LETTER TO THE EDITOR

CRYSTALLOGRAPHIC AND MAGNETIC STRUCTURE OF RbCoCl$_3$ · 2 D$_2$O

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The crystallographic and magnetic structure of RbCoCl$_3$ · 2 D$_2$O were determined mainly by means of neutron diffraction measurements. Below T_N = 2.79 K the magnetic moments are ordered in a canted antiferromagnetic pattern. A metamagnetic phase transition is observed at unusually small field values (H = 18 Oe at T = 2 K).

1. Introduction

The interpretation of the magnetic behaviour of the linear-chain antiferromagnet RbCoCl$_3$ · 2 H$_2$O (T_N = 2.97 K) is severely hampered by the lack of knowledge about the orientation of the magnetic moments in the ordered phase. In a previous paper on the results of dynamic-susceptibility measurements [1] a magnetic order within the chains was proposed similar to that in CsCoCl$_3$ · 2 aq. (aq. = H$_2$O, D$_2$O) [2,3], i.e. a canted antiferromagnetic ordering with a net ferromagnetic moment along the chain direction (c-axis). The relative orientation of the ferromagnetic components was assumed to be parallel within a bc-plane and antiparallel in adjacent bc-planes. The same canted antiferromagnetic model (with ferromagnetic components close to the c^*-direction) has been used by McElearney and Merchant [4] to analyse the results of their zero-field susceptibility and heat-capacity measurements. They conclude that the intrachain exchange inter-

action is predominantly antisymmetric, and that consequently the angle between successive moments is almost 90°.

During the past years we have investigated RbCoCl$_3$ · 2 H$_2$O and the deuterated compound with a variety of experimental techniques in order to obtain a more complete picture of the magnetic properties. In this paper we report on the magnetic structure of RbCoCl$_3$ · 2 D$_2$O (T_N = 2.79 K), which was determined by neutron diffraction experiments and additional susceptibility and NMR measurements.

2. Experimental results

The powder sample was prepared from single crystals grown at 35°C from a solution of CoCl$_2$ and RbCl (molar ratio 4 : 1) in D$_2$O and DCl (20%) by slow evaporation.

The neutron diffraction experiments were performed on the powder diffractometer installed at the HFR at Petten. The diffractometer was used in its standard operation mode, i.e. with a Cu (111) mono-

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chromator yielding a neutron wavelength λ = 2.573 Å, a pyrolytic graphite filter and 30' horizontal collimators in front of the monochromator and the detector. Powder diffraction patterns were recorded at $T \approx$ 300 K, 4.2 K and 1.2 K in the range 0.02 Å^{-1} < $\sin \theta / \lambda$ < 0.36 Å^{-1}. The first two diagrams were used to complement and extend the previous X-ray structure determination at 300 K [5], whereas the magnetic structure in the antiferromagnetic phase was derived from the latter diagram. For the structure refinements, Rietveld's profile-analysis method [6] was applied with the following values for the scattering lengths [7]: 0.708 (Rb), 0.250 (Co), 0.958 (Cl), 0.6672 (D) and 0.5803 (O), in units 10^{-12} cm. For the refinement of the magnetic structure the Co^{2+} form factor given by Watson and Freeman [8] was used.

In the analysis of the diagram recorded at 300 K, the starting values for the cell parameters and the fractional coordinates of the heavy atoms were taken from the X-ray structure determination of the hydrated compound at room temperature [5]. To obtain adequate starting values for the deuterium positions, it was assumed that deuterium bonds exist between the oxygen and chlorine ions. In that case the O—Cl distance should be about 3.2 Å and the D—O—D bonding angle approximately 110°. Only two chlorine neighbours appear to satisfy these conditions.

One of these belongs to a neighbouring chain in the bc-plane, the other one to the nearest CoO₂Cl₄-octahedron within the chain. The above criteria have also been used by McElearney and Merchant to indicate the most probable hydrogen-bond pattern in the hydrated compound [4]. The expected isomorphism with RbCoCl₃ · 2 H₂O (space group C 2/c) was confirmed in the refinement procedure, which yielded the final structural parameters listed in table I. The coordinates of the heavy atoms are in good agreement with the X-ray results [5], with the exception of the y-coordinate for Rb which must be negative (cf. table I in ref. [5]).

