Solid State Communications, Vol. 8, pp. 1001–1005, 1970. Pergamon Press. Printed in Great Britain

THE MAGNETIC STRUCTURES OF $RbNiCl_3$ AND $CsNiCl_3$*

V.J. Minkiewicz, D.E. Cox, and G. Shirane

Brookhaven National Laboratory, Upton, New York 11973, U.S.A.

(*Received* 21 *April* 1970 *by M.F. Collins*)

Powder neutron diffraction measurements were performed on $RbNiCl_3$ and $CsNiCl_3$ at temperatures above and below their respective Néel temperatures of 11°K and 4.5°K. The magnetic superlattice reflections for both compounds can be indexed on the basis of a hexagonal unit cell with dimensions $a = \sqrt{3}\, a_0$ and $c = c_0$, where a_0 and c_0 are the dimensions of the chemical unit cell. The magnetic structure is found to consist of an antiferromagnetic sequence of the spins along the c axis chains, along with a screw spiral propagating in the basal plane. The wavelength of the screw spiral is commensurate with the lattice, and has a value of $3a_0/2$. Single crystal measurements on $RbNiCl_3$ have shown that for $T \gg T_n$ the compound exhibits scattering behavior that is characteristic of a one-dimensional magnetic system.

RECENT neutron scattering measurements on K_2NiF_4,[1] $Mn(HCOO)_2 . 2H_2O$,[2] and $CsMnCl_3 . 2H_2O$[3] have unambiguously demonstrated that real systems can exhibit magnetic properties characteristic of one- and two-dimensional magnetic systems. As a result, these observations have greatly stimulated neutron measurements on other compounds that have these properties.

The compounds $RbNiCl_3$ and $CsNiCl_3$ are two possible candidates in this context. Achiwa[4] has suggested that the magnetic properties of these compounds will simulate those of a linear antiferromagnetic chain for temperatures above their three-dimensional ordering temperatures. The compounds have a structure with $P6_3/mmc(D_{6h}^4)$ symmetry in which the nickel atoms lie on a primitive hexagonal net (see Table 1). If only the $(NiCl_6)^{-4}$ complex is considered, the structure is constructed essentially of linear chains of nickel ions along the c axis that share common (111) faces of distorted chlorine octahedra. The exchange paths that couple nearest-neighbor nickel ions within the basal plane are via two intervening ligands, and therefore the exchange interaction in this plane is expected to be much smaller than that along the c axis. The magnetic susceptibility measurements seem to indicate that this speculation is in fact correct; the measurements above the three-dimensional ordering temperature can be understood if one assumes that the nickel lattice is behaving like a collection of linear antiferromagnetic chains. This paper presents the results of neutron powder diffraction measurements on $RbNiCl_3$ and $CsNiCl_3$ below T_n. In addition, we present preliminary results of single crystal scattering measurements on $RbNiCl_3$. The single crystal measurements furnish direct evidence that there exist strong long-range antiferromagnetic correlations along the c axis for $T > T_n$. Preliminary results of these experiments have been reported elsewhere.[5]

---

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

Table 1. Structural data for $RbNiCl_3$[4] *and* $CsNiCl_3$.[7] *The lattice constants of the chemical cells were found to be* a_0 = 6.92 Å *and* c_0 = 5.87 Å *for* $RbNiCl_3$, *and* a_0 = 7.14 Å *and* c_0 = 5.96 Å *for* $CsNiCl_3$ *at* 5.13°K *and* 2.0°K, *respectively.*

Space Group:	$P6_3/mmc$ (D_{6h}^4)	
Atomic Positions:	Rb^{+1} (Cs^{+1}):	$\left(\frac{1}{3}\,\frac{2}{3}\,\frac{3}{4}\right), \left(\frac{2}{3}\,\frac{1}{3}\,\frac{1}{4}\right)$
	Ni^{+2}:	(000), $(00\frac{1}{2})$
	Cl^{-1}:	$\pm\left(x, 2x, \frac{1}{4}\right), \pm\left(x, \bar{x}, \frac{1}{4}\right), \pm\left(2\bar{x}, \bar{x}, \frac{1}{4}\right)$
	$x(RbNiCl_3)$ = 0.160	
	$x(CsNiCl_3)$ = 0.156	

