Emergence of the isotropic Kitaev honeycomb lattice $\alpha$–RuCl$_3$ and its magnetic properties

Sang-Youn Park$^{1,2}$, Seung-Hwan Do$^{1,3,*}$, Kwang-Yong Choi$^4$, D Jang$^5$, Tae-Hwan Jang$^1$, J Scheffer$^6$, Chun-Ming Wu$^7$, J S Gardner$^{8,9,*}$, J M S Park$^{10}$, Jae-Hoon Park$^{1,11,12,*}$ and Sungdae Ji$^{10,*}$

1 Max Planck POSTECH/Korea Research Initiative, Pohang University of Science and Technology, Pohang 37673, Republic of Korea
2 Pohang Accelerator Laboratory, POSTECH, Pohang 37673, Republic of Korea
3 Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, United States of America
4 Department of Physics, Sungkyunkwan University, Suwon 16419, Republic of Korea
5 Center for Thermometry and Fluid Flow Metrology, Division of Physical Metrology, Korea Research Institute of Standards and Science (KRISS), Daejeon 34113, Republic of Korea
6 Laboratory for Neutron Scattering and Imaging (LNS), Paul Scherrer Institut, Villigen PSI CH-5232, Switzerland
7 National Synchrotron Radiation Research Center, Hsinchu 300092, Taiwan
8 Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States of America
9 Bragg Institute, Australian Nuclear Science and Technology Organisation, Lucas Heights, New South Wales 2234, Australia
10 Advanced Quantum Materials Research Section, Korea Atomic Energy Research Institute, Daejeon 34057, Republic of Korea
11 Department of Physics, Pohang University of Science and Technology, Pohang 37673, Republic of Korea
12 Division of Advanced Materials Science, Pohang University of Science and Technology, Pohang 37673, Republic of Korea

E-mail: seunghwando@gmail.com, jhp@postech.ac.kr and jsungdae@kaeri.re.kr

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Abstract

We present a comprehensive investigation of the crystal and magnetic structures of the van der Waals antiferromagnet $\alpha$–RuCl$_3$ using single crystal x-ray and neutron diffraction. The crystal structure at room temperature is a monoclinic ($C2/m$). However, with decreasing temperature, a remarkable first-order structural phase transition is observed, leading to the emergence of a rhombohedral ($R3$) structure characterized by three-fold rotational symmetry forming an isotropic honeycomb lattice. On further cooling, a zigzag-type antiferromagnetic order develops below $T_N = 6 \sim 6.6$ K. The critical exponent of the magnetic order parameter was determined to be $\beta = 0.11(1)$, which is close to the two-dimensional Ising model. Additionally, the angular dependence of the magnetic critical field of the zigzag antiferromagnetic order for the polarized ferromagnetic phase reveals a six-fold rotational symmetry within the $ab$–plane. These findings

* Authors to whom any correspondence should be addressed.
reflect the symmetry associated with the Ising-like bond-dependent Kitaev spin interactions and underscore the universality of the Kitaev interaction-dominated antiferromagnetic system.

Keywords: Kitaev spin model, quantum magnetism, neutron diffraction

1. Introduction

The Kitaev honeycomb spin model is exactly solvable, and the ground state is described as a quantum spin liquid (QSL) with Majorana fermion (MF) and $Z_2$ gauge fluxes [1]. Beyond the interests of studying pure quantum mechanical states, this system holds promise for quantum computing, particularly through the emergence of non-Abelian anyons resulting from the breaking of time-reversal symmetry. The quest for experimental materials capable of realizing the Kitaev QSL is thus of considerable interest [2, 3].

