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NEUTRON SCATTERING FROM RbCoBr_3 AND RbNiCl_3 (*)

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Résumé. — RbCoBr_3 a été étudié par diffraction de neutrons sur poudre. Les résultats montrent qu'en dessous de $T_N = 36^\circ\text{K}$ ce composé présente une structure antiferromagnétique dans laquelle les spins, dirigés parallèlement à l'axe C sont alternativement $+$ et $-$ le long de cette direction, la configuration des 3 spins dans le plan de base $(++-)$. Cette structure diffère de l'arrangement spiralé obtenu précédemment pour les composés isotypes CsNiCl_3 et RbNiCl_3 . Des mesures sur un monocristal de ce dernier composé montrent que pour $T > 2,27 T_N$, la diffusion magnétique est essentiellement due à des plans perpendiculaires à l'axe C .

Abstract. — Powder neutron diffraction measurements have been performed on RbCoBr_3 . The results indicate that at $T_N = 36^\circ\text{K}$, the compound exhibits a transition to an antiferromagnetic phase in which the spins are alternately aligned along c with a $(++-)$ configuration for the three spins in the basal plane. This is in contrast to the spiral arrangement previously deduced for the isostructural compounds CsNiCl_3 and RbNiCl_3 . Single crystal measurements in the latter compound are presented that demonstrate that for $T > 2.27 T_N$, the magnetic scattering is essentially confined to planes perpendicular to the c^* axis.

Compounds of the CsNiCl_3 type (space group $D6_3/\text{mmc}$) have recently attracted considerable attention. The feature that makes these compounds particularly interesting is that the structural configuration of the $(\text{BX}_3)^{-1}$ complexes suggests that their magnetic properties would simulate those of a linear antiferromagnetic chain [1]. The present paper is concerned with the magnetic structure of RbCoBr_3 and the results of single crystal scattering measurements on RbNiCl_3 .

Standard powder diffraction measurements were performed on RbCoBr_3 both above and below the ordering temperature. The (311) planes of Ge were used to monochromate the beam, and as a result the $\lambda/2$ contaminate was negligible. The measurements at 78°K served to establish that the space group appropriate for the compound is indeed the hexagonal $P6_3/\text{mmc}$ (D_{6h}^4). The weighted R factor for the chemical structure determination was $R = 0.085$. The positions of the atoms in the structure and a comparison between the observed and calculated intensities are given in Table I. The results of the measurements taken at low temperatures are illustrated in figure 1. The lattice constants for the chemical cell for $T = 4.45^\circ\text{K}$ were found to be $a = 7.29 \text{ \AA}$ and $c = 6.19 \text{ \AA}$. The transition temperature was found to be $T_N = 36^\circ\text{K}$. The peaks in the figure labeled M are the additional peaks that are unique to the magnetically ordered phase.

We now discuss the magnetic structure of RbCoBr_3 . The superlattice peaks shown in figure 1 can be indexed on an enlarged hexagonal unit cell with the dimensions $\sqrt{3}a \times \sqrt{3}a \times c$, where a and c refer to the fundamental chemical cell. The a axis of the magnetic cell makes an angle of 30° with the a axis of the chemical cell. The enlarged cell contains six formula units. The three magnetic atoms in the basal plane occupy the (000) , $(\frac{2}{3} \frac{1}{3} 0)$ and $(\frac{1}{3} \frac{2}{3} 0)$ positions; the remaining three are translated at a distance $(00\frac{1}{2})$ from them.

(*) Work performed under the auspices of the U. S. Atomic Energy Commission.

