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Crystal and Magnetic Structures of the Layer Compound $TlMnF_4$

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Abstract. The crystal structure and the magnetic properties of the fluoromanganate(III) $TlMnF_4$ have been investigated. The structure has been refined down to R/wR of 0.057/0.043 in the monoclinic I2/a space group with the unit cell constants a = 539.7(2) pm; b = 544.1(2) pm; c = 1248.4(5) pm; β = 90.19(3)° (Z = 4). $TlMnF_4$ is characterized by a layer structure formed of MnF_6 octahedra sharing their four equatorial corners. Within each octahedron the Mn—F distances range from 178 pm to 215 pm. The intralayer magnetic interaction (J/k) has been evaluated to be approximately −0.45 K by fitting the experimental susceptibility in the 10 − 300 K range using the quadratic layer Heisenberg model. A 3D-antiferromagnetic ordering occurs at T_N = 4.2(5) K. The magnetic cell corresponds to the nuclear one but with a primitive symmetry. The magnetic structure has been refined down to R = 0.058 in the P2′/a′ magnetic group. The Mn^{III} moments are colinear to the b-axis and show antiparallel ordering within the layers.

Kristall- und magnetische Struktur von $TlMnF_4$, einer Verbindung mit Schichtstruktur

Inhaltsübersicht. Die Kristallstruktur und die magnetischen Eigenschaften des Fluoromanganates(III) $TlMnF_4$ wurden untersucht. Die Struktur wurde in der monoklinen Raumgruppe I2/a, Elementarzelle mit a = 539,7(2); b = 544,1(2); c = 1248,4(5) pm, β = 90,19(3)° (Z = 4) auf R/wR 0,057/0,043 verfeinert. $TlMnF_4$ zeigt eine Schichtstruktur, die durch Eckenverknüpfung von MnF_6-Oktaedern über ihre vier äquatorialen Ecken gebildet wird. Die Mn—F-Abstände innerhalb des Oktaeders liegen im Bereich von 178 bis 215 pm. Die magnetische Austauschenergie (J/k) innerhalb der Schicht wurde durch Anpassung der experimentellen Suszeptibilitätsdaten im Temperaturbereich von 10 − 300 K auf der Basis des Heisenbergmodells für quadratische Schichten zu −0,45 K bestimmt. Dreidimensionale antiferromagnetische Ordnung tritt bei 4,2(5) K ein. Die magnetische Zelle entspricht der kristallographischen, jedoch mit primitivem Translationsgitter. Die magnetische Struktur wurde auf R = 0,058 in der magnetischen Raumgruppe P2′/a′ verfeinert. Die magnetischen Momente an Mn^{III} sind colinear zur b-Achse und zeigen antiparallele Ordnung innerhalb der Schichten.

Key words: Thallium tetrafluoromanganate(III), $TlMnF_4$; crystal structure; magnetic structure

Introduction

Many manganese(III) fluorides are known to exhibit chains or layers of corner-sharing octahedra. In addition a structural distortion generally occurs, which is associated to the strong Jahn-Teller effect of Mn^{III} ($3d^4$) due to its high spin configuration.

Several types of materials appeared to be very good models for one- or two-dimensional magnetic systems. Papers dealing with magnetic properties of Mn^{III} fluorides

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built of chains of trans-$[MnF_4F_{2/2}]$ and/or trans$[MnF_2F_{2/2}(H_2O)_2]$ units have been published [1 – 3].

On the other hand $AMnF_4$ (A = K, Rb, Cs, NH_4) phases have been described as layer structures deriving from the $TlAlF_4$-type [4, 5]. The distorted (MnF_6) octahedra are connected by four equatorial vertices. More recently $CsMnF_4$ has been thoroughly investigated [7]. It is of particular interest as it is a characteristic example of a two-dimensional ferromagnet. It crystallizes in the tetragonal P4/n space group and exhibits antiferrodistortive ordering of elongated (MnF_6) octahedra. In good agreement with the Goodenough-Kanamori rules for d^4-d^4 σ-interactions, ferromagnetism has been confirmed by neutron diffraction: the Curie temperature was found to be T_C = 18.9 K; the magnetic moment was 4.04 BM.

