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Magnetic structure of cobalt formate dihydrate : a single crystal determination

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Résumé. — L'étude par diffraction de neutrons non polarisés d'un monocristal de formiate de cobalt montre que sa structure magnétique est décrite par un mode antiferromagnétique A_{xz} pour les ions A et B. Le couplage entre ces deux types d'ions est ferromagnétique. Ces résultats, en accord avec ceux d'une étude par RMN, conduisent à une structure magnétique différente de celle précédemment déterminée pour un échantillon polycristallin deutéré à une température très inférieure à T_N .

Abstract. — An unpolarized neutron diffraction study of a single crystal of cobalt formate $\text{Co}(\text{COOH})_2 \cdot 2 \text{H}_2\text{O}$ indicates that the magnetic structure is described by an antiferromagnetic mode A_{xz} for both the A and B ions. The coupling between these two types of ions is ferromagnetic. These results are consistent with the NMR study but not with the previous determination of the magnetic structure on a powdered deuterated sample at a very low temperature far below T_N .

1. Introduction. — The series of isomorphous formates of transition metal $\text{M}(\text{HCOO})_2 \cdot 2 \text{H}_2\text{O}$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) has been studied by neutron diffraction [1], [2]. The experiments were performed on polycrystalline deuterated samples from which the magnetic structures were derived. Recently [3], an NMR study on single crystals of the cobalt formate dihydrate concluded a different magnetic structure to that previously reported. Therefore a redetermination of the magnetic structure of this salt has been undertaken by neutron diffraction experiments on a hydrated single crystal.

The dihydrated formates of the transition group metals belong to the monoclinic space group $\text{P}_{21/c}$ with four formula units per unit cell. The crystallographic structure of the cobaltous salt has not been determined but it seems a good approximation to assume that the atomic parameters of cobaltous formate are almost the same as for manganous formate [4, 5]. Concerning the magnetic ions, the structure can be schematized as in figure 1. In the monoclinic unit cell the four cobalt atoms are on two sites : the A ions at $(0, 0, 0)$ (A_1) and at $(0, 1/2, 1/2)$ (A_2) and the B ions at $(1/2, 0, 1/2)$ (B_1) and at $(1/2, 1/2, 0)$ (B_2). The A ions are magnetically linked only in the (100) plane by exchange interaction *via* C-O-O bonds and no direct coupling exists between the planes, since the A ions are only coupled to B ions which are not coupled together. The system

Fig. 1. — Schematic representation of the structure of Co formate.

then can be described by a stacking of plane of A ions separated by paramagnetic planes of B ions.

In the two proposed models the magnetic cell is identical to the chemical cell and the ordering consists of an antiferromagnetic mode noted A and a ferromagnetic mode F for both A and B ions.

From the previous powder diffraction experiments, the antiferromagnetic component has been found to be parallel to the monoclinic b axis (A_y) and the ferromagnetic component to be in the x - z plane (F_{xz}) [1, 2], while, from NMR the model consists of an antiferromagnetic component A_{xz} and a ferromagnetic component F_y [3]. Besides, powder neutron diffraction experiments lead to an antiferromagnetic coupling between A and B ions whereas NMR results are consistent with a ferromagnetic coupling.

2. Experiments and results. — Single crystals of cobalt formate dihydrate have been grown by a slow evaporation method as described in [3]. The crystal used has the form and size indicated in figure 2. Neutron diffraction experiments were performed at the reactor Siloe of the CEN-Grenoble using a double axis spectrometer. The crystal was placed inside a cryostat which enables temperatures to be controlled in the range 300 to 1.5 K.

Fig. 2. — Size and morphology of the simple crystal used in neutron diffraction experiments.

Nuclear Bragg peak intensities have been measured at $T = 16$ K i.e. above the Néel temperature $T_N = 5.1$ K. The comparison of these intensities with the square of the structure factors calculated with the atomic positions of manganese formate leads to a scaling factor $K = 1.83 \times 10^{-3}$ and a reliability factor $R = 0.13$. The calculated and observed intensities are listed in table I. The agreement is satisfactorily good indicating that too severe extinction effects are not present in spite of the large size of the crystal.

