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Crystallographic and magnetic structure of $CoCl_2 \cdot 6D_2O$ and $CoBr_2 \cdot 6D_2O$

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High-resolution neutron powder diagrams show that $CoCl_2 \cdot 6D_2O$ and $CoBr_2 \cdot 6D_2O$ are subject to a crystallographic phase transition from monoclinic $C2/m$ to triclinic $P\bar{1}$ on lowering the temperature from 300 to 4.2 K. The magnetic structure can be described by a simple two-sublattice model, magnetic space group $P_{2a}\bar{1}$. Previous four-sublattice models, proposed by various authors, are shown to be incorrect. Single-crystal experiments on both compounds show that the reported anomalous magnetic behavior of these crystals, as deduced mainly from antiferromagnetic-resonance and nuclear-magnetic-resonance measurements, is caused by the occurrence of crystallographic twinning in the low-temperature phase.

I. INTRODUCTION

In the development of our knowledge on phase transitions, low-dimensional magnetic systems play an important role.[1] At this moment much attention, both experimentally and theoretically, is directed towards the Stanley-Kaplan (SK) transition, one of the open spots in our knowledge on critical behavior. The SK transition,[2] predicted only in two-dimensional (2D) Heisenberg and XY systems, is characterized by a divergence of the derivative of the order parameter with respect to the ordering field at nonzero temperature, e.g., of the susceptibility χ for ferromagnetic compounds or the staggered susceptibility χ_{st} for antiferromagnets. Below this Stanley-Kaplan temperature the order parameter (M, respectively, M_{st}) however, remains zero. The SK transition to a quasiordered state has been questioned by many authors, but the theoretical evidence, coming mainly from series expansions, is very strong at least for the 2D XY model.[3]

As indicated by the specific-heat data[4-9] and susceptibility measurements[10-15] the antiferromagnetic compounds $CoCl_2 \cdot 6H_2O$ and $CoBr_2 \cdot 6H_2O$ are good examples of the 2D XY model[16-18]. Long-range order is established at 2.3 K in the chloride[7,8] and at 3.1 K in the bromide.[4,6] The magnetic structure of both compounds was determined by means of nuclear magnetic resonance (NMR),[4,19-21] antiferromagnetic resonance (AFMR),[10,22] and neutron diffraction.[23] The transition to 3D order is caused by small deviations from the ideal 2D XY model (a small amount of anisotropy in the easy plane and weak interlayer coupling). We thought it worthwhile to investigate $CoCl_2 \cdot 6H_2O$ and $CoBr_2 \cdot 6H_2O$ more thoroughly by means of neutron scattering which is directly related to the thermodynamic quantities in the critical region, in order to establish to what extent the transition to long-range order is triggered by the proximity of the SK temperature.

Because of the large incoherent-neutron-scattering cross section of hydrogen, in these experiments a deuterated sample is usually preferred. Although deuteration hardly affects the ordering scheme in most compounds, it was reported to have a striking influence in $CoCl_2 \cdot 6H_2O$ and $CoBr_2 \cdot 6H_2O$.[24-28] For both compounds a change in the magnetic and low-temperature crystallographic structure upon deuteration has been proposed,[27-29] but the 2D XY characteristics seem to be unaffected.[9,16,26] In view of this anomalous behavior we decided to start with a detailed crystallographic and magnetic structure investigation, in order to establish the changes that occur upon deuteration. In this work we report the results of a high-resolution neutron-powder-diffraction experiment on $CoCl_2 \cdot 6D_2O$ and $CoBr_2 \cdot 6D_2O$, from which the low-temperature crystallographic and magnetic structures have been obtained.

II. EXPERIMENTAL

The samples used in the present experiment were grown by slow evaporation at room temperature from a saturated solution of the anhydrates $CoCl_2$ and $CoBr_2$ in D_2O. The neutron-diffraction data were collected on the powder diffractometer, installed at the high flux reactor at Petten. A neutron wavelength of 2.57 Å was used, obtained from the (111) reflection of a copper crystal. Second-order-wavelength contamination was removed by means of a pyrolytic graphite filter.[30] Soller slits with a horizontal divergence of 30′ were placed before the monochromator and in front of the BF_3 counter.