By earlier magnetic measurements [4] a transition from a ferro- to an antiferromagnetic behavior was detected for cations smaller than Cs^+ (A = Rb^+, NH_4^+ or K^+). Thus the investigation of an intermediate member of this series such as $TlMnF_4$ seemed to be worthwhile.

Spectroscopic properties of $TlMnF_4$ have been previously mentioned but the lattice constants have only been deduced from X-ray powder patterns [4].

In the present research we describe both crystal structure of $TlMnF_4$ determined by single-crystal X-ray diffraction and magnetic structure obtained from powder neutron diffraction patterns at low temperature. We have also investigated the powder magnetic properties.

Experimental

1. Synthesis. Mn_2O_3, prepared by decomposition of manganese(II) nitrate [6], was dissolved in aqueous hydrofluoric acid (40%). Separately a Tl^I solution was obtained by dissolving Tl_2CO_3 in a similar 40% HF solution. The two solutions were mixed in such a way that the Tl : Mn molar ratio was 1 : 1. The resulting solution was maintained in a covered polyethylene vessel for several days at about 50 °C. Small dark-brown crystals were grown in those conditions.

2. Elemental analysis. Elemental analysis was carried out at CNRS Service Central d'Analyse. The metallic element concentration was determined using a multielement atomic absorption spectrometer and fluoride ions were titrated using an anion-selective electrode. The concentrations are the following:

— observed: Mn(16.40), Tl(60.80), F(21.51)%
— calculated for $TlMnF_4$ composition: Mn(16.38), Tl(60.35), F(22.67)%.

3. Structural investigation. A small brown crystal was selected for X-ray diffraction measurements on a four circle-diffractometer (Enraf-Nonius) using MoKα-radiation and a graphite monochromator. The lattice constants were refined from 25 high-angle reflections. The main experimental crystallographic data are listed in Table 1.

Table 1 Experimental crystallographic data for $TlMnF_4$

Crystal data	
Formula	$TlMnF_4$
Molecular weight	335.308
Crystal dimensions	approx. $0.1\times0.06\times0.05$ mm^3
Absorption	μ = 455 cm^{-1}, empirical correction
Space group	I2/a, Z = 4
Pseudo symmetry	Imam
Lattice constants	a = 539.7(2) pm
(MoKα)	b = 544.1(2) pm
	c = 1248.4(5) pm
	β = 90.19(3)°
Temperature	293 K
Voluminal mass	ρ = 6.07 g cm^{-3}
Data collection	
Diffractometer	4-circle, CAD4 (Enraf-Nonius)
Radiation	Mo-Kα, graphite monochromator
Scanning-type	ω-scanning
Scanning width	$(1.5 + 0.35\,\mathrm{tg}\theta)°$ and 25% on the left and right side of a reflection for background determinations
Measuring range	$2° < \theta < 30°$, ±h, +k, +l and h k $\bar{l}$
Reflections Total	888
Independent	506; $423 > 5\sigma(F_o)$
Computing	
Structure determination	Patterson methods (SHELXS-86 [8b])
Refinement	minimizing $\Sigma(\Delta F)^2$ (SHELX 76 [8a])
Scattering factors	extracted from [10]
Anomalous dispersion	extracted from [11]
Extinction coefficient	$\varepsilon = 3.5\times10^{-8}$ [8a]
R-values	R = 0.057, wR = 0.043 (31 parameters) [$w = 1/\sigma^2(F_o)$]

Lorentz-polarization correction was made and an empirical absorption correction (Psi-scans) was applied (μ = 455 cm^{-1}). 423 reflections were considered with $F_o > 5\sigma(F_o)$.

The crystal showed only small deviations from an orthorhombic symmetry Imam. This result explains why in an earlier powder work [4] the true monoclinic space group I2/a was not detected.

The structure was determined from a Patterson map and from subsequent Fourier syntheses and could be refined with

Table 2 Atomic coordinates and anisotropic thermal parameters [10^{-20} m^2] for $TlMnF_4$ (space group I2/a)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn	0.25	0.75	0.25	0.011(2)	0.010(2)	0.010(2)	0.000(2)	−0.002(2)	0.002(2)
F1	0.277(2)	0.661(2)	0.114(1)	0.034(7)	0.026(5)	0.016(7)	−0.005(5)	0.007(7)	0.002(6)
F2	0.471(2)	1.066(2)	0.214(1)	0.018(7)	0.023(6)	0.048(11)	0.003(6)	−0.014(8)	−0.016(5)
Tl	0.25	0.2332(3)	0.0	0.0307(8)	0.0204(7)	0.030(1)	0.0	−0.0032(7)	0.0

anisotropic temperature factors for each atom down to a final R = 0.057 and wR = 0.043.[2]) Final position and thermal parameters are reported in Table 2.