Among the material candidates, van der Waals antiferromagnet $\alpha\text{–RuCl}_3$ has garnered much attention as a promising candidate for realizing the Kitaev QSL. The combination of large spin–orbit coupling and electronic correlation of the Ru$^{3+}$ ($4d^7$) ion in Mott insulating state engenders a $J_{ab} = 1/2$ pseudo-spin configuration on a nearly isotropic honeycomb lattice. As a result, the intertwined spatial and spin degrees of freedom result in the bond-dependent Kitaev exchange interaction [4–7]. Numerous spectroscopic and thermo-dynamic measurements have unveiled fractionalized MF spin excitations, affirming a material proximate to the Kitaev QSL state [8–11]. Although this material shows a long-range antiferromagnetic (AFM) ordered ground state below $T_N = 6.5 \sim 14$ K due to non-Kitaev exchange interactions, such as Heisenberg, symmetric anisotropy exchange ($\Gamma$–terms) interactions, and interlayer interactions [12–15], applied magnetic field suppresses the AFM order above $6 \sim 8$ T and gives rise to the putative field-induced QSL state [16–18]. Interestingly, half-quantization of the thermal Hall effects [19–21] and oscillations of thermal conductivity [22] appear in the field-induced phase, which suggests a magnetic field response of the charge-neutral MFs in the QSL. However, more recently, there has been a growing controversy concerning the apparent oscillation-like behavior attributed to multiple magnetic transitions with the sample dependence [23, 24], as well as variation in the thermal Hall coefficient depending on sample [25, 26]. This has complicated the understanding of the MFs in $\alpha\text{–RuCl}_3$.

Considering the inherent structural fragility of van der Waals materials such as $\alpha\text{–RuCl}_3$, the ongoing debate over sample dependence appears to be intricately linked to modifications of the exchange interaction parameters of $\alpha\text{–RuCl}_3$, induced by subtle deformation in its structure. Notably, local symmetry at the Ru-site and the trigonal distortion of RuCl$_6$ octahedron significantly impact the bond-dependent exchanges, $K$ and $\Gamma$ [27]. Furthermore, DFT calculations reveal that the magnitude of the Kitaev interaction can vary depending on the layered structural arrangement [14]. The interlayer interaction environment also changes with a layer-stacking configuration, therefore, the accurate determination of the structure of $\alpha\text{–RuCl}_3$ lies at the center of this controversy. Nevertheless, the crystal structure of $\alpha\text{–RuCl}_3$ has not been uniquely determined yet, and it appears to rely on the crystal growth method [23, 28]. Previous crystallographic analyses have reported multiple structures, including a trigonal structure ($P3_121$) [6, 7, 29] and a monoclinic structure ($C2/m$) for single crystals [30, 31], as well as a monoclinic structure for polycrystalline [31]. These structural variations arise from the subtle difference in the stacking sequence of the honeycomb-lattice layers along the $c$–axis. They also provide different local symmetries that impact the local environment for the electron hopping geometry determining exchange interactions.

In this article, we report the rhombohedral structure of $\alpha\text{–RuCl}_3$ single crystals emerging at low temperatures and examine the Kitaev magnetism in their magnetic properties. At room temperature, the crystal structure is described as a monoclinic ($C2/m$) structure. However, we found a significant first-order structural phase transition from the monoclinic to the rhombohedral structure ($R3$) during cooling and subsequent warming. This transition to $R3$ at low temperature engenders an isotropic honeycomb lattice with three-fold rotational symmetry ($C_3$). As the temperature decreases, our crystal manifests an antiferromagnetic transition at $T_N = 6 \sim 6.6$ K. The neutron diffraction study determines the zigzag antiferromagnetic order in the honeycomb lattice, which is consistent with the preliminary result in the monoclinic structure. The measurements of angle-dependent magnetization within the $ab$–plane reveal distinctive 6–fold easy-axes for the transition from the antiferromagnetic to the polarization phase. This behavior, differing from that observed in $XY$ and Heisenberg magnets, represents a unique symmetry associated with Kitaev spin interaction. Furthermore, the critical exponents of the magnetic order parameter and heat capacity closely resemble those found in the 2D Ising universality, suggesting the representation of the magnetic ordering in a system predominantly governed by Ising-like bond-dependent Kitaev interactions.

