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MAGNETIC STRUCTURE OF THE CANTED 1*D*-ANTIFERROMAGNET $NaBaFe_2F_9$

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$NaBaFe_2F_9$ crystallizes with the Ba_2CoFeF_9 structural type (space group $P2_1/n$, $Z = 4$). In this structure, infinite *cis* double $[M_2F_9]^{3-}$ chains of corner sharing octahedra are isolated one from each other by sodium and barium ions. At 4.5 K, the cell parameters (Å) are found to be: $a = 7.3236(3)$, $b = 17.4525(7)$, $c = 5.4586(2)$, $\beta = 91.840(3)^\circ$. Antiferromagnetic interactions dominate but, below $T_N \simeq 19$ K, a parasitic ferromagnetic component appears with σ_r (4.5 K) = 0.03(1) $\mu_B \cdot$ mole^{-1}.

The magnetic structure ($C_xF_yC_z$ mode) was foreseen by the macroscopic theory of Bertaut and established from neutron powder diffraction. Using the Rietveld profile refinement method, the 4.5 K spectrum was analysed at $\lambda = 1.909$ Å ($R_{\text{Profile}} = 0.093$, $R_{\text{Nucl}} = 0.053$, $R_{\text{Mag}} = 0.126$) and the 4.5–35 K difference spectrum at $\lambda = 2.518$ Å ($R_{\text{Mag}} = 0.049$, $R_{\text{Profile}} = 0.092$). The magnetic moments on two Fe^{3+} sites, lie mainly in the (0 1 0) plane, approximately at 45° from the *a*- and *c*-axes. They form a pseudo *G*-type antiferromagnetic arrangement (μ(Fe1) = 3.60(4) μ_B; μ(Fe2) = 3.61(6) μ_B).

INTRODUCTION

NUMEROUS PHASES were found recently to crystallise with the Ba_2CoFeF_9 structural type (M^{II} = Fe, Co, Ni, Zn; M^{III} = V, Cr, Fe) [1]. The structure is built from infinite isolated *cis* double $[M_2F_9]^{3-}$ chains of corner sharing octahedra. In order to gauge precisely the nature and the strength of the magnetic interactions inside and between such double chains, we have solved first the magnetic structure of $NaBaFe_2F_9$. The crystal structures of this last phase and $NaBaCr_2F_9$ were recently described [2]. These compounds, isotopic with Ba_2CoFeF_9, result from the substitution $Ba^{2+} + M^{2+} \rightarrow A^+ + M^{3+}$; they are representative of the family ABM_2F_9 (A = Na, K; B = Ba, Pb; M^{III} = Fe, Cr, V, Ga) (3, 4). $NaBaFe_2F_9$ was chosen in reason of its high Néel temperature (19.5 ± 0.5 K), as determined by Mössbauer spectrometry [5], compared to that of $NaBaCr_2F_9$ ($T_N < 6$ K).

Experimental

A powder sample of $NaBaFe_2F_9$ was prepared, according to [3], by heating the elementary fluorides at 700°C for 10 hours.

Neutron diffraction patterns were recorded at 35 and 4.5 K on the D1A and D1B powder diffractometers of the HFR of the Laue Langevin Institute (Grenoble) (Table 1). The sample was inserted in a cylindrical vanadium can. The analysis of the 4.5 K and the difference 4.5–35 K spectra was performed with the Rietveld [6] profile refinement method, as modified by Hewat [7].

The nuclear scattering lengths and magnetic form factors were taken from [8] and [9] respectively.

Magnetization and magnetic susceptibility were measured respectively with a Foner vibrating sample magnetometer and a Faraday type balance in the 4.2–293 K temperature range.