If the magnetic structure is described by an anti-

Table I. — Normalized nuclear intensities (in barn/unit cell) measured at $T = 16$ K compared with the calculated values using the atomic positions of the manganese formate.

hkl	Observed F^2	Calculated F^2
002	12.4	11.6
100	4.0	4.3
200	18.3	16.2
300	5.5	5.0
102	6.9	6.0
202	11.8	14.2
020	17.9	14.8
210	45.8	51.0
$\bar{1}10$	1.9	1.7
$\bar{2}02$	1.2	1.16

ferromagnetic mode A and a ferromagnetic mode F , the magnetic structure factor can be expressed by

$$F = [A_A \pm A_B e^{i\pi(h+k)}] [i - e^{i\pi(k+l)}] + [F_A \pm F_B e^{i\pi(h+k)}] [i + e^{i\pi(k-l)}]. \quad (1)$$

Under the hypothesis that the dominant term of the Hamiltonian is a bilinear term, the components A and F must be mutually perpendicular. Therefore the magnetic intensities which appear on reflections characterized by $k + l = 2n + 1$ depend only on the antiferromagnetic component A , whereas reflections with $k + l = 2n$ depend only on the ferromagnetic component.

As in the ordered state there is no increase of the intensity of the reflections with $k + l = 2n$ we can conclude that the ferromagnetic component F is too weak to be detected in an unpolarized neutron experiment ($\mu_F \leq 0.7 \mu_B$).

Some reflections corresponding to $k + l = 2n + 1$ were measured at $T = 1.5$ K. They indicate that the main part of the moment is the antiferromagnetic mode A .

The observation of the (010) reflection indicates unambiguously that the AF component lies in the (a, c) plane (A_{xz}). The intensity of an antiferromagnetic reflection (hkl) is given by

$$I(h, k, l) = (0.27)^2 f^2(h, k, l) \times \sin^2 \alpha_{hkl} 4[A_A \pm A_B e^{i\pi(h+k)}]^2 \quad (2)$$

where $f(h, k, l)$ is the form factor of the Co^{2+} ions [6], α is the angle between A_A or A_B and the scattering vector, the positive sign in (2) corresponds to a ferromagnetic coupling of A and B ions and the negative sign to an antiferromagnetic coupling.

The best agreement between observed and calculated intensities is obtained for a ferromagnetic coupling of A and B ions and a moment direction making an angle of $35 \pm 5^\circ$ with the c axis. The components A_A and A_B are respectively equal to

$A_A = 2.19 \pm 0.5 \mu_B$ and $A_B = 0.71 \pm 0.5 \mu_B$. The observed and calculated intensities are compared in table II.

Table II. — *Magnetic intensities (in barn/unit cell) compared with the calculated values*

<i>hkl</i>	<i>I</i> Obs. (barn)	<i>I</i> Cal. (barn)
—	—	—
001	0.44 ± 0.12	0.47
003	0.47 ± 0.13	0.41
101	0.13 ± 0.11	0.14
201	0.55 ± 0.13	0.47
$\bar{1}01$	0.47 ± 0.13	0.56
$\bar{2}01$	1.90 ± 0.20	1.90
010	0.67 ± 0.15	0.60
$\bar{1}10$	1.80 ± 0.19	1.73

$$A_A = 2.19 \pm 0.50 \mu_B$$

$$A_B = 0.71 \pm 0.50 \mu_B$$

3. **Discussion.** — The results of this neutron diffraction experiment on single crystal cobalt formate dihydrate are consistent with those of a NMR study but not with those obtained from neutron diffraction on deuterated powder samples at 0.4 K. NMR and neutron diffraction on a hydrated single crystal both

lead to an antiferromagnetic mode A_{xz} in which the moments make an angle of 35° with the *c* axis. A ferromagnetic component is deduced from NMR but its value is too small to be measured in an unpolarized neutron experiment. The moment value and the ratio of magnetization of A and B ions derived from the two experiments are consistent within the limits of experimental accuracy. The coupling between the A and B ions is ferromagnetic in the two determinations. The magnetic structure of cobalt formate dihydrate at temperature higher than 1.3 K is described by the mode $A_{xz} F_y$ magnetic group $P_{21/c}$ and a ferromagnetic coupling between A and B ions. The observed value of the magnetic moment of Co^{2+} ions ($2.2 \mu_B$) is rather small and leads for an effective spin value $S = 1/2$ to a *g*-factor ($g = 4.4$) comparable to that ($g = 4.7 \mu_B$) derived from susceptibility experiment [7] performed in the temperature range 10 to 20 K. The reduction of the moment value may be explained in cobalt formate by the effect of the spin-orbit coupling and the crystal field energy which give rise to very anisotropic *g* tensor and small *g* value [8, 9].

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