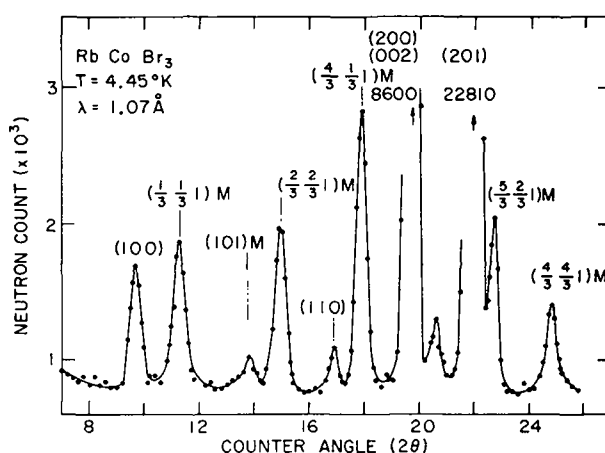


FIG. 1. — The figure contains the results of the powder neutron diffraction measurements on RbCoBr_3 . The reflections labeled M are the additional reflections found in the pattern for $T < T_N$. The reflections are indexed on the fundamental chemical unit cell. The reflection at $2\theta = 20.5^\circ$ could not be indexed.

The magnetic arrangement that satisfactorily reproduces the observed intensities is the collinear model that was first discussed by Corliss et al [2] in a study of CrSe . The spin pattern for the model consists of an antiferromagnetic stacking of the spins along the c axis chains along with a $(++-)$ configuration for the three spins in the basal plane. The observed intensities demand that the spins be directed along the c axis and that the magnetic moment associated with the Co^{+2} ion be $3.4 \pm 0.2 \mu_B$. The magnetic intensities were normalized to the nuclear data taken at 78°K , where, in comparison, a more complete set of data for the chemical structure had been collected. The purely nuclear peaks did not change significantly on decreasing the temperature to 4.45°K . The agreement between the observed and the calculated intensities based on the model is given in Table I. The magnetic structure is illustrated in figure 2. The structure shown in the figure should be contrasted with those found for the isostructural compounds CsNiCl_3 and RbNiCl_3 . In the latter

TABLE I

A comparison of the observed and calculated intensities for RbCoBr₃. The compound was found to belong to the P6₃/mmc (P_{6h}⁴) space group. The Rb⁺ ions are at positions ($\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{2}$) and ($\frac{2}{3}$ $\frac{1}{3}$ $\frac{1}{2}$), the Co²⁺ ions occupy the (0 0 0) and (0 0 $\frac{1}{2}$) positions, while the Br⁻ ions are at $\pm (x, 2x, \frac{1}{4}) \pm (x, x, \frac{1}{4})$, $\pm (2x, x, \frac{1}{4})$ with $x = 0.16$. The reflections are indexed on the fundamental chemical cell.

hkl	$I_{\text{cal}}^{\text{N}}$	$I_{\text{cal}}^{\text{M}}$	$I_{\text{obs}}^{\text{N}}(78^\circ\text{K})$	$I_{\text{obs}}^{\text{M}}(4.4^\circ\text{K})$
(100)	40.2		41.1	
$(\frac{1}{3} \frac{1}{3} 1)$		53.5		58.2
1 0 1	2.0	17.3	< 1.0	16.5
$(\frac{2}{3} \frac{2}{3} 1)$		65.9		59.8
(110)	12.6		10.0	
$(\frac{4}{3} \frac{1}{3} 1)$		103.2		98.4
(200) (002)	351.3		392.1	
(201) (102) $(\frac{5}{3} \frac{2}{3} 1)$	958.7	61.4	893.1	47.6
$(\frac{4}{3} \frac{4}{3} 1)$		24.2		32.1
(202) (211)	259.2		253.7	
(300)	3.5		4.6	
(103)	0.3		< 1.0	
(212)	20.8		20.7	
(220)	276.0		266.8	
(310) (221) (302) } (203) (311) }	314.2		332.0	