RESULTS AND DISCUSSION

The variation of the molar magnetic inverse susceptibility χ_M^{-1} with the temperature is indicative of dominant antiferromagnetic interactions, but, even at room temperature, the Curie–Weiss law is not well obeyed (Fig. 1). Below $T_N = 19.5(5)$ K, previously determined by Mössbauer spectrometry [5], a parasitic

Table 1. Characteristics of data collection and profile refinement

	D1A	D1B
λ (Å)	1.909	2.518
Steps (°)	0.05	0.2
Data collection	$10° < 2\theta < 150°$	$6° < 2\theta < 86°$
Range studied	$2\theta < 121.80°$	$2\theta < 76.80°$
hkl triplets	580	101

ferromagnetic component appears; the remanent magnetization, measured at 4.5 K, is 0.03(1) $\mu_B \cdot \text{mole}^{-1}$. It is noteworthy that a slight accident on the χ_M^{-1} curve occurs around 90 K. This variation corresponds to the magnetic ordering of a small amount of impurity: the ferrimagnetic $Na_5Fe_3F_{14}$ chiolite ($T_N = 92$ K) [10]. It was impossible to eliminate completely the formation of this phase, especially when large quantities of $NaBaFe_2F_9$ were prepared for neutron powder diffraction. This impurity (less than 2%) was found to have very little influence on the refinement of the 4.5 K and, *a fortiori*, the 4.5–35 K difference (Fig. 2) neutron diffraction patterns. However, in a first publication on the subject [3], the presence of a larger amount of $Na_5Fe_3F_{14}$ lead us to give a wrong Néel temperature for $NaBaFe_2F_9$.

No structural phase transition of $NaBaFe_2F_9$ occurs between room temperature and 35 K. At this last temperature, large magnetic diffusion peaks, due to 1D short-range magnetic order are observed on the neutron diffraction spectra. Consequently, the background

Fig. 1. Variation of χ_M^{-1} with the temperature of $NaBaFe_2F_9$.

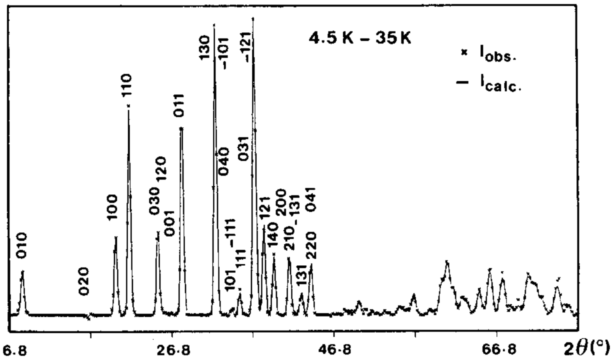

Fig. 2. Observed and calculated 4.5–35 K neutron diffraction spectra of $NaBaFe_2F_9$ at $\lambda = 2.518$ Å.

Table 2. Fractional coordinates and isotropic temperature factors in $NaBaFe_2F_9$ (*) at 4.5 K

Atom	x	y	z	B (Å^2)
Fe(1)	0.4092(6)	0.6249(3)	0.2309(8)	0.60(5)
Fe(2)	0.2698(6)	0.4195(3)	0.2620(9)	0.60(5)
Na(1)	0.3011(15)	0.0377(6)	0.7557(22)	0.72(25)
Ba(1)	0.0602(11)	0.2856(5)	0.7331(16)	1.38(21)
F(1)	0.1383(10)	0.4196(5)	− 0.0429(14)	0.93(9)
F(2)	− 0.0005(9)	0.9226(5)	0.4164(14)	0.72(9)
F(3)	0.2811(10)	0.3111(4)	0.2956(14)	0.93(9)
F(4)	0.4423(10)	0.9193(5)	0.0423(13)	0.93(9)
F(5)	0.2773(10)	0.1651(5)	0.4881(14)	0.61(8)
F(6)	0.2086(9)	0.1648(5)	− 0.0060(15)	0.61(8)
F(7)	0.2401(12)	0.0310(4)	0.2455(16)	0.72(9)
F(8)	0.4333(10)	0.2914(5)	0.8135(16)	0.61(8)
F(9)	0.4000(10)	0.4317(5)	0.5777(14)	0.72(9)

(*) – Estimated standard deviations in parenthesis
Refined cell parameters at 4.5 K. $a = 7.3236(3)$ Å; $b = 17.4525(7)$ Å; $c = 5.4586(2)$ Å; $\beta = 91.840(3)°$.

intensity is difficult to estimate and no profile analysis was undertaken.