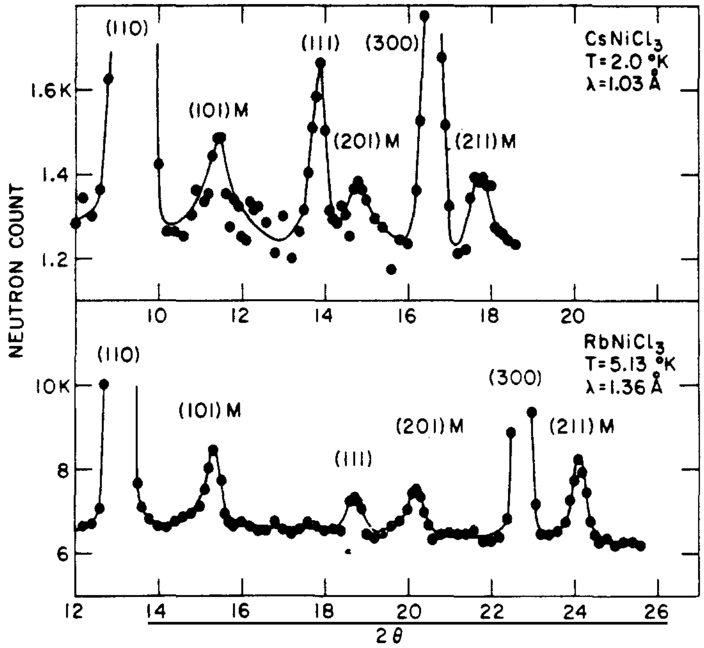

FIG. 1. Powder neutron diffraction data for $RbNiCl_3$ and $CsNiCl_3$ at 5.13 and 2.0°K respectively. The peaks labelled M are the magnetic superlattice reflections. The indexing is based on a hexagonal cell with dimensions $a = \sqrt{3}\,a_0$ and $c = c_0$, where a_0 and c_0 are the dimensions of the hexagonal chemical unit cell.

The powder experiments were performed in the standard manner. Measurements were made both above and below T_n, and as a result, the contribution made by the magnetic scattering was easily identifiable. The higher order wavelength contamination in the neutron beam was negligible. In particular, the $\lambda/2$ contamination was <0.04 per cent because germanium (111) (λ = 1.36 Å) and (311) (λ = 1.03 Å) planes were used to monochromate the beam for the $RbNiCl_3$ and $CsNiCl_3$ experiments, respectively. The observed hexagonal chemical cell dimensions are given in Table 1. The R factors for the chemical structures with the parameters previously quoted were 0.01 and 0.07 for $RbNiCl_3$ and $CsNiCl_3$, respectively. The five low-lying reflections were used in this calculation and the variation in the intensities as a result of the

Table 2. Comparison of observed and calculated intensities for the magnetic peaks. The magnetic intensities are normalized to the nuclear intensities. The value of the magnetic moment is given in units of Bohr magnetons for $RbNiCl_3$ *and* $CsNiCl_3$ *at* 5.13°K *and* 2.0°K, *respectively.*

	$RbNiCl_3$		$CsNiCl_3$	
	I_{obs}	I_{calc}	I_{obs}	I_{calc}
101	98	96	100	94
201	55	59	65	59
211	84	81	69	82
	$\mu = 1.5 \pm 0.15$		$\mu = 1.4 \pm 0.2$	

