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Ordered magnetic frustration
XIV. The magnetic structure of the tetragonal bronze $KMnFeF_6$

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The magnetic structure of the tetragonal bronze-like $KMnFeF_6$ is solved by means of neutron powder diffraction. The structure (space group Pb′a2′) consists of a non-collinear arrangement of spins lying in the (a, b) plane of the crystal cell. Spins belonging to triangular platelets adopt a star arrangement very close to the ideal 120° configuration, whereas the arrangement in square platelets is almost exactly antiparallel. The magnetic structure of $KMnFeF_6$ has been successfully simulated with the program MCMAG by assuming isotropic AF interactions between nearest magnetic neighbours (superexchange interactions).

1. Introduction

Magnetic frustration [1,2] has been shown to be the key element of the magnetic structure and behaviour of a series of transition metal fluorides (see for instance ref. [3] and references therein). In most of these compounds, a non-collinear magnetic structure results from the competition of three antiferromagnetic superexchange interactions between magnetic cations. In this paper, we extend these studies to another structural type where this kind of frustrated triangular platelets is present: the tetragonal tungsten bronze-like structure.

The fluoride $KMnFeF_6$ [4] exhibits a superstructure of the usual tetragonal tungsten bronze type. Its structure, refined from single crystal X-ray diffraction data [5], shows a doubling of the c axis compared to the usual unit cell, due to an ordering of Mn^{2+} and Fe^{3+} cations on the octahedral sites of the structure ($a = 12.765(1)$ Å, $c = 8.002(1)$ Å, space group $P4_2bc$, $Z = 20$). A projection of this structure is shown on fig. 1. All octahedra units share corners and one of the octahedral sites (4b) is occupied statistically by Mn^{2+} and Fe^{3+}, the others (8c) remaining ordered. From one layer to the next along the c axis, manganese and iron ions alternate.

The magnetic behaviour of $KMnFeF_6$ is governed by 180° type M–F–M superexchange.

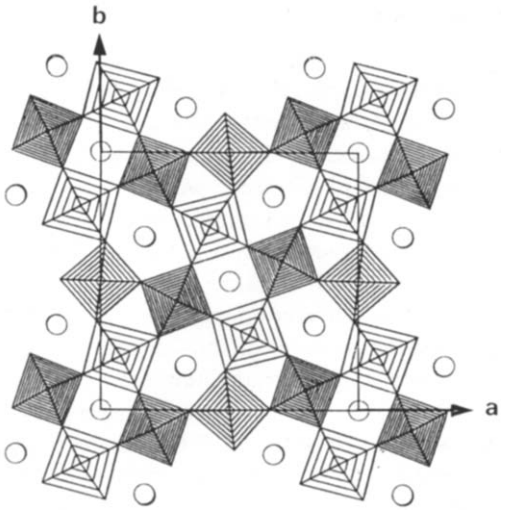

Fig. 1. Crystal structure of the ordered tetragonal bronze $KMnFeF_6$, projected along the c axis. Low, mean and high density hatchings correspond to Mn^{2+}, statistical Mn^{2+}/Fe^{3+} and Fe^{3+} octahedral sites respectively. [MnF_6] and [FeF_6] octahedra alternate along the c axis (open circles = K^+).

Mn^{2+} and Fe^{3+} have the same electronic configuration (d^5) and this kind of coupling configuration is known to lead to antiferromagnetic interactions [6,7]. Magnetic susceptibility measurements agree with an antiferromagnetic behaviour, but the compound exhibits a small remanent magnetization ($0.252\mu_B$/mol at 4.2 K) [8]. It should thus be considered as a ferrimagnet ($T_c = 148$ K, $\Theta = -440$ K). Banks et al. [8] pointed out that the important point is the presence of magnetic constraints in the compound. Indeed the existence of triangular cycles of antiferromagnetic interactions implies magnetic frustration. Two factors confirm this point: the ratio $|\Theta/T_c| \approx 3$ which is much greater than 1 [9] and the lowering of the ordering temperature compared with what it should be in a non-frustrated compound [8].