In a range of $0.02 < \sin\theta/\lambda \leq 0.36$ Å^{-1} powder diagrams for both $CoCl_2 \cdot 6D_2O$ and $CoBr_2 \cdot 6D_2O$ have been recorded in steps of 0.072° in θ at 300 and 4.2 K, i.e., both above and below the reported crystallographic phase transition, which occurs between 77 and 4.2 K.[29] To determine the magnetic structure, diagrams were recorded at 1.2 K, well below the Néel temperature of both $CoCl_2 \cdot 6D_2O$, viz., 2.39 K,[24,31] and $CoBr_2 \cdot 6D_2O$, viz., 3.22 K.[6] For the refinement, Rietveld's[33] profile method was applied, which determines the estimates of the various parameters by finding a least-squares fit between the observed and calculated profile intensities y_i by minimizing the quantity

$$\chi^2 = \sum_i w_i |y_i(\text{obs}) - y_i(\text{calc})|^2/\nu; \qquad (1)$$

w_i is the statistical weight of a data point and ν represents the number of degrees of freedom in the refinement.

In the analysis the scattering lengths were taken from Shull to be, respectively, 0.250 (Co), 0.958 (Cl), 0.679 (Br), 0.580 (O), 0.667 (D), and −0.374 (H) in units of 10^{-12} cm. The Watson and Freeman[32] form factor for Co^{2+} was used. Throughout the paper, standard deviations based on statistics only are given within parentheses in units of the last decimal place.

III. CRYSTALLOGRAPHIC STRUCTURE

From x-ray studies Mizuno[34] determined the crystallographic structure of $CoCl_2 \cdot 6H_2O$ at room temperature to have the monoclinic face-centered space group $C2/m$, with unit-cell dimensions $a = 10.34$ Å, $b = 7.06$ Å, $c = 6.67$ Å, and $\beta = 122°20'$. The unit cell contains two formula units. Cobalt ions are situated on inversion centers and octahedrally coordinated by four oxygen and two chlorine atoms (Fig. 1). The isolated $[CoCl_2O_4]$ clusters show approximate fourfold symmetry around the Cl-Co-Cl axis, which coincides within a few degrees with the a^* axis. The chemical bonding between adjacent ab layers must be considered as relatively weak,[13,23] which is also indicated by the perfect cleavage of the crystals along the (001) plane. The hydrogen parameters have been reported by Kleinberg[23] to be essentially the same as in the isomorphous $NiCl_2 \cdot 6H_2O$.[35] The cell parameters of $CoBr_2 \cdot 6H_2O$ at 300 K, obtained from x-ray studies, are reported by Stroganov *et al.*[36] It is isomorphous with the chloride and its unit-cell dimensions are $a = 11.00$ Å, $b = 7.16$ Å, $c = 6.90$ Å, and $\beta = 124°$.

The effect of deuteration on the crystallographic structure as function of the deuterium percentage x has been deduced mainly from NMR measurements at liquid-helium temperatures. For $x \geq 3.5\%$ in the chloride[27] and $x \geq 55\%$ in the bromide,[28] the number of zero-field proton resonances changes from 4 to 6. Analysis of the pure quadrupole resonance data in the paramagnetic state yields only slightly different parameters for $CoBr_2 \cdot 6H_2O$ and $CoBr_2 \cdot 6D_2O$.[28] These values are very sensitive to structural changes and indicate that the positional rearrangements on deuteration are only small. From their resonance studies (to which we return in Sec. IV) Hijmans *et al.*[28] proposed on group-theoretical arguments a doubling of the crystallographic unit cell along the c axis and a new monoclinic space group $C2/c$ for the low-temperature structure of the deuterated compounds.

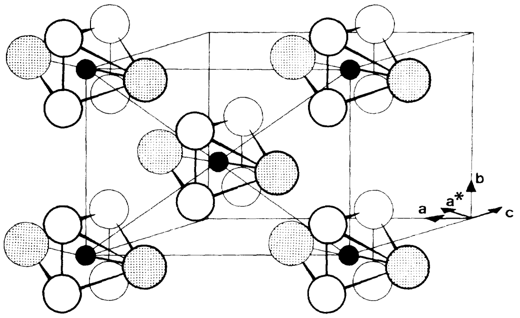

FIG. 1. Face-centered arrangement of the $[CoCl_2O_4]$ clusters in the ab plane of $CoCl_2 \cdot 6H_2O$. Cobalt atoms are small and black, chlorine atoms are shaded, and oxygen atoms have been drawn as open circles.