2. Methods

$\alpha\text{–RuCl}_3$ single crystal was grown by a vacuum sublimation method. A commercial RuCl$_3$ powder (Alfa-Aesar) was thoroughly ground and dehydrated while heating at $200^\circ$ C for 24 h under continuous vacuum and sealed. The sealed quartz ampule is heated at $760^\circ$ C for 24 h using a box furnace, then transferred to a temperature gradient furnace. The
compound was placed in the hot zone of 1080°C, dwelled for 5 h, and the furnace was cooled to 600°C at a rate of 2°C h⁻¹. Single crystals were grown at the cold zone with sizes up to 10 × 10 × 2 mm³ (mass ≤ 120 mg). The dc magnetic susceptibility and specific heat of α−RuCl₃ were measured using a conventional vibrating sample measurement and calorimeter equipped with a commercial Quantum Design Physical Property Measurement System (PPMS Dynacool).

The single crystal x-ray diffraction was performed by using a Huber four-circle diffractometer equipped with the Rigaku x-ray source (Cu target) in the temperature range of T = 4 − 300 K. The monochromatic beam at λ = 1.541 Å was produced by a pyrolytic graphite crystal with a resolution of Δd/d ∼ 7 × 10⁻⁴. The temperature was controlled using a closed-cycle refrigerator with double Be caps.

The single crystal neutron diffraction was performed using the TriCS diffractometer at SINQ in Paul Scherrer Institut (PSI) [32]. The two incident neutron wavelengths of λ = 1.178 Å and 2.314 Å were utilized to measure the nuclear and magnetic Bragg reflections, respectively. The incident beam resolution was Δd/d ∼ 5 × 10⁻³ for λ = 1.178 Å. The crystal structure was refined with the obverse-reverse twin model by using SHELX software [33]. The magnetic structure refinement and representation analysis were carried out using FullProf Suite [34] and SARA/t [35] software, respectively. Temperature-dependent magnetic Bragg peak intensity was collected using the SIKA in the Bragg Institute, Australian Nuclear Science and Technology Organisation using the cold triple-axis spectrometer. A monochromatic incident neutron beam was set to be at a wavelength of λ = 0.01 Å in a vertical focusing pyrolytic graphite monochromator.

3. Experimental results

3.1. Crystal structure

Figures 1(a) and (b) show the temperature dependence of the hexagonal lattice constants a₀ and c₀ estimated by tracking mononclic (0,0,6)₀ and (0,0,4)₀ x-ray diffraction Bragg peaks on α−RuCl₃ single crystal, respectively. These temperature-dependent lattice parameters show significant thermal hysteresis in a temperature range between Tₛ₁ = 166 K and Tₛ₂ = 62 K, indicating a first-order structural phase transition. The thermal hysteresis in a₀ is observed in a temperature range from Tₛ₁ to T⁺ ∼ 115 K, whereas the thermal hysteresis in the parameter c₀ is observed over a wider temperature, ranging from Tₛ₁ to Tₛ₂. This difference indicates the presence of temperature ranges corresponding to three distinct structural states. Figure 1(c) displays the magnetic susceptibility measured with an applied magnetic field along the c-axis and reflects the magnetic response to the structural phase transition. Notably, the susceptibility exhibits significant hysteresis between the temperatures T⁺ and Tₛ₂, which is consistent with the hysteresis temperature range of a₀. This agreement indicates that the magnetic properties are more influenced by changes in the in-plane lattice than the stacking configuration along the c-axis.

To examine the structural symmetry over the transition temperatures, we performed the reciprocal spacing mapping (RSM) scans on the hexagonal (h,k,13)₃ plane at three temperatures: T = 300 K, 80 K, and 10 K. For comparisons, we take reciprocal lattice vector transformations of the monoclinic to hexagonal unit cell, given by a⁺₃ = a⁺₄ = b⁺₄/2 + c⁺₄, 2b⁺₄ = b⁺₄ and c⁺₄ = 3c⁺₄ [see appendix A for details of these lattice vector transformation]. At T = 300 K, the RSM scan presented in figure 1(d) shows five dominant reflections at (1 0 13)₃, (11 13)₃, (1,1,13)₃, (1,2,13)₃, and (2,1,13)₃, which are identified to two pairs of monoclinic (1,±1,4)₃ and (1,±3,4)₃, reflections, and one (2,0,5)₃ reflection, respectively. These reflections satisfy both the reflection condition (hkkl; h + k = 2n) and the mirror symmetry in the ac−plane of the monoclinic space group C2/m. One can also notice two additional weak reflections at (1,0,13)₃ and (0,1,13)₃, which correspond to the 120° twins of the (1,±1,4)₃ reflection.