In this paper, we present the frustrated magnetic structure of $KMnFeF_6$ as determined from neutron diffraction recording. Section 2 is devoted to the experimental part of the work. In section 3, we present the magnetic structure of the compound, which is discussed in terms of magnetic frustration and compared to Monte Carlo simulation results in section 4.

2. Experimental

A powder sample of $KMnFeF_6$ was synthesized by the heating of a stoichiometric mixture of the elementary fluorides. The appropriate amounts of KF, MnF_2 and FeF_3 were weighed, mixed and ground in a glove box under inert atmosphere. The mixture was sealed in a gold tube, then fired for two days at 740 °C under argon.

The neutron diffraction patterns were collected on the high flux powder diffractometer D1B of the Institut Laue–Langevin at Grenoble ($\lambda = 2.52$ Å, $10° < 2\theta < 90°$). The powdered sample was contained in a vanadium can (10 mm diameter) held in a standard helium cryostat with temperature regulation. Two patterns, above and below the ordering temperature (respectively 175 and 5 K) were recorded. The refinements of the crystal and magnetic structures were carried out with the Rietveld program [10] as modified by Hewat [11]. The scattering lengths and magnetic form factors were taken from refs. [12] and [13] respectively.

3. Magnetic structure

The high temperature pattern (175 K) confirms the cationic ordering announced by Banks et al. [5]. For this purpose, it is clear that neutron diffraction has a great advantage on X-ray diffraction because of the opposite signs of the Fermi lengths of manganese and iron [12], which enhance the contrast between these two elements. Unambiguously, we confirm the ordering of manganese and iron cations on the 8c sites of the structure, as well as the statistical occupancy of the 4b site. However, it should be noticed that this Mn/Fe disorder is probably only apparent: most likely these cations are perfectly ordered in each individual row of octahedra along the c axis in order to fulfill Pauling's rules, and the apparent disorder as seen by diffraction techniques would thus originate only from the random arrangement of the rows relative to each other.

The relatively large number of refinable crystallographic parameters (32 parameters for atomic positions only) compared to the limited amount of information available in the 2θ range of the measurement (10°–90°) prevented us from undertaking a refinement of both crystal and magnetic structures. Therefore we conducted the refinement on the difference pattern (5–175 K); the only contribution to the pattern is thus only due to the magnetic moments of magnetic species. Such a procedure has already been successfully applied to the determination of the magnetic structure of $\alpha KCrF_4$ [14]. For the refinements, the magnetic atoms were held fixed at the positions determined by Banks et al. from single crystal data [5]. The absolute value of magnetic moments was obtained by scaling the experimental nuclear pattern to the one calculated with the structural parameters determined by Banks.

Every peak of the difference pattern can be indexed in the nuclear cell. We first chose the magnetic model by using the magnetic space groups classified by Opechowski and Guccione [15]. Space group $P4_2bc$ leads to four magnetic

Table 1
Bertaut's macroscopic theory [16] applied to space group Pba2

Site 4c coordinates of magnetic ions			
spins	atomic coordinates		
S_1	x	y	z
S_2	$-x$	$-y$	z
S_3	$\frac{1}{2}-x$	$\frac{1}{2}+y$	z
S_4	$\frac{1}{2}+x$	$\frac{1}{2}-y$	z

Site 2b coordinates of magnetic ions			
spins	atomic coordinates		
S_1	0	$\frac{1}{2}$	z
S_3	$\frac{1}{2}$	z	

Base vector
$F = S_1 + S_2 + S_3 + S_4$
$G = S_1 - S_2 + S_3 - S_4$
$C = S_1 + S_2 - S_3 - S_4$
$A = S_1 - S_2 - S_3 + S_4$

Base vectors
$F = S_1 + S_3$
$C = S_1 - S_3$

Irreducible representations [a]

modes	x	y	z	
$\Gamma_1(++)$	G_x	A_y	C_z	[Pba2]
$\Gamma_2(+-)$	C_x	F_y	G_z	[Pba'2']
$\Gamma_3(-+)$	A_x	G_y	F_z	[Pb'a'2]
$\Gamma_4(--)$	F_x	C_y	A_z	[Pb'a2']