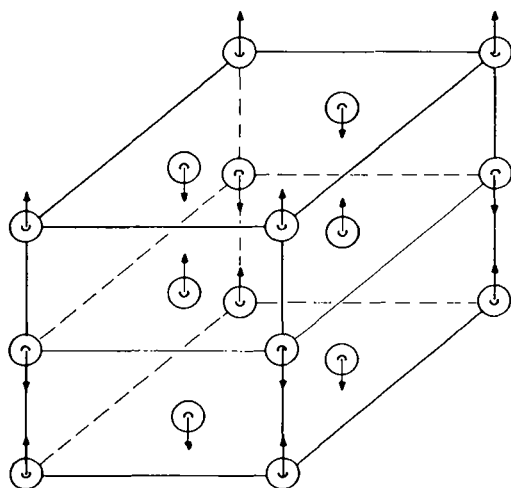


FIG. 2. — The figure illustrates the magnetic structure of RbCoBr₃ for $T = 4.45^\circ\text{K}$. This type of structure was first considered by Corliss et al. The Co²⁺ ions are shown in their positions in the enlarged hexagonal magnetic unit cell with dimensions $\sqrt{3}a \times \sqrt{3}a \times c$. The a axis of the magnetic cell makes an angle of 30° with the a axis of the fundamental chemical unit cell.

case, the structure was found to be an antiferromagnetic stacking of the spins along the c axis, along with a screw spiral propagating in the basal plane [3].

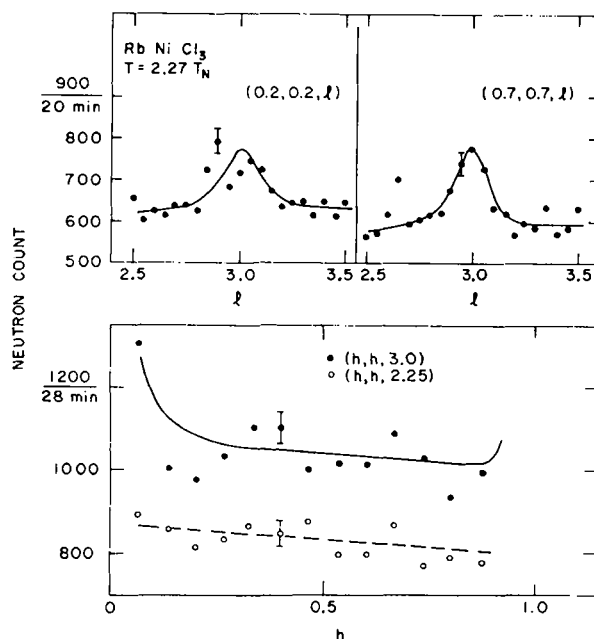


FIG. 3. — The figure illustrates the results of single crystal measurements on RbNiCl₃. The results demonstrate that for $T \cong 2.27 T_N$, the magnetic scattering is confined to planes perpendicular to the c^* axis. The two profiles in the upper half of the figure are scans through the plane at $3 c^*$. The profiles in the lower half are scans «on» and «off» the ridge of the scattering from the same plane.

The compound RbNiCl_3 exhibits a three-dimensional magnetic transition at $T_N = 11^\circ\text{K}$ [1]. Achiwa [1] has noted that the chemical structure of compounds of the CsNiCl_3 type strongly suggests that they will simulate the magnetic properties peculiar to an antiferromagnetic chain. The broad maxima observed [1] in the susceptibility of several compounds of this type can, in fact, be understood on the basis of this assumption. The results of the scattering measurements are illustrated in figure 3. The data shown in the figure clearly demonstrate that for $T \lesssim \frac{1}{2} T_N$, the magnetic scattering is essentially confined to planes that inter-

sect the c^* axis at positions lc^* where l is odd. Measurements were made with the crystal oriented in both the [100] and [110] zones to confirm that the scattering was planar rather than rod-like. This type of scattering has been observed in $\text{CsMnCl}_3 \cdot 2\text{H}_2\text{O}$ [4] and $(\text{CH}_3)_4\text{NMnCl}_3$ [5]. The two profiles shown in the top half of the figure are scans «through» the plane of scattering, while the bottom half contains profiles of scans «on» and «off» of the scattering plane. To conclude, the measurements present definitive proof that for $T \lesssim \frac{1}{2} T_N$, RbNiCl_3 simulates the magnetic behavior of an antiferromagnetic chain.

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