On the other hand, the RSM scan at T = 10 K (T < Tₛ₂) shows a significant change in the reflection pattern (see figure 1(e)). In particular, the (1,1,13)₃ and (1,2,13)₃ reflections, corresponding to the (1,±3,4)₃, disappear and the (1,0,13)₃ 6-fold reflections appear. This transformation denotes the transition to a hexagonal from a monoclinic structure below Tₛ₂. To understand the 6−fold reflection pattern, we consider two relevant space groups, P3₁12 and R3. The P3₁12 space group allows all 6−fold Bragg reflections, while the R3 space group (−h+k+l=3n) accounts for the 6−fold Bragg reflections by considering the reverse twin (h−k+l=3n) in the hexagonal layered crystal, similar to CrI₃ [36]. Moreover, in the temperature range of hysteresis, the RSM scan at 80 K during the warming process (see figure 1(f)) only displays the hexagonal pattern, while the scan at the same temperature during the cooling process (see figure 1(g)) reveals both monoclinic and hexagonal patterns. This discrepancy indicates that structural phase segregation occurs only upon cooling in the temperature range Tₛ₂ < T < T⁺.

To determine the low-temperature crystal structure, we performed single crystal neutron diffraction measurements at T = 5 K, and collected 370 peaks indexed with the hexagonal notation. We also performed a Rietveld refinement on the two crystal structure models R3 and P3₁12, where the obverse-reverse twin [33]. Figures 2(a) and (b) provide a comparison between the observed and calculated structure factors for the two models. The R3 model yields lower refinement reliability factors (R₁ = 0.114 and wR₂ = 0.250) compared to P3₁12 (R₁ = 0.382 and wR₂ = 0.709), thus offering a more accurate representation of the low-temperature crystal structure. The determined structural information is given in table 1.

13 The R3 structure allows four types of twin-laws, corresponding to identity, 2−fold rotational transformations in the [a−b]−, [a+b]−, and c−axes [37]. However, the refinement considering the simultaneous fitting of the four twin laws does not converge. Consequently, we restricted our model to a two-twin domain model for the obverse-reverse twin, and we found that the R3 with the 2−fold rotational transformation for the [a−b]−axis yields the lowest R−value.
Figure 1. Temperature-dependent hexagonal lattice parameters (a) $a_h$ and (b) $c_h$. Vertical dashed lines are guides for the structural transition temperatures, $T_{S1}$, $T_{S2}$, $T^*$. The data measured while cooling (warming) are indicated with blue (red) circles. (c) Magnetic susceptibility of sample $\sharp 2$ measured with an applied magnetic field along the $c -$axis. (d) Reciprocal space mapping (RSM) scans on a hexagonal $(h, k, 13)_h$ plane at $T = 300$ K. The color scale bar represents the diffracted x-ray intensity. White dashed lines are guides for the hexagonal reciprocal space in the $(h, k, 13)_h$ plane. The collected RSM scan shows strong five Bragg peaks (yellow circles), representing the monoclinic $C_2/m$ space group. (e) RSM scan at $T = 10$ K. Six-folded Bragg reflection peaks represent either the $P_3112$ space group or the $R\bar{3}$ space group with reverse-twinning of the peak marked with yellow circles. RSM scans measured at $T = 80$ K upon (f) warming and (g) cooling. On warming, the RSM exhibits the hexagonal pattern, whereas it shows both monoclinic and hexagonal patterns on cooling. (h) Reciprocal unit vectors in the monoclinic ($\hat{a}_m^*, \hat{b}_m^*, \hat{c}_m^*$) and hexagonal phases ($\hat{a}_h^*, \hat{b}_h^*, \hat{c}_h^*$).