4. Magnetic measurements. Magnetic measurements were performed on powder sample with a SQUID magnetometer in the 2 – 300 K temperature range. The applied field ranged from 0 to 5 T. A correction for diamagnetic contribution was taken into account.

5. Neutron diffraction measurements. Neutron diffraction experiments were carried out at the high flux reactor of the Institut Laue-Langevin in Grenoble using the D1B powder diffractometer which is equipped with a large position-sensitive detector (PSD). Diffractograms were recorded with the incident wavelength λ = 252.2 pm. The powder sample was set in a vanadium container and a $4° \leq 2\theta \leq 84°$ angular domain has been covered. Patterns were registered between 1.5 and 200 K using a liquid helium cryostat. Crystallographic and magnetic structures were determined using the Rietveld profile refinement technique with the Young program [12]. The nuclear scattering lengths and the magnetic form factors were taken from reference [13] and [14] respectively.

Results and Discussion

1 Crystal structure

$TlMnF_4$ has a layer structure deriving from the $TlAlF_4$-type, i.e. formed by $[MnF_6]$ octahedra sharing their four equatorial corners (Fig. 1). As for $CsMnF_4$ the Jahn-Teller effect of the d^4 high-spin configuration leads to a strong elongation of the octahedra (Table 3). The directions of the long axes (Mn—F2 = 215 pm) constitute an antiferrodistortive arrangement within the layers. The shorter Mn—F distances correspond to bridging bonds (Mn′—F2 = 186 pm) and very short terminal bonds (Mn—F1 = 178 pm).

The layers differ from those of $CsMnF_4$ by the bridge angles Mn—F—Mn which decrease from 161.9° for $CsMnF_4$ to 146.5° for $TlMnF_4$, and by the puckering type. The layers alternate with the 12-coordinated Tl^+ ions (see. Fig. 6, Table 3).

We have recently investigated the structural and magnetic properties of the hydrates $Tl[MnF_4(H_2O)]$ and $Tl_2[MnF_5] \cdot H_2O$ [3], both showing octahedral transchain structures.

2 Magnetic behavior

The temperature dependence of the reciprocal molar susceptibility for powder samples is plotted in Fig. 2. In the investigated temperature range a linear variation is observed with a small θ_p value of −7 K. The experimental Curie constant (C_M = 2.87) is in good agreement with the usual values found for manganese(III) compounds.

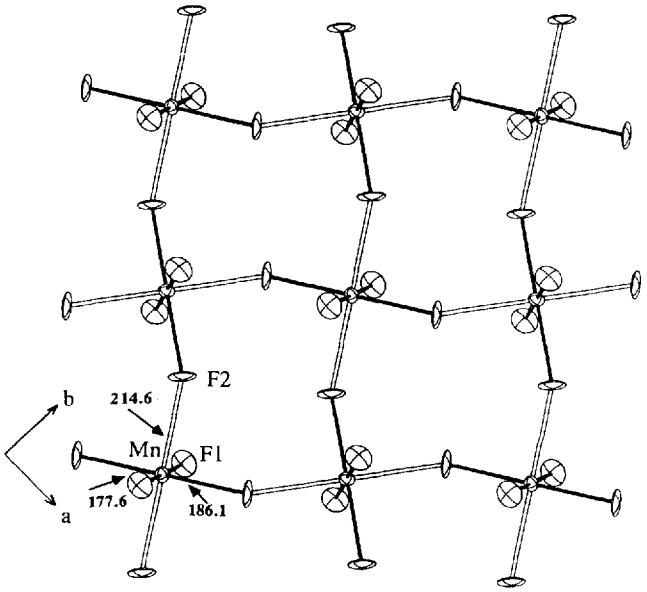

Fig. 1 Arrangement of MnF_6 octahedra in $TlMnF_4$: (a, b) plane; white double lines: elongated axes; Mn—F distances in pm (ORTEP drawing [9]: thermal ellipsoids at the 50% probability level)