The analysis of the diffraction pattern recorded at 4.2 K shows that the structure is the same as at 300 K, and that the contraction of the unit cell between 300 and 4.2 K is slightly anisotropic: $\Delta a/a$ = 0.010, $\Delta b/b$ = $\Delta c/c$ = 0.006 (cf. table I).

In the powder diagram recorded at 1.2 K two weak additional peaks are observed at small scattering angles. These magnetic reflections may be indexed as ($\bar{1}01$) and (101). A comparison with the magnetic space groups that are compatible with the crystallographic space group C 2/c shows that only two of those, viz. C_p 2/c and C_p 2'/c, lead to reflections with both $(h + k)$ and l odd. Refinement computations were carried out for both cases and the most probable structure was selected on basis of the final magnetic R-

Table I

Structural parameters of RbCoCl₃ · 2 D₂O at room temperature and at 4.2 K. Standard deviations based on statistics only are given in parentheses, in units of the last decimal place. R is defined in terms of observed and calculated intensities Y_i : R = 100 × $\Sigma_i |Y_i^{obs} - Y_i^{calc}| / \Sigma_i Y_i^{obs}$.

	300 K	C 2/c		4.2 K	C 2/c	
	x	y	z	x	y	z
Co	0	0	0	0	0	0
Rb	$\frac{1}{4}$	$-\frac{1}{4}$	0	$\frac{1}{4}$	$-\frac{1}{4}$	0
Cl(1)	0	0.200(2)	$\frac{1}{4}$	0	0.203(2)	$\frac{1}{4}$
Cl(2)	0.1403(4)	0.243(2)	0.0517(9)	0.1428(4)	0.243(2)	0.0541(8)
D(1)	0.1042(8)	−0.266(2)	0.280(1)	0.1038(7)	−0.271(2)	0.283(1)
D(2)	0.0900(7)	−0.420(3)	0.123(2)	0.0904(5)	−0.431(2)	0.115(1)
O	0.0885(10)	−0.273(3)	0.160(2)	0.0965(8)	−0.274(3)	0.165(2)
a	15.724(2) Å			15.563(2) Å		
b	5.6283(6) Å			5.5957(5) Å		
c	8.748(1) Å			8.6961(8) Å		
β	118.326(7)°			118.444(6)°		
R	6.5			6.2		

Table II
Ordered magnetic moments of $RbCoCl_3 \cdot 2 D_2O$ and
$CsCoCl_3 \cdot 2 D_2O$ [3]. $H = 0$, $T = 1.2$ K.

$RbCoCl_3 \cdot 2 D_2O$		$CsCoCl_3 \cdot 2 D_2O$	
μ_{Co}	2.4(2) μ_B	μ_{Co}	2.5(2) μ_B
μ_b	2.3(1) μ_B	μ_c	2.4(2) μ_B
μ_{ac}	0.7(3) μ_B	μ_a	0.7(2) μ_B
μ_a	−0.4(11) μ_B		
μ_c	0.3(6) μ_B		

factor. The best fit was obtained with space group $C_p 2'/c$ ($R = 23$, to be compared with $R = 51$ for $C_p 2/c$) and the magnetic moment components listed in table II. Further evidence for the occurrence of the magnetic space group $C_p 2'/c$ was obtained from NMR measurements. Symmetry considerations, combined with the experimental result that the local field is zero at the Rb positions and unequal to zero at the Co sites, permit the groups $C_p 2'/c$ and $C 2'/c'$. The latter group has to be rejected on the basis of the neutron diffraction results.

The small component μ_{ac} of the magnetic moment in the ac-plane was calculated from the total moment and its component along the b-axis (table II). Due to the large uncertainty in the components μ_a and μ_c the direction of μ_{ac} cannot be determined from the powder-diffraction data. Additional dynamic-susceptibility measurements [9] indicate that the principal axes of

Fig. 1. Magnetic structure of $RbCoCl_3 \cdot 2 D_2O$.

the susceptibility tensor in the ac-plane are very close to the crystallographic a and c^*-axes, in accordance with the location of the principal axes in the hydrated compound [4,9]. The direction c^* where the susceptibility reaches its maximum value, may be identified with the direction of μ_{ac}. The combination of the susceptibility and diffraction results yields the magnetic structure in zero field, shown in fig. 1. In each chain a canted antiferromagnetic ordering exists, with a canting angle $\phi = (17 \pm 5)°$ between the moments and the b-axis, and ferromagnetic alignment of the components μ_{ac}. The resulting ferromagnetic moments of the chains are aligned parallel in the bc-plane, whereas the relative orientation in adjacent bc-planes is antiparallel.