In the present work the structural parameters of $NiCl_2 \cdot 6H_2O$ (Ref. 35) have been used as starting values of the atomic positions in the refinement of the room-temperature neutron powder diagrams of $CoCl_2 \cdot 6D_2O$ and $CoBr_2 \cdot 6D_2O$. Convergence of the refinements was rapid and the $C2/m$ structure resulted for both compounds at 300 K. The final parameters, shown in Table I, are only slightly different from the x-ray parameters of $CoCl_2 \cdot 6H_2O$.[34] The deuterium percentages in the samples, as obtained from refinement of the deuterium scattering length, are 87(2) at.% in the chloride and 91(3) at.% in the bromide. In the diagrams no evidence was found for the presence of impurities. The use of different temperature factors did not alter the final results significantly, because of the uncertainty in the background at high angles and the small region of $\sin\theta/\lambda$ covered.

Analysis of the 4.2 K diagrams showed clearly that the low-temperature crystallographic symmetry is neither $C2/m$ nor the proposed $C2/c$. As can be seen in Fig. 2, striking splittings occur, especially for the $(22\bar{2})$ reflection, which forces us to reject any monoclinic space group and to as-

TABLE I. Structural parameters of $CoCl_2 \cdot 6D_2O$ and $CoBr_2 \cdot 6D_2O$ at room temperature and at 4.2 K. The low-temperature data are presented with respect to a triclinic unit cell, which has been chosen completely analogous to the monoclinic cell at 300 K. In the room-temperature data, atoms which are related by mirror symmetry are denoted with a prime and have been given separately for easy comparison with the 4.2 K results. Standard deviations based on statistics only are given in parentheses, in units of the last decimal place. χ^2 is defined in Eq. (1).

	$CoCl_2 \cdot 6D_2O$ 300 K $C2/m$				$CoCl_2 \cdot 6D_2O$ 4.2 K $P\bar{1}$				$CoBr_2 \cdot 6D_2O$ 300 K $C2/m$				$CoBr_2 \cdot 6D_2O$ 4.2 K $P\bar{1}$		
	x	y	z		x	y	z		x	y	z		x	y	z
Co	0	0	0	Co	0	0	0	Co	0	0	0	Co	0	0	0
Cl	0.272(1)	0	0.167(2)	Cl	0.275(1)	0.000(1)	0.172(2)	Br	0.280(1)	0	0.172(2)	Br	0.281(1)	−0.002(2)	0.180(2)
$O_{(1)}$	0.034(1)	0.211(1)	0.255(3)	$O_{(1)}$	0.033(2)	0.208(2)	0.258(2)	$O_{(1)}$	0.035(1)	0.203(1)	0.239(1)	$O_{(1)}$	0.035(2)	0.205(2)	0.263(2)
$O'_{(1)}$	0.034(1)	0.789(1)	0.255(3)	$O_{(2)}$	0.028(2)	0.796(2)	0.252(2)	$O'_{(1)}$	0.035(1)	0.797(1)	0.239(1)	$O_{(2)}$	0.031(2)	0.788(2)	0.231(2)
$O_{(2)}$	0.270(2)	0	0.701(3)	$O_{(3)}$	0.274(2)	0.012(2)	0.691(3)	$O_{(2)}$	0.284(1)	0	0.698(2)	$O_{(3)}$	0.277(1)	0.012(2)	0.701(2)
$D_{(1)}$	0.110(2)	0.310(2)	0.284(3)	$D_{(1)}$	0.106(2)	0.301(2)	0.281(3)	$D_{(1)}$	0.107(1)	0.302(1)	0.277(1)	$D_{(1)}$	0.111(2)	0.301(2)	0.278(2)
$D'_{(1)}$	0.110(2)	0.690(2)	0.284(3)	$D_{(2)}$	0.107(2)	0.692(2)	0.287(3)	$D'_{(1)}$	0.107(1)	0.698(1)	0.277(1)	$D_{(2)}$	0.111(2)	0.701(2)	0.269(2)
$D_{(2)}$	0.444(1)	0.231(1)	0.225(2)	$D_{(3)}$	0.440(2)	0.224(2)	0.224(2)	$D_{(2)}$	0.451(1)	0.241(1)	0.224(1)	$D_{(3)}$	0.452(2)	0.240(2)	0.245(2)
$D'_{(2)}$	0.444(1)	0.769(1)	0.225(2)	$D_{(4)}$	0.439(2)	0.768(2)	0.224(3)	$D'_{(2)}$	0.451(1)	0.759(1)	0.224(1)	$D_{(4)}$	0.442(2)	0.761(2)	0.212(2)
$D_{(3)}$	0.182(2)	0	0.539(3)	$D_{(5)}$	0.181(2)	0.016(2)	0.543(2)	$D_{(3)}$	0.189(1)	0	0.546(2)	$D_{(5)}$	0.197(1)	0.010(2)	0.541(2)
$D_{(4)}$	0.272(2)	0	0.840(4)	$D_{(6)}$	0.264(1)	0.011(3)	0.820(3)	$D_{(4)}$	0.273(1)	0	0.818(2)	$D_{(6)}$	0.274(1)	0.011(2)	0.840(3)
a		10.4105(11) Å		a		10.3719(10) Å		a		11.0146(11) Å		a		10.9770(11) Å	
b		7.0715(5) Å		b		7.0188(4) Å		b		7.1741(4) Å		b		7.1262(4) Å	
c		6.6477(5) Å		c		6.5733(4) Å		c		6.9138(4) Å		c		6.8455(5) Å	
α		90°		α		88.912(4)°		α		90°		α		89.376(4)°	
β		122.017(5)°		β		122.230(5)°		β		124.770(6)°		β		124.946(5)°	
γ		90°		γ		89.729(4)°		γ		90°		γ		89.802(4)°	
x		87(2) at.%		x		86(2) at.%		x		93(1) at.%		x		89(2) at.%	
χ^2		2.45		χ^2		1.85		χ^2		3.44		χ^2		4.5	