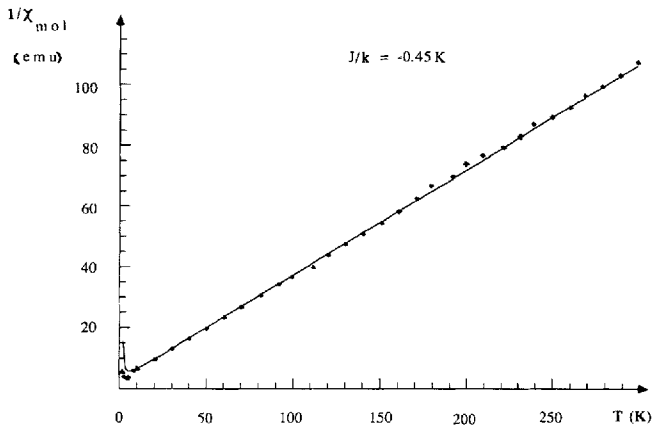

Fig. 2 Temperature dependence of the reciprocal susceptibility of $TlMnF_4$

The exchange constant between Mn atoms within a plane (J/k) has been calculated by fitting the susceptibility data to the quadratic layer Heisenberg antiferromagnetic model as described by *Lines* [15]. Fitting was based on the following equation:

$$\frac{Ng^2\beta^2}{J_{\chi(T)}} = 3\theta + \sum_{n=1}^{\infty} \frac{Cn}{\theta^{n-1}},$$

where $\theta = kT/JS(S+1)$, g is the Lande factor, N the number of spins in the lattice, Cn are coefficients calculated from the general formalism of ref. [16].

[2]) The structure factor tables have been deposited in the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information, W-7514 Eggenstein-Leopoldshafen 2, with number CSD-55 897.

This method allowed to fit the broad susceptibility maximum which experimentally characterizes two-dimensional quasi-Heisenberg antiferromagnets. It yielded an intralayer exchange constant: $J/k = -0.45$ K. The weakness of this value can account for the low value of the 3D-ordering antiferromagnetic temperature (see below).

According to Goodenough-Kanamori rules, an antiferrodistortive (MnX_6) octahedra arrangement is generally associated with a ferromagnetic behavior, whereas a ferrodistortive structural arrangement leads to antiferromagnetism. X-ray and neutron diffraction studies on $CsMnF_4$ seemed to confirm such an assumption: the antiferrodistortive arrangement observed for this material induces a bulk ferromagnetism [5]. On the other hand the magnetic J/k value obtained for $TlMnF_4$ at first sight contradicts the above rules: $TlMnF_4$ exhibits an intralayer antiferromagnetic behavior associated with an antiferrodistortive structural arrangement.

If we compare the layer structure of $TlMnF_4$ with that of $CsMnF_4$ we observe actually that the exchange angles Mn—F—Mn are quite different from each other. In $TlMnF_4$ this angle is about 146.5°, which corresponds to a deviation from the ideal angle (180°) stronger than that of $CsMnF_4$ (161.9°). In such conditions the mixtures of the d_{xz} and d_{yz} Mn^{3+} orbitals forming π-bonds with the p_x and p_y orbitals of fluorine have to be considered; these couplings which are responsible for antiferromagnetism strongly compete with the e_g-pσ-e_g interactions. This trend is in good agreement with that previously observed in other series of Mn^{III} fluorides [2].

3 *Magnetic structure*

A neutron diffraction study has been carried out down to 1.34 K (Fig. 3). The study of the temperature dependence of the intensity of some magnetic peaks in the 1.34 – 20 K temperature range has allowed to determine the 3D-magnetic ordering temperature $T_N = 4.2(5)$ K (see Fig. 4). The magnetic peaks which appear below T_N can be indexed in the nuclear cell but with a primitive lattice. The unit cell constants at 1.34 K are the following: a = 536.1(2) pm; b = 539.7(2) pm; c = 1243.5(3) pm; $\beta = 89.20(1)°$.

Various magnetic configurations have been tested to fit the observed intensities. The best result, which corresponds to a magnetic R-factor of 0.058, with $R_{magn} = 100 \times \Sigma[I_{magn}(obs) - I_{magn}(calc)]/\Sigma I_{magn}(obs)$ can be described as follows: in the magnetic cell the magnetic atoms are assigned to two different sites: Mn1 (1/4, 3/4, 1/4); Mn2 (3/4, 1/4, 3/4).

