compounds. Only  $R$ -atoms are shown. For  $T < 7$  K  $\text{HoCu}_2$  has a  $c$ -axis modulated moment component in  $b$ -direction, for the other compounds there are no  $c$ -axis modulation.

$\text{Tb}(\text{Cu}, \text{Ni})_2$

For higher Ni-concentration in  $\text{Tb}(\text{Cu}_{1-x}\text{Ni}_x)_2$  compounds a ferromagnetic component appears because the electron concentration is lowered. This effect was confirmed for  $\text{Tb}(\text{Cu}_{0.9}\text{Ni}_{0.1})_2$  at 4.2 K [8]. Here, the magnetic moments have ferromagnetic components in the  $c$ -direction and the remaining  $a$ -components form

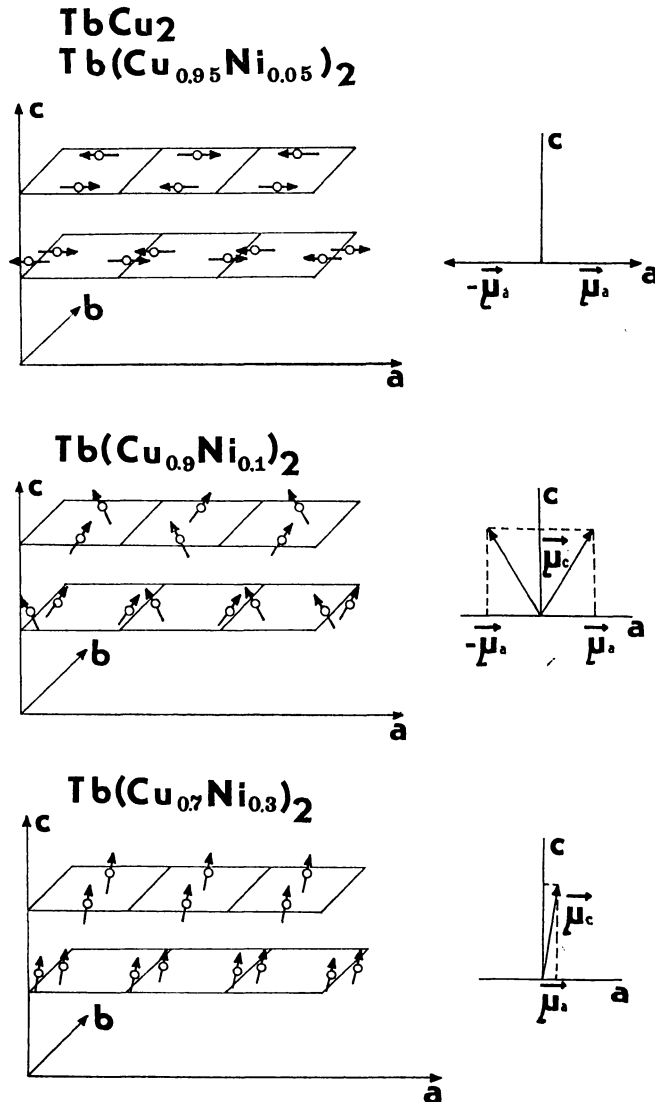


Fig. 4. The influence of Ni-concentration in  $\text{Tb}(\text{Cu}_{1-x}\text{Ni}_x)_2$  compounds on their magnetic structure at 4.2 K. For  $0 \leq x \leq 0.1$  two types of Tb-magnetic moments in tripled magnetic cell of double layer structure are schematically represented. In case of  $\text{Tb}(\text{Cu}_{0.7}\text{Ni}_{0.3})_2$  the magnetic structure is collinear and therefore the magnetic cell is the same as the chemical one.

a structure of TbCu<sub>2</sub>-type (Fig. 4). In case of the Tb(Cu<sub>0.7</sub>Ni<sub>0.3</sub>)<sub>2</sub> compound, profile analysis of the diffraction pattern revealed a pure collinear ferromagnetic structure (i.e.  $\mathbf{q} = 0$  only) with magnetic moments in the ( $a, c$ ) plane, near the  $c$ -axis (Fig. 4) [8].

#### DyCu<sub>2</sub>

The neutron diffraction patterns obtained for DyCu<sub>2</sub> are similar to those obtained for TbCu<sub>2</sub> and can be interpreted similarly. However, due relatively poor statistics (Dy has a high neutron absorption cross-section), we were not able to analyse the temperature dependence of the magnetic structure in detail.