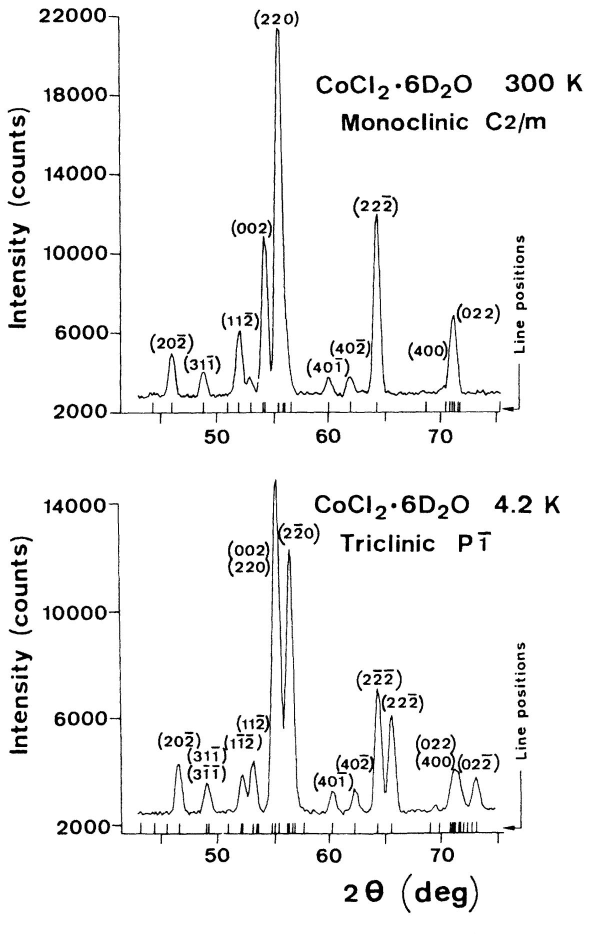

FIG. 2. Central part of the neutron powder diagrams of $CoCl_2 \cdot 6D_2O$ at room temperature and 4.2 K. Only the most intense reflections are indicated. Especially the $(22\bar{2})$ reflection clearly shows a splitting in the low-temperature diagram, indicating that the system has undergone a phase transition from monoclinic to triclinic.

sume a triclinic one. Since the inversion center at the cobalt site has to be maintained, as indicated by the presence of six proton lines in the NMR spectrum and by NMR measurements on the halogens,[27-29] the low-temperature space group is $P\bar{1}$. For the sake of simplicity a triclinic unit cell was chosen, completely analogous to the face-centered monoclinic one. Note, however, that the elementary parallelopiped is only half of this unit cell and contains one molecular unit. The final parameters of the 4.2 K refinement of both compounds are also presented in Table I. It was found that the geometry of the three water molecules in the final structure had the expected values, i.e., a distance of $O-D \approx 1$ Å and angle $D-O-D \approx 110°$. The reliability of the final model was tested by varying the initial values of variables, but all different sets did converge to the same point.