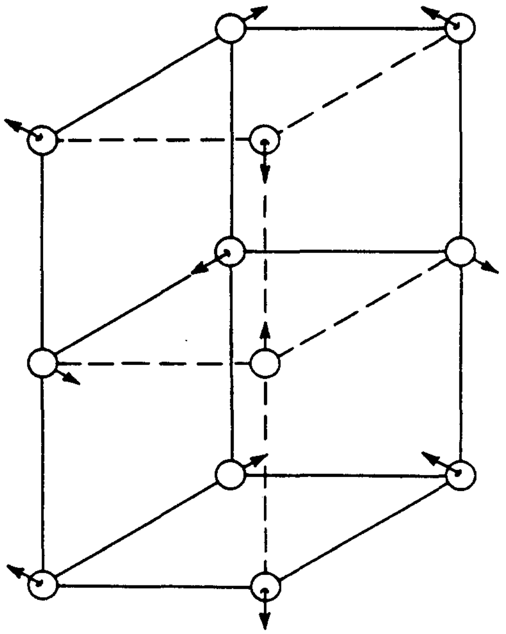

FIG. 2. An illustration of the magnetic structure of $RbNiCl_3$ and $CsNiCl_3$. The structure consists of an antiferromagnetic sequence of moments along c, and a screw spiral propagating in the basal plane. The wavelength of the spiral is $3a_0/2$; as one proceeds along the a_0 direction, the spins rotate by 120° in the a.c. plane.

Debye–Waller factor was assumed to be negligible.

The neutron powder patterns below T_n are shown in Fig. 1. The peaks labelled M are the superlattice reflections unique to the magnetically ordered phase. The superlattice peaks can be indexed on the basis of a hexagonal cell with dimensions $a = \sqrt{3}\,a_0$ and $c = c_0$, where a_0 and c_0 are the dimensions of the hexagonal chemical unit cell. The magnetic structure that most satisfactorily accounts for the observed intensities is illustrated in Fig. 2. The agreement between the observed and calculated intensities is given in Table 2. Using the nuclear reflections to put the intensities of the magnetic reflections on an absolute scale, we found that the Ni^{+2} ion has a magnetic moment extrapolated to 0°K of $1.6 \pm 0.15\mu_B$ and $1.5 \pm 0.2\mu_B$ in $RbNiCl_3$ and $CsNiCl_3$, respectively Normally, the Ni^{+2} ion is expected to have a moment of approximately $2\mu_B$. The difference between this value and the experimental results could possibly be the result of either a zero point spin deviation or covalency effects, or a combination of the two. However, in view of the difficulty in reliably estimating the contribution made by both effects, the question as to whether the experimental results can be understood on this basis should be regarded as being unresolved.

The magnetic structure is best described as consisting of an antiferromagnetic sequence of the spins along the c axis chains, coupled with a screw spiral array in which the spins rotate in a plane perpendicular to the basal plane. The wavelength of the screw spiral is commensurate with the chemical lattice, and has a magnitude of $3a_0/2$. We note that since the wavelength of the spiral is commensurate with the chemical lattice, we do not necessarily have to describe the structure as a 'spiral' at all. However, we prefer this description because the structure is thereby more easily visualized.

There are two points that must be made concerning the structure. The first is concerned with the phase angle that the 'initial spin' makes with the c axis, and the second with the direction of the spin components in the basal plane. The structure can be generated by the following expression

$$\hat{S}_{n,m} = \hat{S}_{/\!/} \cos(\underline{\lambda}\cdot\underline{R}_{n,m}+\theta_0) + \hat{S}_{\perp} \sin(\underline{\lambda}\cdot\underline{R}_{n,m}+\theta_0) \qquad (1)$$

where $\hat{S}_{n,m}$ is a unit vector along the spin direction of the m'th atom in the n'th unit cell with position vector $R_{n,m}$, $\hat{S}_{/\!/}$ is a unit vector along c, $\hat{S}_{\perp}$ is a unit vector in the basal plane, and

$$\underline{\lambda} = \frac{1}{3}(\underline{a}_0^* + \underline{b}_0^*) + \underline{c}_0^*.$$

The structure that is illustrated in Fig. 2 is one for which $\theta_0 = 0$. The value of θ_0 cannot be determined by neutron scattering measurements. We have *set* $\theta_0 = 0$ to retain the c axis as a unique spin direction, which is strongly suggested by the results of the magnetic susceptibility measurements.[4] As far as the second point is concerned, the measurements were performed on powder samples, and therefore in the averaging process, any information concerning the direction of $\hat{S}_{\perp}$ within the basal plane is completely lost. In Fig. 2, $\hat{S}_{\perp}$ has been set perpendicular to a purely for the purposes of illustration.