Irreducible representations

modes	x	y	z
$\Gamma_1(++)$	–	–	C_z
$\Gamma_2(+-)$	C_x	F_y	–
$\Gamma_3(-+)$	–	–	F_z
$\Gamma_4(--)$	F_x	C_y	–

[a] The magnetic space groups [15] corresponding to the coupling modes are given in brackets.

space groups, but only one of them allows ferrimagnetism ($P4_2b'c'$), the ferromagnetic component being oriented along the c axis of the structure. Attempts to refine in this space group led to a reliability factor higher than 0.45. Therefore, as often for frustrated magnetic structures, we had to lower the symmetry and consider subgroups of $P4_2bc$. Refinements in tetragonal space group $P4_2$ did not improve the results, but we got a significant improvement by considering the orthorhombic space group Pba2 (coincidentally, the crystal structure of the bronze $K_{0.6}FeF_3$ [4] is also described in this space group).

The passage from $P4_2bc$ to Pba2 splits the general positions (8c) of $P4_2bc$:

x, y, z (1) $\quad -y, x, \frac{1}{2}+z$ (2)
$-x, -y, z$ (3) $\quad y, -x, \frac{1}{2}+z$ (4)
$\frac{1}{2}-x, \frac{1}{2}+y, z$ (5) $\quad \frac{1}{2}+y, \frac{1}{2}+x, \frac{1}{2}+z$ (6)
$\frac{1}{2}+x, \frac{1}{2}-y, z$ (7) $\quad \frac{1}{2}-y, \frac{1}{2}-x, \frac{1}{2}+z$ (8)

into two sets of general positions (4c) of Pba2 (namely 1–3–5–7 and 2–4–6–8). Similarly the site (4b) of $P4_2bc$ is split in two sets of sites (2b) in Pba2.

Table 2
Refined magnetic moments of $KMnFeF_6$. The cations were held fixed on the atomic positions determined by Banks et al. [5]

Atoms	Atomic positions			Magnetic moments (μ_B)			
	x	y	z	M_x	M_y	M_z	total M
Mn^{2+}	0.0758	0.2144	0.9996	−3.22(19)	2.96(32)	0	4.38(36)
Fe^{3+}	0.2901	0.4244	0	4.87(18)	3.09(31)	0	5.77(32)
Mn^{2+}/Fe^{3+}	0	0.5	0	0.49(49)	−4.63(16)	0	4.66(21)

When applied to space group Pba2, Bertaut's macroscopic theory [16] leads to 4 modes, three of them having ferromagnetic components (Γ_2, Γ_3, Γ_4, see table 1). The refinement in the mode Γ_4 (space group Pb′a2′) gave the best result. The components of the moments along the c axis, always refined to zero within the standard deviation, were thereby held fixed to 0 in final refinements. A first refinement without any constraint gave, within the standard deviation, magnetic moments of equal amplitude for the two manganese sites, as well as for the two iron sites. Therefore moments carried by atoms of the same nature in consecutive bronze layers were later constrained to the same value. The best reliability ($R_I = 0.067$) was obtained for the values of magnetic moments given in table 2. Observed and calculated patterns are shown on fig. 2 and the magnetic structure is represented in fig. 3.

