Magnetic Structure of $NaCoF_3$

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The room-temperature (paramagnetic) structure of $NaCoF_3$ has orthorhombic symmetry ($Pbnm$-D_{2h}^{16}). It is found, using neutron diffraction, that this compound undergoes a magnetic transition at $T_n \sim 74$ °K to an antiferromagnetic mode of the type G. Magnetic measurements showed that this mode was accompanied by a weak ferromagnetic component. It is found that in order to comply with symmetry, one must interchange a and b (the cell edges) previously reported by Rudorff.

I. INTRODUCTION

The structure of the compound $NaCoF_3$ has been investigated by several authors, using x-ray,[1,2] nuclear magnetic resonance,[3] and optical absorption[4] measurements. Rudorff *et al.*[1] found that the room-temperature structure of $NaCoF_3$ belongs to the orthorhombic space group $Pbnm$ ($a = 5.42$ Å, $b = 5.60$ Å, $c = 7.79$ Å). Okazaki *et al.*,[2] on the other hand, found that it belongs to the space group $P2_12_12_1$. Petrov *et al.*[3] reported that $NaCoF_3$ does not become antiferromagnetic down to 77 °K. Pizarev *et al.*[4] reported a Néel temperature of ~35 °K. We report here the results of neutron powder diffraction and magnetic susceptibility measurements undertaken at the IRR-2 (Israel Research Reactor 2) and the Weizmann Institute of Science in order to determine the magnetic structure and the Néel temperature in $NaCoF_3$.

II. EXPERIMENTAL

The material $NaCoF_3$ was precipitated from a mixture of boiling solution of hydrated cobaltous chloride and of sodium fluoride. Prior to the mixing, the sodium fluoride solution was acidified with hydrofluoric acid. The precipitate was dried in a vacuum oven at 200 °C for about 2 h. The final product was a pink-violet powder. The gravimetric analysis of the dried powder yielded Co – 42.46%, F – 40.0% (calculated: Co – 42.42%. F – 41.09%).

Neutron diffraction patterns of $NaCoF_3$ at room, liquid-nitrogen, and liquid-helium temperatures are shown in Fig. 1. The cryostat with no sample in it exhibits two aluminum reflections (111) at $2\theta = 25.5°$, which amounts to about 50% of the reflection in Fig. 1 and (200) at $2\theta = 29.5°$, which amounts to about 80% of the reflection appearing in Fig. 1. The reflections (011) and (101) were not resolved with 1.03 Å neutrons (Fig. 1). The intensity I (011, 101) of the magnetic reflection of the (011, 101) doublet was measured as a function of temperature and is shown in Fig. 2. A transition temperature of ~74 °K was obtained. The doublet (011, 101) was separated, using long-wavelength neutrons (~2 Å). The difference pattern of this doublet between liquid-helium temperature (antiferromagnetic state) and liquid-nitrogen temperature (paramagnetic state) is shown in Fig. 3. An intensity ratio of $I(011/I(101) \sim \frac{1}{3}$ was obtained.

The magnetization of a sample of the same material was measured as a function of temperature in a vibrating sample magnetometer (VSM). The transition temperature obtained from these measurements was ~74 °K. The measurements show also that the sample has a weak ferromagnetic component in the antiferromagnetic region.

III. RESULTS AND DISCUSSION

According to Rudorff *et al.*,[1] the structure of $NaCoF_3$ belongs to the orthorhombic space group $Pbnm$-D_{2h}^{16} with the magnetic Co^{++} ions occupying the special positions 4b. We have worked out the conditions limiting possible magnetic reflections for the different sites in $Pbnm$ for the different modes of magnetic structure and listed them in Table I. The appearance of the magnetic reflection (011, 101) in the 4.2 °K diffraction pattern indicates that the spin arrangement is according to mode G, whereas the intensity ratio $I(011)/I(101) \sim \frac{1}{3}$ indicates that it is G_y.

The magnetic modes derived from the space group $Pbnm$ for the positions 4b are given in Table II. Modes that belong to the same irreducible representation are listed in the same row.

The weak ferromagnetic component observed in the VSM measurement is, according to Table II, inconsistent with a magnetic structure G_y. This discrepancy is removed if we interchange a and b, i.e., $a = 5.60$ Å, $b = 5.42$ Å, and $c = 7.79$ Å; or if one wants to keep the convention $a < b < c$, the space group should be taken as $Pnam$. This change means that the line (h, k, l) becomes now (k, h, l). The reflections reported by Rudorff *et al.*,[1] indexed this way, remain consistent with the space group $Pbnm$.[6] The experimental results in the new notation become $I(011)/I(101) \sim 3$, which yields G_x for the magnetization which is consis-

