# Zigzag type magnetic structure of the spin $J_{eff}$ = ½ compound α-$RuCl_3$ as determined by neutron powder diffraction

**C. Ritter**
Institut Laue Langevin, 71 Avenue des Martyrs, 38000 Grenoble, France

E-mail: ritter@ill.fr

**Abstract.** Using high intensity powder neutron diffraction the magnetic structure of α-$RuCl_3$ has been determined. Following the magnetic propagation vector κ = (½, 0, ½) the $J_{eff}$ = ½ spins of $Ru^{3+}$ adopt a Zigzag type arrangement on the honeycomb lattice of the layered $P3_112$ structure. The magnetic moments are oriented perpendicular to the trigonal axis. Similarities and differences to previously published single crystal data are discussed. The low value of the magnetic moments, $\mu_{Ru}$ = 0.5(1) $\mu_B$ indicates a possible closeness of α-$RuCl_3$ to the Kitaev spin liquid state.

## 1. Introduction

The importance of the spin-orbit coupling (SOC) in determining the electronic ground state of transition metal oxides has recently been a focus of both theoretical and experimental efforts [1-6]. On the theoretical side the Kitaev model [7-11]], which describes the interactions of spins $J_{eff}$ = ½ on a honeycomb lattice by including bond dependent exchange interactions resulting from the SOC, is a rare example of exactly solvable models with highly nontrivial properties such as a quantum spin-liquid state and fractional statistics. However, being highly artificial, the model is difficult to realize in a real-world material. A number of promising candidates have been proposed in strongly spin-orbit coupled 5*d* transition-metal oxides (such as $Na_2IrO_3$ [3] and $Li_2IrO_3$ [5]), which have the requisite bond-directional interactions of the form in the Kitaev model. The search for the Kitaev spin-liquid has recently been extended to 4*d* transition-metal compounds with α-$RuCl_3$ [12-14] as one of the possible candidates as it crystallizes in a layered structure where the $Ru^{3+}$ ($4d^5$) ions sit on a honeycomb lattice and see a nearly perfect $RuCl_6$ octahedral environment [15]. Under the combined effect of the crystal field and the spin-orbit coupling $J_{eff}$ states having spin and orbital character develop [1]. The on-site Coulomb repulsion leads to the double degenerate $J_{eff}$ = 3/2 bands having lower energy and being fully occupied while the remaining electron occupies a $J_{eff}$ = ½ band and determines the magnetism [12].

Although magnetic susceptibility data had indicated a finite-temperature long-range magnetic order at a magnetic transition temperature of about 14 K [16], the determination of its magnetic structure is of crucial importance in assessing the proximity to the Kitaev quantum spin liquid state. Here we present the results from the first neutron powder diffraction measurements which strongly support the presence of a Zigzag type magnetic order, quite similar to that of $Na_2IrO_3$. In the low temperature neutron diffraction patterns, we have observed three magnetic Bragg peaks which could be indexed with a propagation vector κ = (½, 0, ½). Using magnetic symmetry analysis, the

refinement of these peaks was possible with an allowed irreducible representation and confirmed the three-dimensional nature of the magnetic order despite the fact that neighboring Ru-Cl layers are weakly coupled by van der Waals forces.

## 2. Experimental

α-$RuCl_3$ crystals were prepared by vacuum sublimation. $RuCl_3$ powder was sealed in a quartz ampoule and heated to 750◦C and kept for 2 weeks. Black and thin crystals were grown in the cold zone. For the powder measurements these crystals were powdered. High resolution and high intensity neutron powder diffraction experiments were done on the diffractometers D2B and D20 respectively, both situated at the Institut Laue Langevin at Grenoble, France. The high resolution data were taken at room temperature using a neutron wavelength of λ = 2.39 Å while low temperature data were recorded using a standard Orange cryostat on D20 at 1.8 K and at 50 K with λ = 2.41 Å. On D20 a radially oscillating collimator suppressed any scattering from the sample environment; at both temperatures data were collected for 6 hours. The Rietveld refinement program FULLProf [17] was used to analyse the data, magnetic symmetry analysis was done using the program BASIREPS [18, 19].