Magnetic moments of both Mn1 and Mn2 atoms appear to be colinear to the b-axis and antiparallel to each other with a value of 3.1(3) BM. The refined neutron diffraction pattern corresponding to such a hypothesis is given in Fig. 5. The expected value of the resulting magnetic moment is about 3.5 BM for a magnetic ion with S = 2. However, due to the low value of the Neel temperature this difference can be attributed to an incomplete saturation of the moment at 1.34 K. Observed and calculated intensities for such a model are collected in Table 4. We can describe therefore the magnetic structure as formed of Mn^{III} atoms antiferromagnetically coupled inside

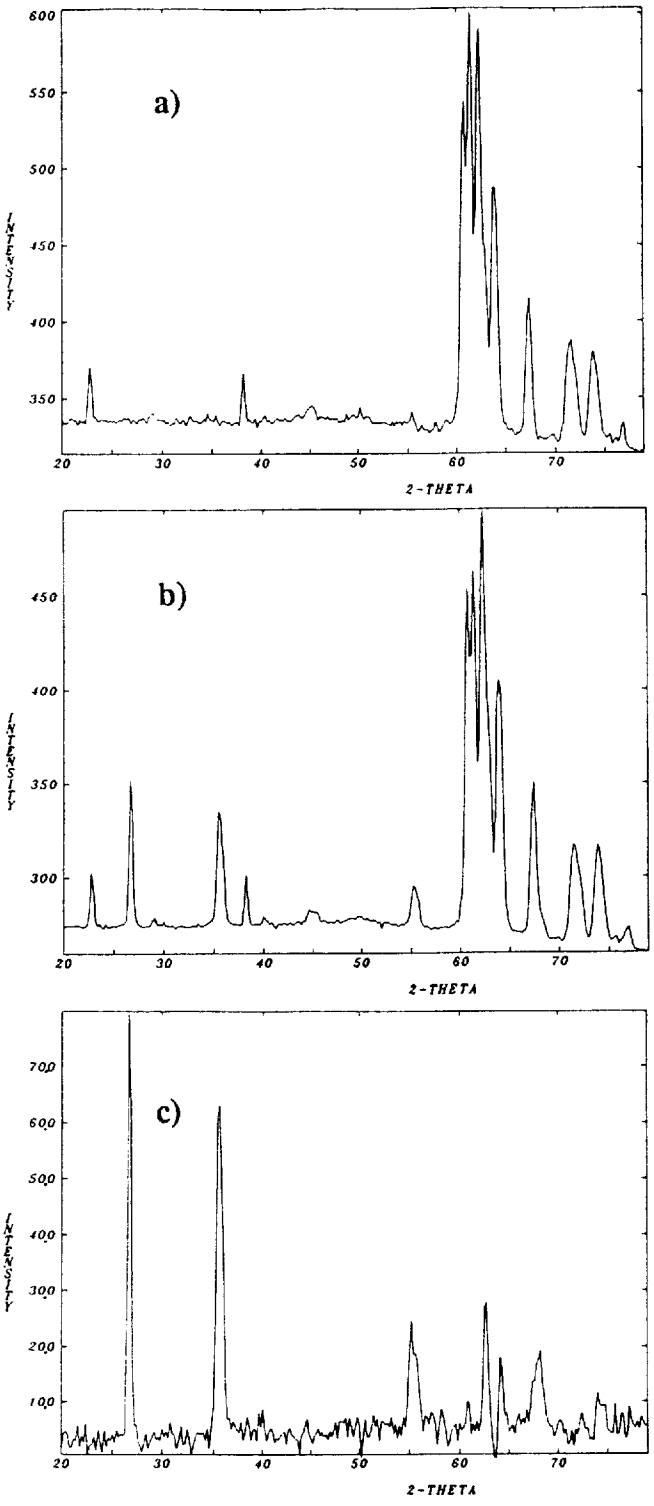

Fig. 3 Experimental neutron diffractograms of $TlMnF_4$ at T = 8 K[a]), T = 1.34 K[b]) and difference pattern[c])