Figure 2(c) displays the determined $R\bar{3}$ rhombohedral structure of $\alpha-$RuCl$_3$. The unit cell consists of three honeycomb layers with the interlayer distance 5.64 Å, and each layer stacks with a translation vector $(\vec{b} - \vec{a} + \vec{c})/3$. The Ru-ions occupy the $6c$ Wyckoff position at $(0,0,z)$ with a single atomic position variable $z$ in the $R\bar{3}$ space group. This Ru sub-lattice forms an isotropic honeycomb lattice with $C_3$ rotational symmetry at low temperatures ($T < T_{S2}$), distinct from the high-temperature monoclinic $C_2/m$ phase with a distorted honeycomb lattice. It is worth noting that the Ru–Cl–Ru bond angle in the edge-shared octahedral environment is 94.09°. According to the quantum chemistry calculations [38], the Kitaev interaction becomes ferromagnetic (FM) with a near maximum value around this bond angle, while the Heisenberg interaction is minimized.

3.2. Magnetic structure

Based on the determined low-temperature rhombohedral structure, we examined the magnetic structure of the AFM state below the $T_N$. We used the TriCS diffractometer at SINQ [32] with incident neutron wavelength $\lambda = 2.314$ Å to collect magnetic reflection peaks. The observed magnetic reflections are explained by the ordering vector $\vec{k} = (0, 1, 1)_h$. We performed a representation analysis using SARAh [35], and the magnetic representation $\Gamma_{mag}$ is decomposed into the two irreducible representations (IR) $\Gamma_1$ and $\Gamma_2$ for two Ru sites $(0,0,\pm z)$ with inversion symmetry. The basis vectors for the magnetic moment in $\Gamma_1$ and $\Gamma_2$ are listed in table 2. $\Gamma_1$ is identified by spins aligned along the zigzag chain direction, while $\Gamma_2$ is characterized by spins aligned along the stripe direction (see the yellow and blue connections in figures 3(a) and (b)).
ment reliability factors with representation of the zigzag and stripe magnetic structures. Therefore, the zigzag magnetic structure describes the antiferromagnetic ordering in \( \alpha - \text{RuCl}_3 \). The determined magnetic structure is exhibited in figures 3(c) and 5(b). The refined magnetic moment is 0.73(3) \( \mu_B \) per Ru atom. It lies within the \( ac \)-plane with tilting angle of 48.3(3)\(^\circ\) from the \( ab \)-plane\(^\circ\), which corresponds to the face diagonal direction of the RuCl\(_3\) octahedron (middle of the \( x- \) and \( y- \) cubic axes). This deviation from the cubic axis indicates the influence of the off-diagonal exchange matrix \( \Gamma \)-term \([39, 40]\), and the minimal Hamiltonian model is \( J - K - \Gamma \). Meanwhile, the moment of the Kitaev-Heisenberg zigzag antiferromagnet is predicted to align along the cubic axes \([39, 40]\).

Figure 4(a) shows the temperature dependence of the magnetic order parameter obtained from the integrated intensity of the magnetic Bragg peak at (0, \( \frac{1}{2}, 1 \))\(_h\). By fitting the power law equation \((1 - T/T_N)^\beta\), the Néel temperature and the critical exponent are determined with \( T_N = 6.3(5) \) K and \( \beta = 0.11(1) \), respectively. The extracted \( \beta \) value is smaller than those of 3D Ising (\( \sim 0.33 \)) or Heisenberg (\( \sim 0.37 \)) model and is closer to the 2D Ising honeycomb model (\( \beta = \frac{1}{4} \)) \([41]\). This 2D Ising-like critical behavior is also observed in the magnetic specific heat \( C_M \). The inset of figure 4(b) shows the heat capacity \( C_p \), and the lattice contribution \( C_L \) obtained from an isostuctural non-magnetic ScCl\(_3\). The \( C_M \) is extracted by subtracting \( C_L \) from \( C_p \), and compared with the theoretical \( C_M \) in the 2D Ising honeycomb model \([42]\) with \( T_N = 6.55 \) K with a scale factor of 0.19 (see figure 4(b)). The simulated \( \lambda \)-shape peak closely matches the linewidth and slope of the measured \( C_M \) below 8 K.