## 3. Results and Discussion

Figure 1 shows the room temperature high resolution D2B data which can be refined within the nuclear spacegroup $P3_112$ with lattice constants of a = 5.9510(4) Å and c = 17.1001(14) Å. The structure is characterized by a strong layer type structure where the coherence between the layers along the crystallographic c-axis is only determined by Van der Waals forces [20].

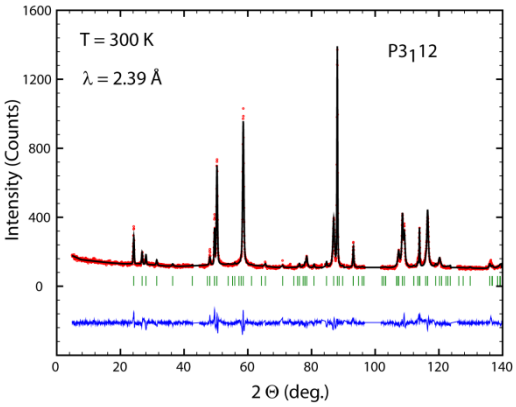
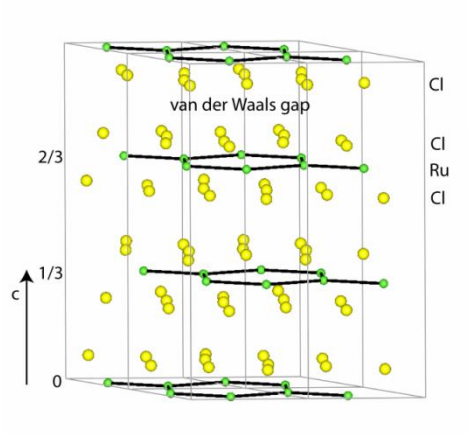



**Figure 1.** Observed (red dots), calculated (black line), and difference pattern of α-$RuCl_3$ at 300 K refined in $P3_112$. The tick marks indicate the calculated position of the Bragg peaks.



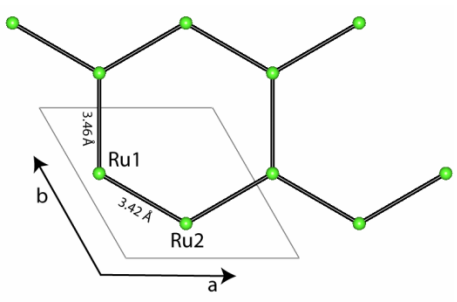



**Figure 2.** Layer type structure of α-$RuCl_3$ showing the van der Waals gap (left), honeycomb lattice formed by the two Ru sites (right).

Figure 2 shows the structure of α-$RuCl_3$ and the two dimensional honeycomb lattice formed by the two Ru-sites which are both situated on the Wykoff site 3*a* with $x$ = 0.436(8) for Ru1 and $x$ = 0.769(5) for Ru2. The Ru-Ru distances within the honeycomb lattice are not exactly similar; there are two different Ru1 – Ru2 distances amounting to 3.46 and 3.42 Å.

The magnetic scattering developing below $T_N$ is very weak and is only visible in the difference pattern created by subtracting the high intensity data taken at 50 K from those taken at 1.8 K. Figure 3 displays this difference data with the presence of three magnetic reflections. These reflections can be indexed with the magnetic propagation vector κ = (½, 0, ½) or equivalent (0, ½, ½) and (½, ½, ½). The up-down feature visible at 2Θ = 24.5° is created by the slight thermal expansion between 1.8 K and 50 K which leads to an incomplete subtraction of the nuclear 003 reflection.