Table 3 Interatomic distances [pm] and angles [deg] in $TlMnF_4$

Mn—F1	2×	177.6(10)	Tl—F1,F1[i])	2×	273(1)
Mn—F2	2×	186.1(10)	Tl—F1[j])[g])	2×	298(1)
Mn[a])—F2	2×	214.6(10)	Tl—F2[k])[l])	2×	307(1)
			Tl—F1[a])[h])	2×	322(1)
mean Mn—F		192.8	Tl—F1[k])[l])	2×	342(1)
			Tl—F2[g])[j])	2×	348(1)
F1—Mn—F2		88.5(5)			
F1—Mn—F2[b])		89.2(6)	mean Tl—F		315
F2—Mn—F2[b])		88.2(5)			
			in plane:		
Mn—F2—Mn[a])		146.5(7)	Mn · · · Mn	4×	383.2(2)
			between planes:		
			Mn · · · Mn	2×	624.2(3)

Symmetry operations: [a]) 0.5+x, 1−y, z; [b]) x−0.5, 2−y, z; [c]) 1−x, y−0.5, 0.5−z; [d]) 0.5+x, 2−y, z; [e]) 1−x, −y, −z; [f]) −x, −y, −z; [g]) 1−x, 1−y, −z; [h]) −x, 1−y, −z; [i]) 0.5−x, y, −z; [j]) x−0.5, 1−y, z; [k]) x, y−1, z; [l]) 0.5−x, y−1, −z