### 3.3. DC and AC magnetization

In this section, we investigate the angular dependence of the magnetization of \( \alpha - \text{RuCl}_3 \) single crystal with a rhombohedral lattice. Figure 5(b) shows the in-plane crystal structure of \( \alpha - \text{RuCl}_3 \), representing a Ru honeycomb lattice. In this figure, the two symmetric axes for parallel and perpendicular to the honeycomb bond directions are indicated with blue and orange arrows, which correspond to the (2, 1, 0) and (0, 1, 0) directions in the reciprocal lattice, respectively. We aligned \( \alpha - \text{RuCl}_3\) single crystal along these directions using Laue diffraction (see figure 5(a)) and performed dc magnetization measurements at \( T = 1.8 \) K. The obtained magnetization (\( M \)) curves are shown as solid lines in figure 5(c). The magnetization curves for both field directions show kinks near 1 T and \( 6 \sim 7 \) T, and these become clearer in the first derivative curves, d\( M \)/dT (see figure 5(c)). According to the previous neutron diffraction \([43]\), the spin-flop-like transition at \( m_H \sim 1 \) T anomaly is attributed to the redistribution of the 120° twinned zigzag AFM domains by the magnetic field, while the upper critical transition indicates the transition from the zigzag AFM to a partially polarized spin state \([18, 44]\). Notably,

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**Table 1.** Structural parameters at 5 K refined by a space group \( R3 \) with an obverse-reverse twin model.

| atom/site | \( x \) | \( y \) | \( z \) |
|-----------|-------|-------|-------|
| Ru (6c)   | 0.31786(45) | 0.33413(42) | 0.41181(12) |
| Cl (18f)  | 0.31786(45) | 0.33413(42) | 0.41181(12) |

These structures are commonly referred to as the zigzag and stripe structures, respectively. We also note that these two magnetic structures have opposite alignments between two adjacent interlayer Ru ions, i.e. the AFM (FM) coupling in the \( \Gamma_1 \) zigzag (\( \Gamma_2 \) stripe) order (see the ellipsoids in figures 3(a) and (b)).

For the collected integrated intensity of magnetic Bragg peaks, we performed Rietveld refinement on both magnetic structures. Figures 3(c) and (d) compare the refinement results between the zigzag and stripe magnetic structures. Notably, the zigzag structure gives lower refinement reliability factors with \( R_1 = 0.072 \) and \( wR_2 = 0.053 \), in comparison with \( R_1 = 0.136 \) and \( wR_2 = 0.179 \) for the stripe structure.
this easy axis repeats every 60°. The face diagonal of the octahedron is the easy axis. Furthermore, determined by neutron diffraction, which indicates that the maximum value at 6 T for the direction along the magnetic moment of the RuCl\(_3\) in figure shows a broad peak near 6 T. Figure 3. Illustration of (a) zigzag and (b) stripe magnetic structures represented in the R3 space group with a magnetic propagation vector \(k = (0, 1, 1)\). The two magnetic structures are distinguished by whether the spins are aligned along (a) zigzag chain or (b) stipe directions, as indicated by the yellow and cyan lines. Blue and green spheres indicate the two sub-lattices of Ru sites (Ru\(_1\) and Ru\(_2\)), and arrows indicate the directions of their magnetic moments. Grey dotted lines indicate the unit cell of the \(R3\) structure. Comparison of observed and calculated magnetic structure factor for (c) zigzag and (d) stripe magnetic structure models.

Table 2. Basis vectors \(\psi_i\)’s of two irreducible representations (\(\Gamma_1\) and \(\Gamma_2\)) obtained from the space group \(R3\) with the magnetic propagation vector \(k = (0, 1, 1)\). Each \(\Gamma\) consists of two Ru sites at \(z = \pm 0.3333\). The basis vector components along the hexagonal crystallographic axes.

| BVs     | \(\Gamma_1\) (zigzag) | \(\Gamma_2\) (stripe) |
|---------|------------------------|-----------------------|
| \(\psi_1\) | (1, 0, 0) | (1, 0, 0) |
| \(\psi_2\) | (0, 1, 0) | (0, 1, 0) |
| \(\psi_3\) | (0, 0, 1) | (0, 0, 1) |
| \(\psi_4\) | (1, 0, 0) | (0, 1, 0) |
| \(\psi_5\) | (0, 1, 0) | (0, 0, 1) |
| \(\psi_6\) | (0, 0, 1) | (0, 0, 1) |