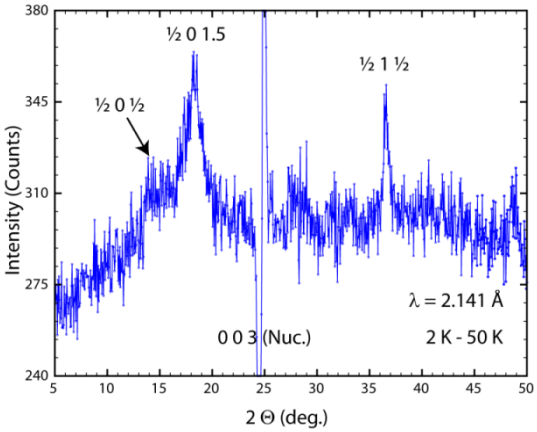



**Figure 3.** Purely magnetic diffraction pattern created as difference between data taken at 2 K and 50 K. Magnetic reflections are indexed in the nuclear unit cell.

Magnetic symmetry analysis for κ = (½, 0, ½) in spacegroup $P3_112$ shows that the Wykoff site 3*a* is split into two different orbits resulting in four independent Ru-sites in the unit cell. The original 3-fold site is split into a 2-fold site with the atoms on *x*, -*x*, *z* (Ru1(2)_1) and *x*, *x*-*y*, -*z* (Ru1(2)_2) and the unique site at -2*x*, -*x*, 0 (Ru1(2)_3). There are two different allowed irreducible representations (IR) which are listed in Table 1 together with their corresponding basis vectors (BV). For the determination of the magnetic structure of α-$RuCl_3$ one has to use not only the information on the presence and intensity of the measured magnetic peaks but as well on the absence of certain magnetic reflections. Nevertheless one will have to assume certain conditions to be valid in order to find stable solutions for the refinement. As a first condition it will be assumed that all Ru-sites possess equal magnetic moment values. The second condition which limits then sufficiently the number of free refinable parameters is to assume the magnetic spins to adopt a collinear structure. A collinear arrangement perpendicular to the trigonal axis can be described using a combination of BV1 and BV2 of IR1 while a collinear arrangement parallel to the trigonal axis is described by BV2 of IR2. Within each IR one can further choose between an antiferromagnetic coupling between the sites Ru1 and Ru2 defining the so-called Stripe model and a ferromagnetic coupling between the Ru1 and Ru2 sites which gives the so-called Zigzag model.

**Table 1.** Irreducible representations (IRs) and their basis vectors (BVs) for the Wykoff site 3*a* in space group $P3_112$ with κ = (½, 0, ½). Note that the threefold site is split into two orbits: 1) *x*, -*x*, ⅓ and *x*, 2*x*, ⅔ and 2) -2*x*, -*x*, 0

| Ru on *x*, –*x*, ⅓ | | IR1 | | Ru on -2*x*, –*x*, 0 | IR1 |
|---|---|---|---|---|---|
| | BV1 | BV2 | BV3 | BV1 | |
| *x*, *y*, *z* | 100 | 010 | 001 | *x*, *y*, *z* | 210 |
| *x*, *x*-*y*, -*z* | 110 | 0-10 | 00-1 | | |

| | | IR2 | | | | IR2 | |
|---|---|---|---|---|---|---|---|
| | BV1 | BV2 | BV3 | | BV1 | BV2 | BV3 |
| *x, y, z* | 100 | 010 | 001 | *x, y, z* | 0-10 | 010 | 001 |
| *x, x-y, -z* | -1-10 | 010 | 001 | | | | |

Figure 4 displays these two different models in case of IR2, e.g. with spins parallel to the trigonal axis (compare with Figure 2). The last degree of freedom for the refinement of these collinear models consists in the choice between a ferromagnetic or an antiferromagnetic coupling between the Ru1(2)_1 and the Ru1(2)_3 site. This last choice determines the sequence in which the Ru-layers are ordered in direction of the c-axis (Figure 5).