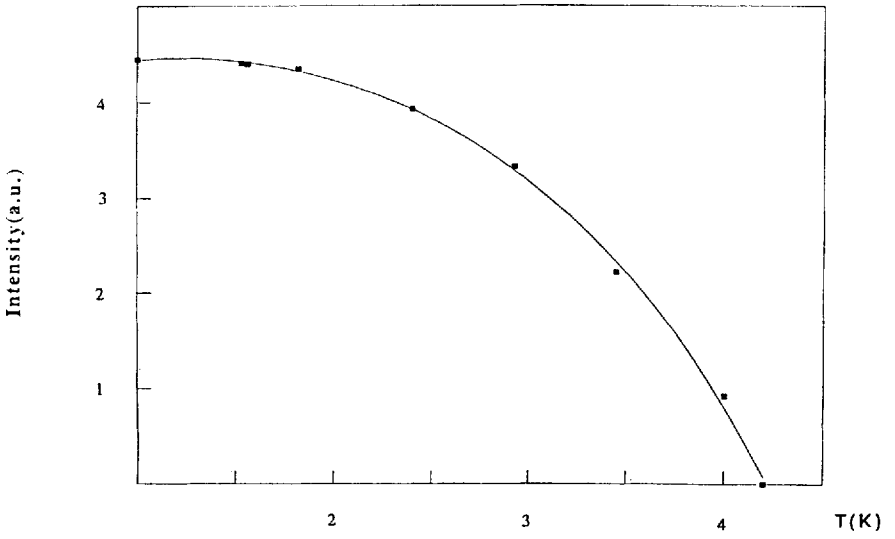

Fig. 4 Temperature dependence of the (100) magnetic peak

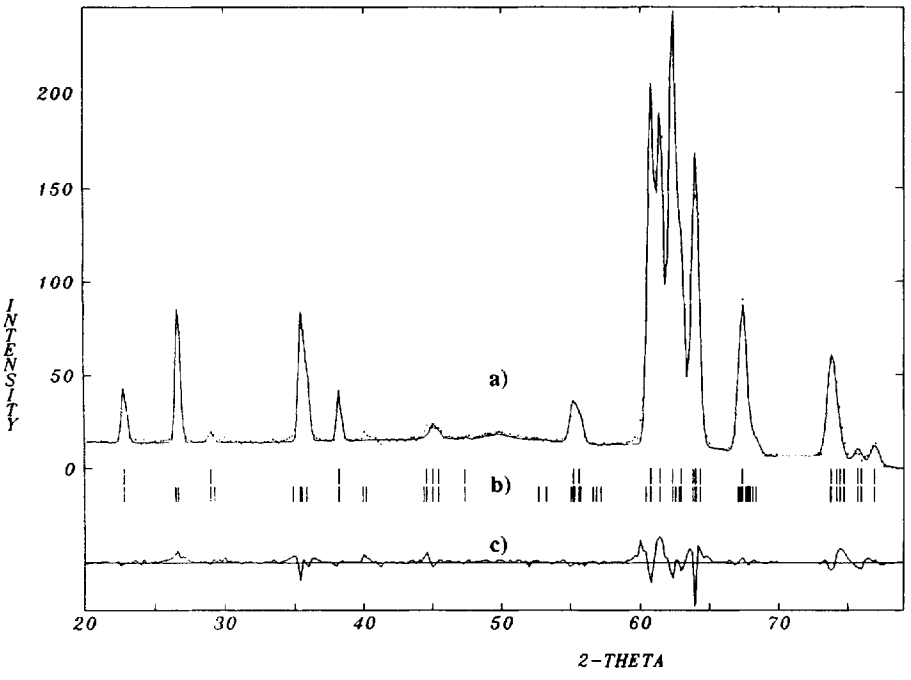

Fig. 5 Refined neutron diffraction pattern of $TlMnF_4$ at T = 1.34 K [calculated profile intensities (full line) a); positions of nuclear peaks (above) and magnetic peaks (below) b); difference spectrum c)]

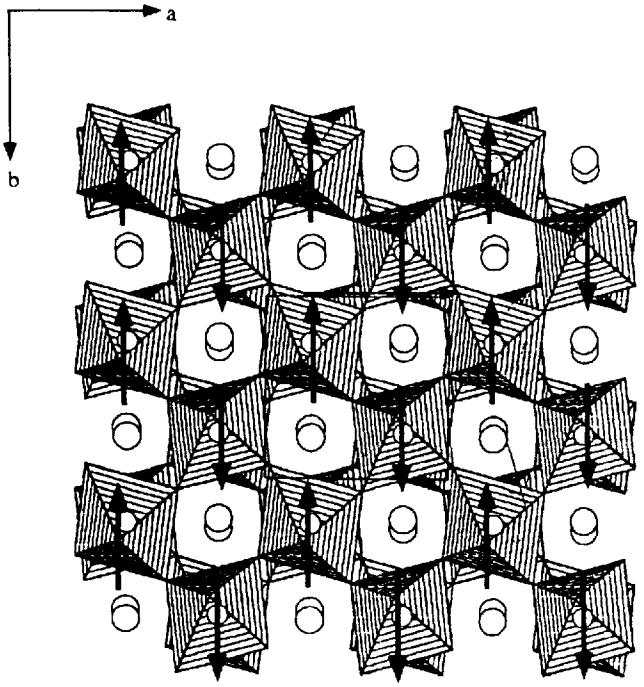

Fig. 6 Magnetic structure of $TlMnF_4$

Table 4 Observed and calculated intensities of magnetic reflections for $TlMnF_4$ at T = 1.34 K

h k l	$I_{calc.}$	$I_{obs.}$	h k l	$I_{calc.}$	$I_{obs.}$
1 0 0	3264	3716	$\bar{1}$ 0 4	553	613
1 0 2	1700	1990	1 2 0	161	172
0 1 2	1489	1453	2 1 0	631	701
$\bar{1}$ 0 2	1686	1723	1 2 2	195	201
1 0 4	562	569	$\bar{2}$ 1 2	524	539
0 1 4	850	887	$\bar{1}$ 2 2	197	206
			$\bar{2}$ 1 2	518	558

a layer and ferromagnetically coupled between two alternating planes with a compensated resulting moment as shown in Fig. 6. This scheme corresponds to the P2′/a′ magnetic group.

Conclusions

The structural and magnetic data obtained for $TlMnF_4$ point out the strong influence of the Mn—F—Mn bridging angle on the magnetic couplings: an antiferromagnetic ordering is observed instead of the ferromagnetic behavior which could be expected as a consequence of the antiferrodistortive structural ordering shown in Fig. 1. This result illustrates the competition between σ- and π-superexchange mechanisms for low bridging angles. It confirms the previous investigations on the Mn^{III} chain compounds $A_2MnF_5 \cdot xH_2O$ (A = monovalent cation; x = 0 or 1) in which the intrachain antiparallel exchange constant has been shown to decrease strongly with decreasing Mn—F—Mn bridging angles [2]. The small negative values of the intralayer exchange constant (J/k = −0.45 K) thus gives an indication of the presence of both parallel and antiparallel coupling mechanisms within a layer.

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