We have also attempted to fit the data with other spin configurations, in particular the 'umbrella' and collinear models that were considered by Corliss *et al.* in a study of CrSe.[6] We found that none of the high symmetry models could account for the observed intensities of the superlattice reflections. Specifically, the 'umbrella' model failed to reproduce the observed low ratio of the intensity of (101)M to (211)M. The collinear model is also unable to account for the observed ratio with the spin axis either perpendicular or parallel to c. If this latter condition is relaxed, however, it is possible to obtain agreement for the *purely magnetic* peaks. If the spin axis makes an angle of 45° with the c axis, one obtains *exactly* the same agreement as is given in Table 2, albeit with a slightly altered value for the magnetic moment. This model is inadequate, however, because the (111) reflection would then contain a magnetic contribution amounting to approximately 35 per cent of the nuclear intensity. We observed that the intensity of the (111) reflection did not change significantly when the sample was cooled through T_n.

The results of the single crystal measurements on $RbNiCl_3$ can be summarized as follows. For $T > T_n$ the magnetic scattering manifests itself in two forms: as *planes* of scattering perpendicular to the c_0^* axis, which intersect the axis at positions $l c_0^*$ where l is odd, and as normal three-dimensional critical scattering *peaks* which are superimposed on the planes, and which dominate the scattering near T_n. These peaks occur at reciprocal lattice positions that coincide with the magnetic reciprocal lattice positions of the ordered phase. For $T \gtrsim 4T_n$, the peaks have essentially disappeared, and all that remains are the *planes* of scattering normal to the c_0^* axis. The interpretation of these results is straightforward. The planes of scattering reflect the fact that even for $T \gtrsim 4T_n$, there are strong long-range antiferromagnetic spin correlations along the c axis. Immediately above T_n the magnetic system behaves in the normal manner. As the temperature is increased, the 'three-dimensional characteristics' continuously decrease until for $T \sim 4T_n$ the three-dimensional behavior is essentially lost, and the system is then stimulating the characteristics of a linear antiferromagnetic chain as was first proposed by Achiwa.[4] This unique type of magnetic scattering was recently observed by Skalyo *et al.* in $CsMnCl_3 \cdot 2H_2O$.[3]

Acknowledgements – We would like to acknowledge a helpful exchange of information and discussions with N. Achiwa and J. Skalyo, Jr.

REFERENCES

1. BIRGENEAU R.J., GUGGENHEIM H.J. and SHIRANE G., *Phys. Rev. Lett.* 14, 720 (1969); BIRGENEAU R.J., GUGGENHEIM H.J. and SHIRANE G., *Phys. Rev.* (in press); SKALYO J. Jr., SHIRANE G., BIRGENEAU R.J. and GUGGENHEIM H.J., *Phys. Rev. Lett.* 23, 1394 (1970).
2. SKALYO J. Jr., SHIRANE G. and FRIEDBERG S.A., *Phys. Rev.* (in press).
3. SKALYO J. Jr., SHIRANE G., FRIEDBERG S.A. and KOBAYASHI H., *Bull. Am. Phys. Soc.* 15, 337 (1970).
4. ACHIWA N., *J. Phys. Soc. Japan* 27, 561 (1969).
5. MINKIEWICZ V.J., COX D.E. and SHIRANE G., *Bull. Am. Phys. Soc.* 15, 338 (1970).
6. CORLISS L.M., ELLIOTT N., HASTINGS J.M. and SASS R.L., *Phys. Rev.* 122, 1402 (1961).
7. TISHCHENKO G.N., *Trans. Inst. Kristallogr. Akad. Nauk. USSR* 11, 93 (1955).

Измерения порошювой диффракции нейтронов производились на $RbNiCl_3$ и $CsNiCl_3$ при температуре выше и нюке их соответствующих температур Нииля II$^\circ$K и 4,5°K. Магнитные сверхрешеточные отражения можно выразить для обоих соединений в виде гексагональной единичной ячейки с размерами $a = \sqrt{3}a_0$ и $c = c_0$, где a_0 и c_0 - размеры химическюй единичной ячейки. Магнитная структура состоит из антиферромагнитного ряда спинов по цепочкам оси c, вместе с червячной спиралью вращающейся в базовой плоскюсти. Длина волны спирали пропорциональна ячейки, величина ютoрой $3a_0/2$. Измерения $RbNiCl_3$ на монокристалле показали, что при $T \gg T_H$ это соединение проявляет эффект рассеяния, характерный для одномерной магнитюй системы.