#### HoCu<sub>2</sub>

The neutron diffraction measurements between 2.5 and 15 K on a powdered HoCu<sub>2</sub> sample have shown that below  $T_N = 10$  K there are additional reflections corresponding to magnetic satellites of reciprocal lattice points  $K$  for which  $h + k + l$  are even. Particularly, between 7 and 10 K, the antiferromagnetic structure can be described by the wave vector  $\frac{1}{3}\mathbf{a}^*$  describing the same magnetic structure as found in TbCu<sub>2</sub> near  $T_N$  – region I, see Fig. 3b. Below 7 K the neutron diffraction data contain two sets of magnetic reflections. The first set represents the commensurate component of a longitudinally modulated structure with wave vector  $\mathbf{q}_1 = \frac{1}{3}\mathbf{a}^*$  being the same as for above 7 K. The second set of reflections is new and corresponds to a magnetic structure which is incommensurably modulated along the  $c$ -axis. These additional peaks appear as satellites around reflections having  $h + k + l$  even. It can be shown, that these new components of the magnetic structure can be described by two transversally modulated waves with wave vectors  $\mathbf{q}_2$  and  $2\mathbf{q}_2$ , respectively – see Fig. 5. Here  $\mathbf{q}_2 = q_c \cdot \mathbf{c}^*$ ,  $q_c = 0.300 \pm 0.005$ . The transversal

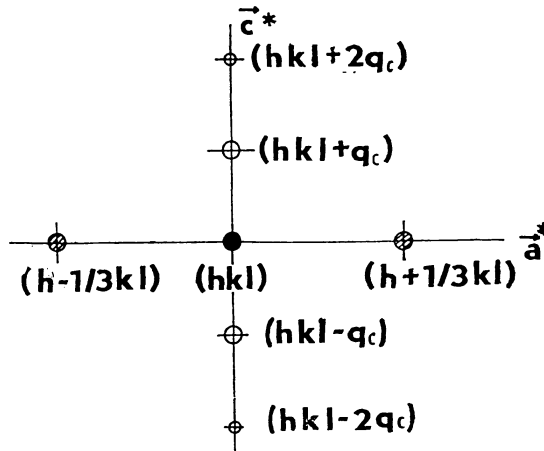


Fig. 5. The (010) plane of the reciprocal space for the case of HoCu<sub>2</sub> below 7 K. The full circle corresponds to the reciprocal point  $(hkl)$  with  $h + k + l$  even. The hatched and open circles correspond to the satellites with the propagation vectors  $\pm\mathbf{q}_1$  and  $\pm\mathbf{q}_2$  (or  $\pm 2\mathbf{q}_2$ ), respectively.

character of these components is responsible for observed  $(0, 0 \pm q_c)$  and  $(0, 0, \pm 2q_c)$  peaks. The moments corresponding to  $q_2$  and  $2q_2$  are parallel to the  $b$ -axis. Hence, these components can be expressed as

$$M_{q_2}(\mathbf{e}_j + \mathbf{R}_n) = \gamma_{q_2} \cos [q_2(\mathbf{e}_j + \mathbf{R}_n)]$$

$$M_{2q_2}(\mathbf{e}_j + \mathbf{R}_n) = \gamma_{2q_2} \cdot \cos [2q_2(\mathbf{e}_j + \mathbf{R}_n)]$$

where  $j = 1$  to 4 and  $\gamma_{q_2} \parallel \gamma_{2q_2} \parallel \mathbf{b}$ . The existence of  $2q_2$  waves indicates a non-sinusoidal