Clearly, the differences between the 300 and 4.2 K structures are rather small. In the $P\bar{1}$ structure the vanishing of mirror planes and twofold axes leads to a change in the number of inequivalent deuterium positions from four to six, while three inequivalent oxygen positions are found. Special attention is drawn to the small deformation of the rectangular oxygen surrounding of the cobalt ion. In reciprocal space the angles α^* and γ^* show a deviation from 90°, as a consequence of the triclinic deformation. The deviation angles are $\delta = 1.457(4)°$ and $\epsilon = 1.007(4)°$, respectively in $CoCl_2 \cdot 6D_2O$, and $\delta = 0.899(4)°$ and $\epsilon = 0.677(4)°$ in $CoBr_2 \cdot 6D_2O$.

IV. MAGNETIC STRUCTURE

The magnetic ordering scheme of $CoCl_2 \cdot 6H_2O$ has been obtained by Kleinberg[23] from single-crystal neutron diffraction. It consists of antiferromagnetic (001) planes with an antiferromagnetic coupling between adjacent planes. A corresponding doubling of the c axis gives a magnetic unit cell twice the size of the chemical cell [Fig. 3(d)]. In the transformed system $(a+2c,\ b,\ c)$ the magnetic space group can be denoted as $C_{2c}2/m'$ in the notation of Opechowski (C_c2/c according to Belov). The direction of the magnetic moments is in the ac plane and close to the c axis. The magnetic structure of $CoBr_2 \cdot 6H_2O$ is assumed to have the

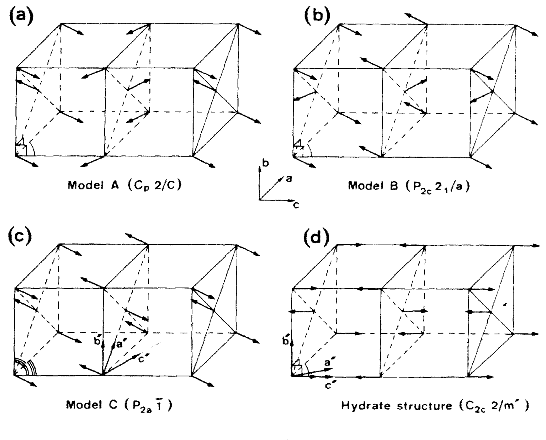

FIG. 3. Models, proposed for the magnetic ordering scheme in $CoBr_2 \cdot 6D_2O$ and $CoCl_2 \cdot 6D_2O$. The monoclinic four-sublattice models A and B were proposed by Benoit *et al.* (Ref. 27) and Hijmans *et al.* (Ref. 28). The triclinic two-sublattice model C is the result of this study. Spin directions are close to the bc plane in these models. For comparison the magnetic structure of $CoCl_2 \cdot 6H_2O$ (Ref. 23) is also shown (d). Note that the magnetic space groups of model C and the hydrate structure are denoted in the notation of Opechowski with respect to the axes, indicated by primes.

same characteristics, but here the direction of the moments deviates 8° from the c axis towards the c^* axis.[17] The effect of deuteration on the magnetic structure of both compounds has been reported to be rather anomalous for deuterium percentage $x \geqslant 3.5$ at.% in the chloride[27] and $x \geqslant 55$ at.% in the bromide.[28]

Above these values NMR measurements reveal a doubling of the internal-field directions on the halogen atoms. Both sets are related to each other by mirror symmetry with respect to the ac plane. Also the AFMR spectrum has been observed to split into two components. Resonance originally observed with the magnetic field along the c axis, now occurs in the bc plane at angles symmetrically around the c axis. Benoit *et al.*[27] have suggested that the magnetic moments could be divided into two antiferromagnetic sets, each turned away from the ac plane, but in opposite directions. For both compounds the canting angle ϕ should vary continuously with deuterium percentage up to $\phi \approx 32°$ in the completely deuterated samples.[27,28]