Figure 4. (a) Temperature dependence of the integrated intensity of the magnetic Bragg peak at \((0, 1, 1)\). The blue solid line is the power-law fit, \((1 - T/T_N)^{\beta}\), with \(T_N = 6.3(5)\) K and \(\beta = 0.11(1)\). (b) Magnetic heat capacity \(C_p\) of \(\alpha\)-RuCl\(_3\) (red and blue circles) and scaled 2D Ising honeycomb model fit (solid line). The inset shows the heat capacity \(C_p\) (green circles) of \(\alpha\)-RuCl\(_3\) and the lattice contribution \(C_L\) (dashed line). \(C_p\) exhibits the magnetic transition at \(T_N = 6.55\) K. The \(C_M\) is extracted by subtracting \(C_L\) from \(C_p\) (see the text below). The red and blue circles indicate \(C_M\) above and below \(T_N\), respectively.

To investigate the detailed angular dependence of the \(H_c\), magnetization curves were measured with fields rotating from 0° to 360° with 5° step in the \(ab\)-plane. The critical fields were obtained from the Gaussian fitting to the \(dM/dH\) curves, as shown in figure 5(c). The extracted peak center and peak width are plotted as dots and error bars in the polar plot shown in figure 5(d), and the direction is compared to the geometry of the RuCl\(_3\) octahedron. As shown, the critical field oscillates with hexagonal symmetry with the \(H_c\) reaching its minimum value at 6 T for the direction along the magnetic moment determined by neutron diffraction, which indicates that the face diagonal of the octahedron is the easy axis. Furthermore, this easy axis repeats every 60°, and this symmetry within the plane is distinct from \(XY\) and Heisenberg spin lattices, which have continuous symmetry in the plane. This characteristic is possibly linked to the \(Z_6\) symmetry of the Kitaev–\(\Gamma\) spin interaction [39, 40].

The \(ac\)–magnetization sensitively detects subtle phase transitions. Figures 5(e) and (f) show the real part of the \(ac\)–magnetic susceptibility \(\chi_{ac}'\) measured at various temperatures with magnetic fields along \((2, 1, 0)\) and \((0, 1, 0)\) directions near \(H_c\). At \(T = 1.8\) K, the \(\chi_{ac}'\) curve exhibits a distinctive angular dependence, similar to the \(dc\)–magnetization. However, for the magnetic field along the \((2, 1, 0)\), two broad peaks are visible at 6 T and 6.5 T (see the black arrows in figure 5(e)). The second peak gradually shifts to the left with increasing temperature and merges with the first peak above 3 K. This double-transformation feature indicates the emergence of
an intermediate phase under a magnetic field. Recent neutron diffraction experiments investigating this phase have shown that it is associated with a change in the periodicity of the zigzag AFM along the $c$–axis, referred to as Zigzag2 (ZZ2), and that the emergence of this phase is attributed to inter-layer interactions [44]. It is worth noting that the intermediate phase boundary we observed here slightly differs from the previous reports [44, 45]. While the lower boundary of the ZZ2 phase at 6 T is consistent with the previous value, our measurements indicate an upper boundary at 6.5 T, which is lower than the reported 7 T. Furthermore, the intermediate phase observed for $H||[0, 1, 0]$ is not apparent in our sample. This discrepancy indicates that the phase boundary of the ZZ2 phase can vary with a sample dependence.

4. Discussions

As mentioned above, the local symmetry of Kitaev magnets significantly influences the bond-dependent terms. The transition from a monoclinic ($C2/m$) to a rhombohedral ($R3$) structure, which establishes $C3$ rotational symmetry and forms an isotropic honeycomb lattice, leads to an adjustment of the exchange parameters, consequently affecting the Weiss constant $\Theta_{CW}$ in the Curie-Weiss formula\textsuperscript{15}. Therefore, the sharp change in magnetic susceptibility that occurs simultaneously with structural deformations within the $ab$–plane (see figure 1(c)) shows a close correlation between structural change and tuning of the spin Hamiltonian parameters. It is also worth noting that Raman spectroscopy measurements of our sample revealed an enhanced spectral weight of the continuum excitation in the rhombohedral than the monoclinic structure [46], which underscores the intimate relationship between the structural configuration and the stability of MFs in this material.