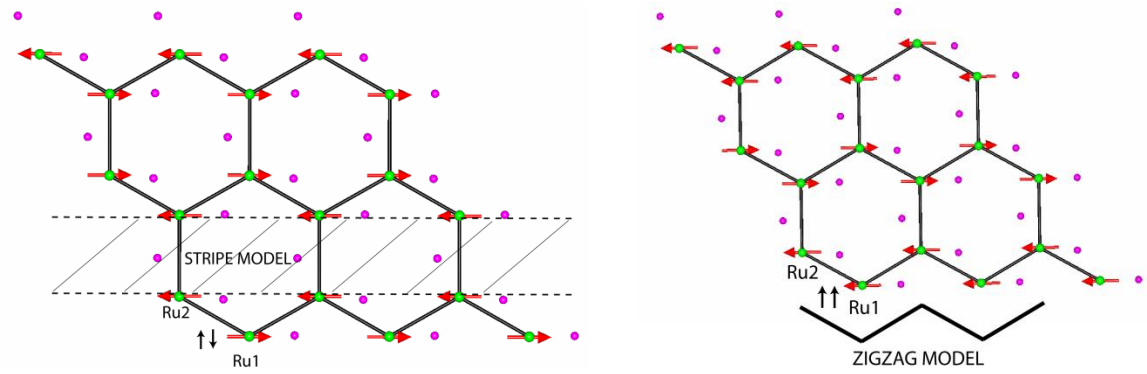



**Figure 4.** Arrangement of Ru-spins corresponding to the Stripe model resulting from an antiferromagnetic coupling of Ru1 and Ru2 sites (left); corresponding to the Zigzag model resulting from a ferromagnetic coupling of Ru1 and Ru2 sites (right).

Testing the different possible collinear magnetic arrangements it became immediately clear that only IR1 is able to reproduce the measured magnetic reflections: All models using IR2 create a too strong magnetic (½ 0 ½) peak and a too weak (½ 0 3/2) peak. The stripe model of IR2 creates furthermore a strong (-½ 1 3/2) reflection which is not seen in the data. In a similar way it is possible to show that using IR1 the stripe model creates again a strong (-½ 1 3/2) reflection and too weak intensity at the position of the (½ 0 3/2) reflection.

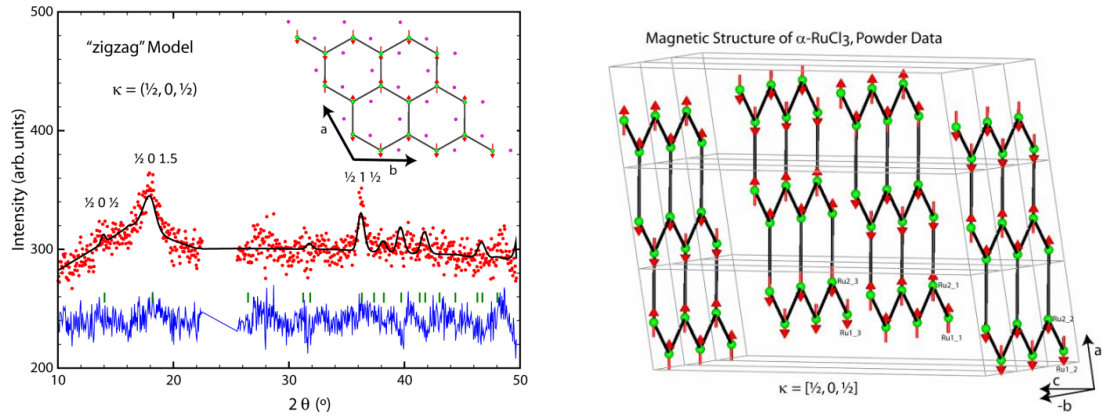



**Figure 5.** Observed (red dots), calculated (black line), and difference pattern of the purely magnetic diffraction pattern of α-$RuCl_3$ (left). The tick marks indicate the calculated position of the magnetic Bragg peaks. Magnetic structure with a Zigzag type arrangement on the honeycomb lattice (right) and an antiferromagnetic alignment of the Ru1(2)_1 and the Ru1(2)_3 sites.