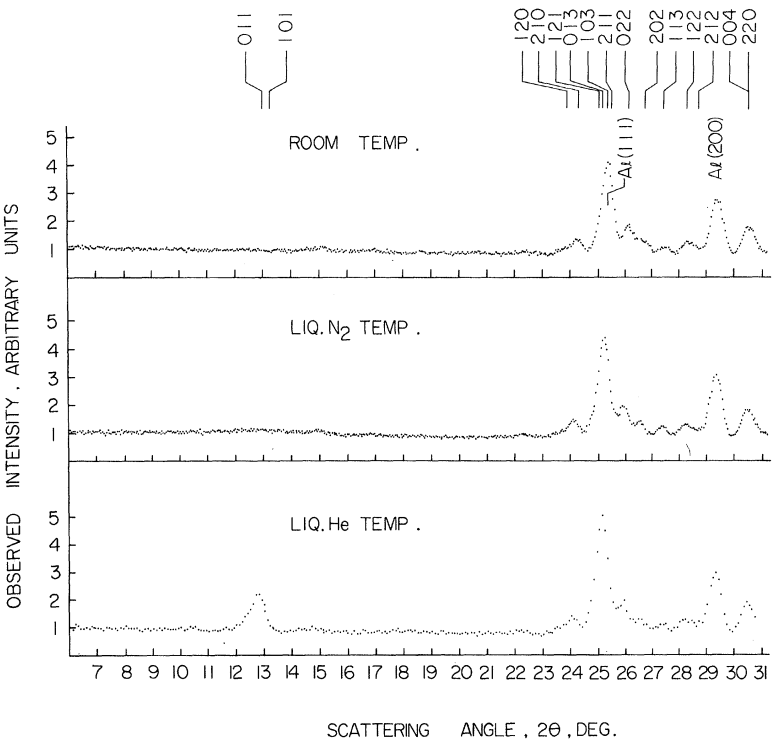

FIG. 1. Observed neutron ($\lambda \sim 1.03$ Å) diffraction patterns of $NaCoF_3$.

tent with a ferromagnetic component F_z in the z direction.

The pair of modes G_x and F_z is found in many magnetic compounds with this type of symmetry.[7,8] In these compounds, the antiferromagnetic axis is generally parallel to the shorter edge of the basal plane. In $NaCoF_3$, however, we found the antiferromagnetic axis parallel to the longer edge of the basal plane.

Our treatment of the magnetic modes was based on the assumption that *Pbnm* is the space group of $NaCoF_3$. A comment regarding Rudorff's[1] and Okazaki's[2] assignments of *Pbnm* and $P2_12_12_1$ may therefore be in place here. The space group *Pbnm* requires that $h0l$ reflection be present only with $h+l=2n$ and that $0kl$ have $k=2n$. Rudorff lists reflection 012 (very weak), 013 (medium), 023 (very weak) as present, thus violating in the first two instances the extinction condition on $0kl$. If the a and b axes are interchanged as we propose,

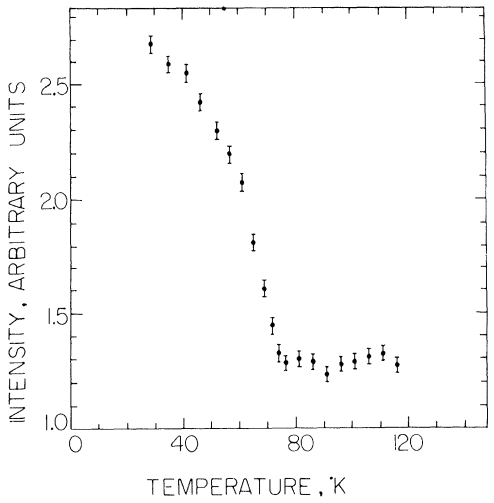

FIG. 2. Temperature dependence of the intensity of the (011, 101) magnetic reflection in $NaCoF_3$.

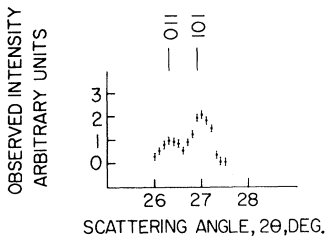

FIG. 3. Difference pattern of the doublet (011, 101) between liquid-helium temperature and liquid-nitrogen temperature at wavelength of 2.0 Å.

TABLE I. Allowed magnetic reflections in $Pbnm$-D_{2h}^{16}.

Site	Reflection	Condition set on	Magnetic mode[a,b] F	G	A	C
$4a, 4b$	hkl	$h+k$	+	−	+	−
		l	+	−	−	+
	$0kl$	k	+	−	+	−
	$h0l$	$h+l$	+	+	−	−
$4c$	$h00$	h	+	+	−	−
	$0k0$	k	+	−	+	−
	$00l$	l	+	°	−	•

[a]The magnetic modes F, G, A, and C are defined in Ref. 5.

[b]+even; −odd; °not allowed.

the rule $h+l=2n$ is now violated for the first and the third reflections. This raises a question of the validity of Rudorff's assignment of $Pbnm$ (and our assignment of $Pnam$). This question cannot be settled with the data available to us. As already mentioned above, according to Okazaki *et al.*[2] the correct space group is $P2_12_12_1$.[6] The transformation properties of the magnetic modes under $P2_12_12_1$ are the same as under the respective twofold screws of $Pbnm$ and Table II is left unchanged. Our conclusion that the antiferromagnetic axis is parallel to the longer edge of the basal plane in $Pbnm$ is therefore also valid for $P2_12_12_1$.

TABLE II. Allowed magnetic modes derived from the paramagnetic space group $Pbnm$ for the positions $4b$.

A_x, G_y, C_z
F_x, C_y, G_z
C_x, F_y, A_z
G_x, A_y, F_z

Comparison of the intensity of the magnetic reflection $I(011, 101)$ to that of $NaNiF_3$ and $YFeO_3$ yields the following relations for the magnetic moments: $\mu_{Co^{++}} \sim 1.7\,\mu_{Ni^{++}}$ and $\mu_{Co^{++}} \sim 0.72\,\mu_{Fe^{++}}$, which is in fair agreement with the "spin only" values.[9]

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[6]According to Okazaki *et al.* (Ref. 2), the space group is $P2_12_12_1$. This, however, does not change the conclusion mentioned above. It is interesting to note that the space group $P2_12_12_1$ has no mirror planes (as $Pbnm$ has) and will therefore allow a magnetoelectric effect (which is not allowed in $Pbnm$).

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