At 4.5 K, all the new magnetic reflections are indexed in the nuclear cell; the parameters are given in Table 2. A severe overlap of the reflections occurs, even at low Bragg angles, at 1.909 Å on D1A, and the magnetic (0 1 0) reflection cannot be observed ($2\theta < 8°$). Consequently the D1A pattern was used to adjust the atomic coordinates and isotropic thermal motion factors using the magnetic vector components refined from the 4.5–35 K difference D1B diagram and inversely.

The starting set of atomic coordinates was taken from the previous single crystal X-ray structure determination [2]. Four magnetic models were sought using the macroscopic theory of Bertaut [11] from two independent symmetry elements (2_1 axis at $x = \frac{1}{4}, z = \frac{1}{4}$; n plane at $y = \frac{1}{4}$). The S_i and R_i ($i = 1, 4$) magnetic moments are taken respectively at Fe1 and Fe2 sites; their corresponding atomic coordinates can be obtained from Table 2 and Table 3. For each sublattice ($M = \mathrm{S, R}$) the linear combinations of the moments: $F = M_1 + M_2 + M_3 + M_4$, $G = M_1 - M_2 + M_3 - M_4$, $C = M_1 + M_2 - M_3 - M_4$, $A = M_1 - M_2 - M_3 + M_4$ give the ferromagnetic or antiferromagnetic modes of coupling. The base vectors, in the irreducible representation of $P2_1/n$, lead to four modes which are suitable with Fe1 and Fe2 sublattices.

Only the Γ_1 magnetic mode ($C_xF_yC_z$) allows to fit the observed and calculated intensities. The reliability R factors establish as follows:

	D1A	D1B
F^2	0.060	0.049
Nuclear	0.053	–
magnetic	0.126	0.049
profile	0.093	0.092
Weighted profile	0.106	0.083
expected	0.034	0.018

The final atomic coordinates, thermal motion factors and magnetic components are listed in Tables 2 and 3. The atomic positions do not differ markedly at 4.2 and 300 K. Within the accuracy of the refinement, the ferromagnetic component along b is very weak, as given by the magnetic measurements.

The magnetic moments at Fe1 and Fe2 sites lie mainly in the (0 1 0) plane at ~ 45° from the a- and c-axes (Fig. 3). They point in the direction of the upper or lower Fe^{3+} neighbours in the chain. Their relative orientation is almost antiferromagnetic like in a G-type antiferromagnet and this is consistent with the susceptibility measurements at high temperature.

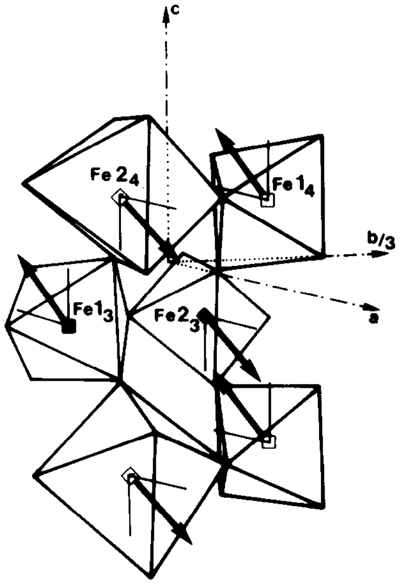

Fig. 3. Orientation of the magnetic moments in a double $[M_2F_9]^{3-}$ chain of $NaBaFe_2F_9$.

Table 3. Coordinates of the magnetic Fe^{3+} ions ($M_i = S_i$, R_i), refined magnetic moments of S_1 ($Fe1_1$) and R_1 ($Fe2_1$) at 4.5 K and irreducible representation of M in the $P2_1/n$ space group

Coordinates				
M_1	x	y	z	
M_2	$-x$	$-y$	$-z$	
M_3	$1/2+x$	$1/2-y$	$1/2+z$	
M_4	$1/2-x$	$1/2+y$	$1/2-z$	
Moment (μ_B)				
	M_x	M_y	M_z	M
S_1	2.49(3)	0.02(7)	−2.51(3)	3.60(4)
R_1	−2.64(3)	0.33(9)	2.36(4)	3.61(6)
Mode				
$\Gamma_1(++)$	C_x	F_y	C_z	
$\Gamma_2(+-)$	G_x	A_y	G_z	
$\Gamma_3(-+)$	A_x	G_y	A_z	
$\Gamma_4(--)$	F_x	C_y	F_z	

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