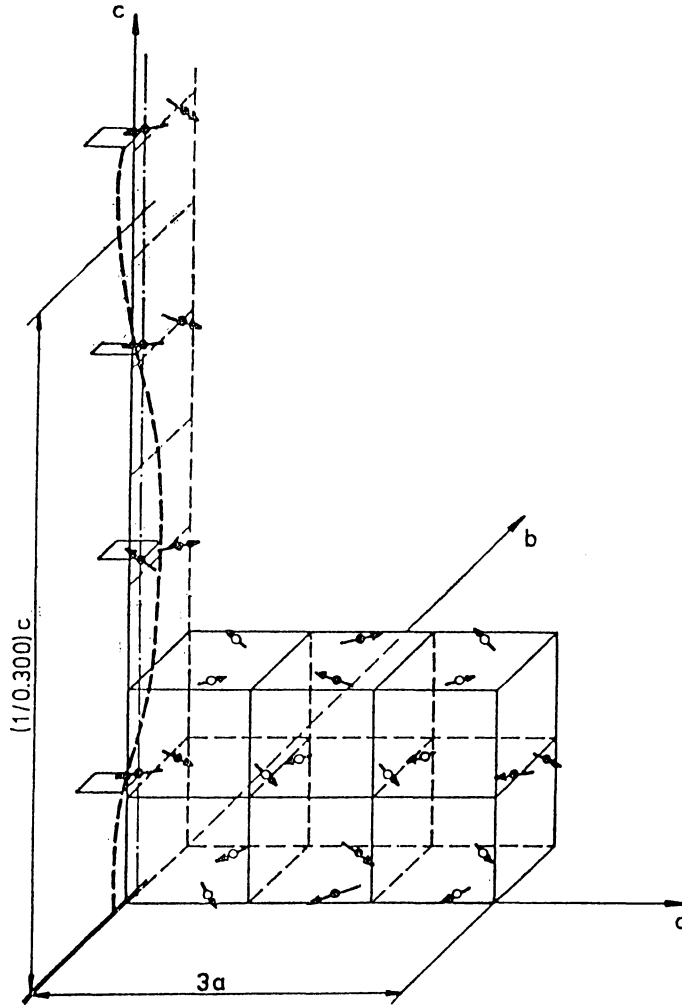


Fig. 6. Illustration of the magnetic structure of  $\text{HoCu}_2$  below 7 K. For simplicity only the first harmonic of the transverse  $c$ -axis modulated moment component is shown. The full (●) and open (○) symbols correspond to Ho-atoms where the longitudinal  $a$ -axis modulated moments are  $M$  and  $M/2$ , respectively.

modulation in the structure. The resulting magnetic structure of  $\text{HoCu}_2$  below 7 K is then a non-collinear incommensurably modulated structure with magnetic moments lying in the  $(a, b)$  plane – see Fig. 6 and Fig. 3c. The increase in Ni-concentration in the  $\text{Ho}(\text{Cu}, \text{Ni})_2$  system gives rise to a ferromagnetic component for  $\sim 10\%$  Ni similarly to the results for  $\text{Tb}(\text{Cu}, \text{Ni})_2$  [6].

### $\text{ErCu}_2$

In case of  $\text{ErCu}_2$  neutron diffraction powder patterns obtained between 1.5 K and  $T_N = 12$  K revealed a rather complicated antiferromagnetic structure with a strong temperature dependence of the propagation vector. In spite of many attempts to interpret the powder patterns obtained for  $\text{ErCu}_2$ , we have not been able to describe the magnetic structure satisfactorily. We can say only the magnetic structure is most probably incommensurably modulated – because the  $\text{Er}^{3+}$  is non-Kramers ion, the modulated structure cannot be stable at  $T = 0\text{K}$  and therefore we can expect a transition to unmodulated phase at very low temperatures. It seems that in spite of the low-symmetrical character of  $\text{ErCu}_2$  the problem of its magnetic structure will be necessary to solve by means of single crystal measurements.