The magnetic moment of the iron III cations is slightly too large compared to what one would expect for a d^5 cation ($S = \frac{5}{2}$). This could be related to the fact that the refinement is based on a difference pattern: indeed the temperature difference is rather large (170 K) and changes in Debye–Waller factors and small shifts in atomic positions, although not considered in the refine-

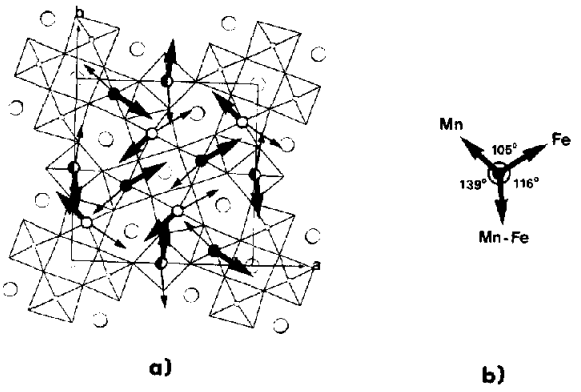

Fig. 3. The magnetic structure of $KMnFeF_6$: (a) The magnetic moments are lying in the (a, b) plane. Arrows with the same thickness represent magnetic moments carried by atoms located in the same layer (full circles = Fe^{3+}, open circles = Mn^{2+}, split circles = Mn^{2+}/Fe^{3+}). (b) Star spin configuration in the triangular platelets of the structure.

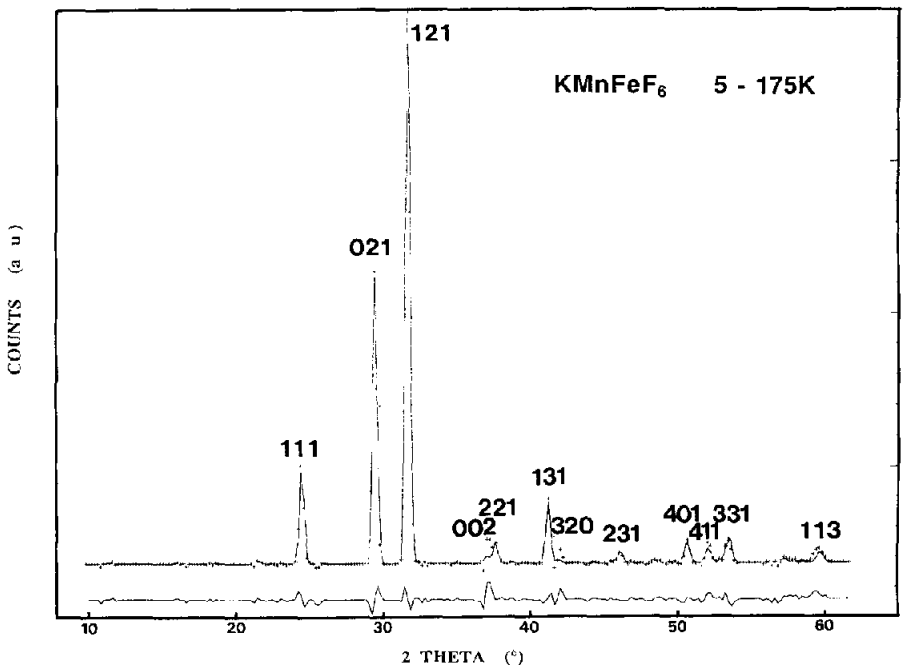

Fig. 2. Observed (+) and calculated (line) magnetic profiles for $KMnFeF_6$ (5–175 K). The difference pattern (obs.–calc.) is shown on the lower part of the figure.

ment, cannot be excluded. The relatively large value of the remanent magnetization ($0.84\mu_B$/mol) compared to the experimental value ($0.252\mu_B$/mol) should be seen as a consequence of the large magnetic moment of Fe^{3+}. However we believe that the orientation of the magnetic moments as determined above is globally correct, because it corresponds to what might be expected from this kind of frustrated arrangement. As a matter of fact, the spin configuration in the frustrated triangular platelets (see fig. 3b) is very close to the ideal 120° star configuration already encountered in HTB–FeF_3 [17] and to the spin arrangement in the triangular platelets of $\alpha KCrF_4$ [14]. The almost strictly antiferromagnetic alignments of spins in square platelets and along the c axis of the structure are also in good agreement with expected unfrustrated antiferromagnetic couplings.