Only the Zigzag model in IR1 together with an antiferromagnetic arrangement between the Ru1(2)_1, Ru1(2)_2 and the Ru1(2)_3 sites is able to refine consistently the intensities of the measured magnetic reflections. Figure 5 shows the final refinement of the neutron difference pattern 2 K - 50 K together with the arrangement of the magnetic spins within the honeycomb layer. Using the scalefactor as determined from the refinement of the purely nuclear pattern recorded at 50 K and the atom coordinates as determined from the high resolution D2B data the magnetic moment value was determined to $\mu_{Ru}$ = 0.5(1) $\mu_B$. The relatively large error bar attached to the refined value is related to the unavailability of a magnetic form factor for $Ru^{3+}$ and the use of the $Fe^{3+}$ form factor instead. The broadening of the magnetic (½ 0 3/2) can be related to a limited coherence length along the crystallographic c-direction induced by the presence of stacking faults.

In the following this result will be compared to previous results on α-$RuCl_3$ obtained by Sears et al. [13] from single crystal neutron diffraction. This group found the presence of two magnetic reflections (½ 0 1) and (½ 0 2) and a magnetic propagation vector κ = (½, 0, 0). The data were not refined and no specific magnetic structure was proposed. Surprisingly single crystal data and powder data find different magnetic propagation vectors. It must be supposed that it is the effect of the stacking faults and the different coherence lengths in a single crystal compared to a powder which leads to this different behaviour. Starting from the magnetic structure determined here from the powder data it is, however, possible to find strong similarities to the data presented by Sears et al.: assuming the same Zigzag type magnetic order and assuming the same orientation of the magnetic moments in direction perpendicular to the trigonal axis one can simulate with κ = (½, 0, 0] the expected magnetic peaks and finds that the by far strongest magnetic reflections are the (½ 0 1) and (½ 0 2) reflections which are exactly the two reflections found by Sears et al. Assuming, on the contrary, a stripe type arrangement in IR1 or a magnetic moment orientation parallel to the trigonal axis corresponding to IR2, reflections not measured by Sears et al. are calculated in the model with κ = (½, 0, 0). This means that apart from the different magnetic propagation vectors both data sets agree in the basic magnetic arrangement of the Ru-spins on the honeycomb lattice. The differences are limited to the arrangement of the Ru-layers in c-direction as can be seen when comparing Figure 6 which displays the simulated magnetic structure for the single crystal data of Sears et al. and Figure 5 which displays the refined solution of the powder data.

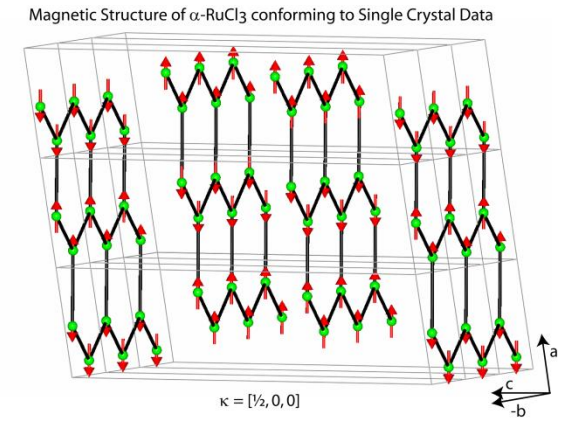



Figure 6. Proposed magnetic structure of α-$RuCl_3$ using the information from the single crystal data of Sears et al. [13] with the magnetic propagation vector κ = (½, 0, 0).

## 4. Summary

The magnetic structure of α-$RuCl_3$ has been determined from the refinement of high intensity neutron powder diffraction data. The magnetic propagation vector κ = (½, 0, ½) is different from the one found before from single crystal data. A collinear arrangement of the Ru-spins on the honeycomb lattice in a way so as to form Zigzag chains with moments perpendicular to the trigonal axis is, however, able to explain powder and single crystal data. The magnetic moment value amounts to about 0.5(1) $\mu_B$ and is

therefore strongly reduced compared to the expected value for a $J_{eff}$ = ½ spin indicating possibly the closeness of the system to the Kitaev spin-liquid state [21].

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[21] During the final preparation of this manuscript we became aware of related unpublished work on neutron diffraction of a single crystal of α-$RuCl_3$ which reports the existence of (½ 0 1) and (½ 0 3/2) magnetic reflections. Both reflections can be explained by the here proposed Zigzag type magnetic structure with spins pointing in a direction perpendicular to the trigonal axis.