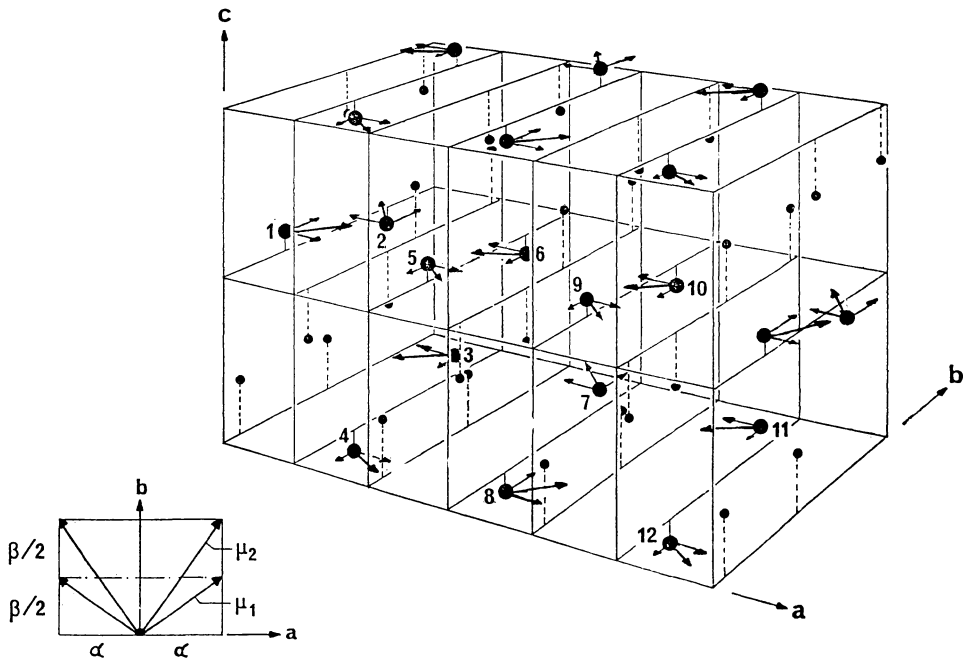


Fig. 7. The magnetic unit cell of  $\text{TmCu}_2$  at 5 K. The large and small full circles represent thulium and copper atoms, respectively. The transversal modulated component in  $b$ -direction, unmodulated component in  $a$ -direction and resulting moment are marked by appropriate arrows. Magnetic moments of magnitude  $\mu_1$  and  $\mu_2$  are situated in positions 3, 4, 5, 6, 9, 10 and 1, 2, 7, 8, 11, 12, respectively.

## TmCu<sub>2</sub>

TmCu<sub>2</sub> is an antiferromagnet below  $T_N = 6.3$  K. The neutron diffraction pattern obtained at 5 K contains two types of magnetic reflections: satellites ( $h \pm \frac{1}{3}, k, l$ ) where  $h + k + l$  is odd and non-satellite magnetic peaks ( $h, k, l$ ),  $h + k + l$  even. A detailed analysis of the observed pattern revealed that the moment component connected with the first type of reflections is transversally modulated with propagation vector  $\frac{1}{3}\mathbf{a}^*$  and moments parallel to the  $\mathbf{b}$ -direction. The second type of reflections is responsible for a moment component parallel to the  $\mathbf{a}$ -axis, similar to the  $\alpha$ -component in TbCu<sub>2</sub>. The resulting magnetic structure in TmCu<sub>2</sub> is noncollinear (see Fig. 7 and Fig. 3d) and may be described (see conditions (8')) by

$$(10) \quad \begin{aligned} M_{1,n} &= -\alpha + \beta \cos\left(\frac{1}{3}\mathbf{a}^* \cdot \mathbf{R}_n\right) \\ M_{2,n} &= \alpha + \beta \cos\left(\frac{1}{3}\mathbf{a}^* \cdot \mathbf{R}_n\right) \\ M_{3,n} &= \alpha - \beta \cos\left(\frac{1}{3}\pi + \frac{1}{3}\mathbf{a}^* \cdot \mathbf{R}_n\right) \\ M_{4,n} &= -\alpha - \beta \cos\left(\frac{1}{3}\pi + \frac{1}{3}\mathbf{a}^* \cdot \mathbf{R}_n\right) \end{aligned}$$

where  $\alpha \parallel \mathbf{a}$  and  $\beta \parallel \mathbf{b}$ . This structure has two magnetic moments  $\mu_1$  and  $\mu_2$  given by

$$\mu_1 = \sqrt{(\alpha^2 + \frac{1}{4}\beta^2)} \quad \text{and} \quad \mu_2 = \sqrt{(\alpha^2 + \beta^2)}$$

This model was tested by profile analysis of powder pattern. The reliability factors were  $\sim 16\%$  for the nuclear and  $\sim 26\%$  for the magnetic structure. In spite of the rather large  $R$ -factors we find the model reasonable because the data was collected at 5 K which is only just above the next transition temperature (4.3 K). Therefore, there may be a mixture of magnetic phases in the powder sample.

The foregoing examples of magnetic structures have demonstrated both advantages and disadvantages of neutron powder diffraction in case of low-symmetrical magnetic materials. We have seen that we can study complex magnetic structures successfully on powdered specimens, but there are special cases, mainly dealing with the problem of right indexing, high neutron absorption and temperature homogeneity of the sample, when single crystal measurement seems to be of advantage.

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