4. Monte Carlo simulation and discussion

In order to check the compatibility of our assumptions with the results presented in the previous section, we undertook a Monte Carlo simulation of the magnetic structure of $KMnFeF_6$. For this purpose, we used the computer program MCMAG [18], which has been designed to simulate the magnetic structure of any 3D lattice of spins interacting through given coupling constants [19]. This program is specially suitable for finding the non-trivial ground states of frustrated magnetic structures. For this simulation, we focused on a single tetragonal bronze type layer, namely the plane where frustration occurs in the structure. For the sake of simplicity we assumed that all the nearest neighbour interactions (taken as antiferromagnetic) have equal strength, which seems reasonable in consideration of the spin canting in the compound. Each magnetic atom having a d^5 electronic configuration, the same spin amplitude ($5\mu_B$) was assigned to every site of the lattice, and an isotropic XY spin model was used.

The simulation evidenced the degeneracy of the ground state. As a matter of fact, besides the classical rotation degeneracy, two different sets of spin arrangements with the same energy have been found, depending on the initial spin configuration. These two configurations are shown in fig. 4. They cannot be deduced one from each other by a simple spin rotation; they represent two different chiralities in triangular platelets. This type of degeneracy has already been evidenced in simpler lattices such as the frustrated triangular lattice (see for instance refs. [20,21]). It originates from the existence of two different ground state spin configurations for a single platelet. A difference can be established between these two types of arrangements by considering their chiralities defined as $\chi = \Sigma_{\text{triangle}}\theta/2\pi$; the angle θ is the smallest rotation angle from one spin to the neighbour, the sign being defined by the direction of rotation chosen for the summation around the triangle [21]. For a ground state configuration, $\theta = \pm 120°$ and χ can take the values $+1$ or -1. These two chiralities are notified by the signs + and − in fig. 4. As can be seen on this figure, in the case of a tetragonal tungsten bronze type layer, each of the two ground state configurations is associated with one chirality type and only one. This is at variance from the AF frustrated triangular lattice, where both chiralities occur in each configuration [21].

By comparing figs. 3a and 4, it can be seen that the magnetic structure of $KMnFeF_6$ corresponds almost exactly to the spin configuration with chirality -1. Although the two chiralities possess the same exchange energy, one can postulate, in the case of $KMnFeF_6$, that a slight anisotropy

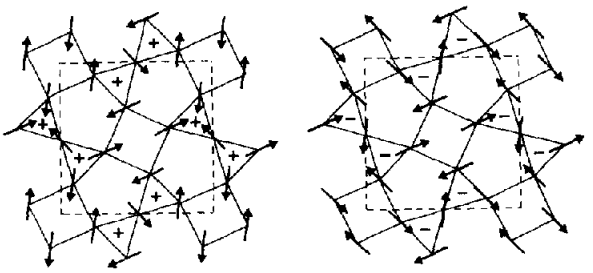

Fig. 4. The two spin configurations obtained from the Monte Carlo simulation of the magnetic structure of a tetragonal bronze layer with AF interactions (XY model). The signs indicate the chirality of the spin arrangement in the triangular platelets. The configuration with chirality – (right part) is to be compared with the magnetic structure of $KMnFeF_6$ as determined by neutron diffraction (fig. 3a).

removes the degeneracy in favor of the configuration with chirality -1.

5. Conclusion

From neutron powder diffraction patterns, we have determined the frustrated magnetic structure of $KMnFeF_6$. The canted spin configuration, which lowers the space group symmetry, is due to competition between AF superexchange interactions in the triangular cycles of the structure. In contrast, spins connected by unfrustrated interactions order antiferromagnetically. We have used the program MCMAG to simulate the magnetic structure of $KMnFeF_6$ with an XY spin model, suitable for isotropic exchange between d^5 cations. The magnetic structure of $KMnFeF_6$ corresponds to one of the two degenerate ground state configurations found by the program. A comparison with the magnetic structures of other fluorides with the same topology could be fruitful. The magnetic structure of $CsCoF_4$, described elsewhere [22], gives some insight on the behaviour of an Ising type spin system on a similar frustrating topology.

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