Since all magnetic single-crystal measurements showed mirror symmetry with respect to the ac plane, previous authors assumed that the low-temperature crystallographic structure although unknown, remained monoclinic. Two possible magnetic structures were proposed, which both contain four sublattices and coincide with the hydrate structure for $\phi = 0$. In model A [Fig. 3(a)][27,28] the moments situated in one ab layer belong to one antiferromagnetic set and are canted with respect to the moments in adjacent layers. This structure was considered the most probable one because of the relatively weak interactions between moments in neighboring ab planes. It can be described with the magnetic space group C_p2/c on a crystallographic cell with a doubled c axis. From this magnetic ordering scheme Hijmans *et al.*[28] proposed the low-temperature crystallographic structure to be $C2/c$. The second model B [Fig. 3(b)] shows antiferromagnetic bc planes, whereas the neighboring moments in the ab faces are canted with respect to one another.[27] In the notation of Opechowski model B has the magnetic space group $P_{2c}2_1/a$, which is equivalent to $P_{2a}2_1/c$. It is clear that both models are incompatible with the triclinic crystallographic structure reported in Sec. III. Even if we permit a slight triclinic distortion, these four-sublattice models still require a magnetic unit cell four times as large as the crystallographic elementary parallelopiped.

In the present study, the neutron powder diagrams recorded at 1.2 K show that the crystallographic structures are the same as at 4.2 K (Table I). No evidence was found for a larger crystallographic unit cell. The diagrams reveal a simple antiferromagnetic ordering, consisting of two sublattices for both compounds. Only magnetic reflections with $h + k = 2n + 1$ and $l = n + \frac{1}{2}$ are present, which indicates antiferromagnetic (001) planes with an antiferromagnetic coupling between adjacent planes. The magnetic space group can be denoted as $P_{2a}\bar{1}$. Because of the small number of observable magnetic reflections, the determination of the direction of the moments is rather inaccurate. For $CoCl_2 \cdot 6D_2O$ the best fit is obtained with $M_a = 0.1(4)$, $M_b = -1.5(2)$, $M_c = 1.5(4)$ and a total moment of $M = 2.1(1)$ in units of Bohr magnetons (μ_B). For the bromide the results are $M_a = 0.3(3)$, $M_b = -1.6(3)$, $M_c = 1.4(3)$, and $M = 2.10(6)\,\mu_B$. In both compounds the magnetic moments are near the bc plane and turned away from the c axis over an angle of some 45(15)°. This magnetic structure will be called model C and is shown in Fig. 3(c).

The simple magnetic ordering scheme proposed here seems to contradict the reported NMR and AFMR measurements on single crystals,[27,28] which apparently show *two* antiferromagnetic sets of magnetic moments, each turned away from the ac plane and related to each other by mirror symmetry. However, it is obvious that these phenomena can be caused by the creation of crystallographic domains (twins) due to the phase transition from monoclinic to triclinic. It is easy to see that the deformation of the monoclinic unit cell can generate two different triclinic cells, related by reflection symmetry, which in a powder diagram are indistinguishable.

To detect the presence of such crystallographic domains, a preliminary neutron scattering experiment was performed at 300 and 4.2 K, using both a $CoBr_2 \cdot 6D_2O$ and a $CoCl_2 \cdot 6D_2O$ single

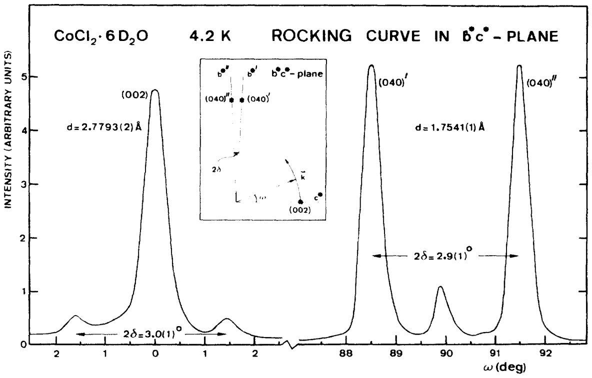

FIG. 4. Rocking curves of the (002) and (040) reflections in a single crystal of $CoCl_2 \cdot 6D_2O$ at 4.2 K, in the reciprocal b^*c^* plane. In the insert it is shown that the high-intensity reflections are related to two domains, indicated by primes and double primes, respectively.

crystal. In the reciprocal b^*c^* plane, where the deviation from monoclinic should be the most clearly visible, rocking curves have been taken to observe the (002) and (040) reflections. Whereas at room temperature these nuclear Bragg reflections are single, at 4.2 K a clear splitting of the (040) reflection is observed, indicating the anticipated domain structure.