Dynamic-susceptibility measurements on $RbCoCl_3 \cdot 2H_2O$ display the same characteristics as were found for the deuterated compound so it may be expected that the magnetic structures of both materials are the same.

3. Discussion

The present determination of the magnetic structure shows that $RbCoCl_3 \cdot 2 D_2O$ is not a linear-chain system with almost exclusively Dzyaloshinsky–Moriya exchange interactions, in contrast to the conclusion of McElearney and Merchant for the hydrated compound. The magnetic structure is indeed very similar to that of $CsCoCl_3 \cdot 2 D_2O$ [3]. In both systems the canting angle is about 17°, and the magnetic moments of the Co^{2+}-ion are equal within the experimental uncertainty (table II). On basis of the present results it is not possible to distinguish between the two possible orientations of the magnetic moment with respect to the ligand octahedron. However, on the analogy of the magnetic structure of $CsCoCl_3 \cdot 2H_2O$ [2] it is expected that the moment is oriented along the direction close to the $Co-O-Cl_{(2)}$ plane. In this context it is noteworthy that in the compounds $CsFeCl_3 \cdot 2 H_2O$ and $RbFeCl_3 \cdot 2 H_2O$ the magnetic moments are aligned almost parallel to the $Fe-Cl_{(1)}$ direction. Generally, when Co^{2+} and Fe^{2+} ions are exposed to the same ligand field their magnetic moments are perpendicular to each other [10].

In spite of the similarity between the magnetic structures of $CsCoCl_3 \cdot 2$ aq. and $RbCoCl_3 \cdot 2$ aq. in zero field, there is a striking difference between their

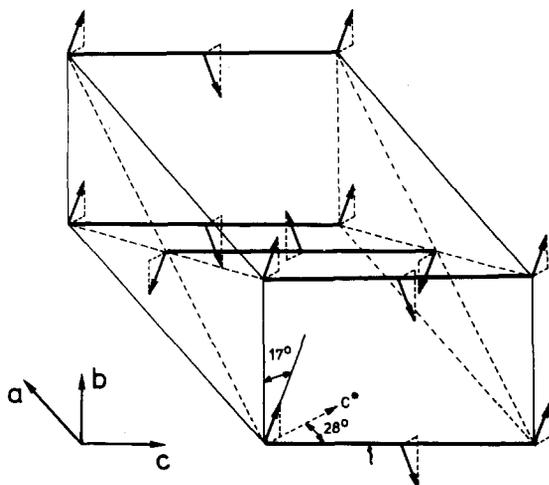behaviour in a magnetic field applied along the weak ferromagnetic component. In $RbCoCl_3 \cdot 2 H_2O$ and $RbCoCl_3 \cdot 2 D_2O$ a metamagnetic phase transition is observed at unusually small field values, $H = 37$ Oe and 18 Oe, respectively, at $T = 2$ K. At the transition, the magnetic moments with a component μ_{c*} anti-parallel to the field are reversed, which results in a parallel alignment of μ_{c*} in adjacent bc-planes. In $CsCoCl_3 \cdot 2 H_2O$ the metamagnetic transition involves the same reversal of moments in alternate planes, but takes place at $H(T = 0) \approx 2.85$ kOe [2]. Obviously, the antiferromagnetic interaction between the chains in neighbouring bc-planes, which are separated by Rb ions, is very much weaker than the coupling between the ac-planes in the Cs compound. This is quite remarkable because the analogous interionic distances and bonding angles in the superexchange-interaction path $Co-Cl_{(1)}-X-Cl_{(1)}-Co$ (X = Cs, Rb) differ by at most 3.4%. Possibly the different magnetic properties are related to different symmetry properties of the 3d wave functions in the ligand field, as the Co^{2+}-ion is surrounded by a strongly distorted cis-octahedron in $CsCoCl_3 \cdot 2$ aq. and an almost regular trans-octahedron in $RbCoCl_3 \cdot 2$ aq. A detailed report about the magnetic properties of $RbCoCl_3 \cdot 2$ aq. will be published soon [9].

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