For the chloride the effect is most distinct and the measured profiles at 4.2 K are shown in Fig. 4. The apparent splitting of the (040) reflection has the expected magnitude, viz., $2\delta = 2.9°$, whereas the (002) reflection is unaffected. Obviously two dominant regions are present, in which the *ac* planes make an angle with respect to one another. This corresponds to a parallel shift of the hardly distorted *ab* planes, but in opposite directions. A minor effect is indicated by the weak-intensity satellites of the (002) reflection, which also show a splitting of 2δ and which are related to the small central peak at the position of the monoclinic (004) reflection. These correspond to a less-important type of twinning, in which adjacent *ab* layers are canted in opposite directions. In the bromide the same features are met, but here the splitting angles are 1.8°, in agreement with the value expected from the powder diagram results.

V. DISCUSSION

Analysis of the neutron powder diagrams of $CoCl_2 \cdot 6D_2O$ and $CoBr_2 \cdot 6D_2O$ at 300 and 4.2 K clearly yields a crystallographic phase transition from monoclinic $C2/m$ to the low-temperature triclinic $P\bar{1}$ structure, for both compounds. The $P\bar{1}$ structure is completely compatible with the reported doubling of the NMR-absorption lines due to the deuterons originally positioned on the mirror plane *ac*.[27,28] The differences between the low-temperature and room-temperature structures are rather small. This is in agreement with the small differences between the quadrupole interaction quantities at 77 and 4.2 K in $CoBr_2 \cdot 6D_2O$.[29] Also the differences with the hydrated compounds are only small, as expected.[28]

Neutron-diffraction experiments on single crystals of both $CoBr_2 \cdot 6D_2O$ and $CoCl_2 \cdot 6D_2O$ reveal the occurrence of crystallographic domains below the transition temperature, at which the compounds become triclinic. Unit cells in different domains are related to each other by mirror symmetry. This explains why previous authors assumed a four-sublattice model to describe the magnetic structure of both compounds. The 1.2 K powder diagrams indicate that the only essential change in magnetic structure upon deuteration is a rotation of the moments away from the *ac* plane over an angle of 45(15)°.

This large angle, responsive to the only small deformation of the oxygen surrounding of the cobalt ions, is not surprising and supports the large amount of isotropy in the *bc* plane of $CoBr_2 \cdot 6D_2O$ and $CoCl_2 \cdot 6D_2O$. Kopinga *et al.*[6] calculated that for the bromide this effect can be caused by an increase of the anisotropy in the easy plane from 5% up to 7.5%. Recalculations of the internal fields on the deuterium positions presented in this work, assuming the domain effects proposed here, yield a better agreement with experiment than previous values, calculated from the magnetic ordering scheme of model *A*.[37]

We can conclude that the main features of the interpretation of previous measurements on $CoBr_2 \cdot 6D_2O$ and $CoCl_2 \cdot 6D_2O$ are unaffected by the crystallographic phase transition reported here. Both compounds appear to be good examples of the 2D *XY* model. However, the occurrence of crystallographic twins undoubtly will complicate further critical scattering experiments on these compounds.

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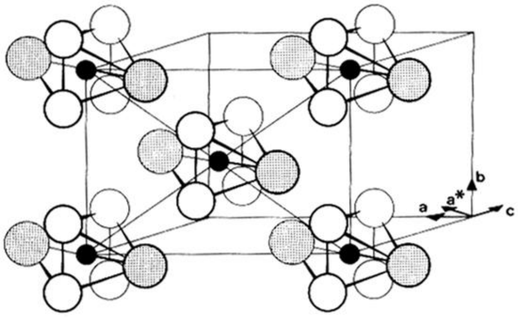

FIG. 1. Face-centered arrangement of the $[CoCl_2O_4]$ clusters in the *ab* plane of $CoCl_2 \cdot 6H_2O$. Cobalt atoms are small and black, chlorine atoms are shaded, and oxygen atoms have been drawn as open circles.