Further, the structural transition from $C2/m$ to $R3$ results in alteration in interlayer interactions. Specifically, the rhombohedral and monoclinic structures differ in terms of the number and distances of their nearest interlayer interactions. In the rhombohedral structure, there is only one nearest interlayer interaction, with a distance of 5.64 Å (in this study), whereas

\textsuperscript{15} According to a molecular mean-field calculation with a particular magnetic field direction, the Weiss constant is defined as following: $\Theta_{CW} = \frac{4(K + 1)}{\sum_{ij} J_{ij}} H \cdot J_{ij} \cdot H$, where $H$ and $J_{ij}$ are magnetic field and exchange tensor, respectively. For $H||[0, 0, 1]$, $\Theta_{CW} \propto -(3J + K + 2\Gamma)$. For $H||[1, 0, 0]$, $\Theta_{CW} \propto -(3J + K - \Gamma)$ [27].
the monoclinic structure features four nearest interlayer interactions at distances of 6.04 Å ~ 6.07 Å [31]. The change in both the magnitude and number of interlayer interactions plays an important role in determining the low-temperature physical properties of $\alpha$–RuCl$_3$. Additionally, we noticed that the recent 3D pair-distribution function analysis of the $\alpha$–RuCl$_3$ structure by Sears et al. [47] revealed that there is a mixed phase of rhombohedral and monoclinic stacking at low temperatures, due to stacking disorder occurring during the structural phase transition. This disorder arises from imperfect c-layer stacking attributed to weak van der Waals coupling, inevitably leading to stacking faults. In this case, the coexistence of monoclinic and rhombohedral stacking is likely to introduce multiple bond distances for interlayer interactions, thereby contributing to multiple transition temperatures and critical fields.

In light of these findings, we note the reported sample-dependent variations in the physical properties of $\alpha$–RuCl$_3$ thus far. As shown in the figure C1, our sample’s $T_N$ falls within the range of 6 to 6.6 K, which is slightly lower than the previously reported $T_N$ in the range of 7 to 8 K for single crystals [13, 30, 48] and 13 K for polycrystalline samples [31]. Furthermore, we have similar deviations in the critical field $H_C$ compared to previous reports [44, 45], with the intermediate magnetic phase (ZZZ phase) being notably suppressed in our sample. Based on the comprehensive discussion above, we propose two potential factors contributing to the observed variations in $T_N$ and $H_C$. First, the adjustment of bond-dependent exchanges ($K, \Gamma$) within the rhombohedral structure may lead to these reduced $T_N$ and $H_C$ values. Second, the distinct interlayer interactions between rhombohedral and monoclinic structures, coupled with unavoidable stacking disorders and faults, create a complicated interplay influencing the control of $T_N$ and $H_C$. The in-depth understanding of variability may provide a plausible explanation for the multiple transitions observed in magnetization data and resolve the issue in terms of the thermal conductivity oscillations [23]. Furthermore, the coupling between low-energy phonons propagating in the out-of-plane direction and MFs has been suggested as a critical factor in determining the magnitude of the thermal Hall coefficient [49, 50]. As a result, the layer stacking and/or stacking fault has a profound impact on the explanation of the quantization of the thermal Hall effect. Accurately determining the structural configuration of $\alpha$–RuCl$_3$ and its coupling to magnetic properties is central to resolving the ongoing controversies on this material.

5. Conclusion

We report x-ray and neutron diffraction studies on structural phase transitions of high-quality $\alpha$–RuCl$_3$ single crystals. Our findings reveal a clear transition from $C2/m$ to $R3$ structure during cooling, accompanied by a change from monoclinic to rhombohedral stacking. These structural modifications not only impact the local hopping environment of bond-dependent exchange interactions, such as Kitaev- and $\Gamma$-terms, but also induce changes in interlayer interactions. Consequently, the low-temperature physical properties are influenced by the type of low-temperature structure, contingent upon the presence or absence of structural transitions in the sample. This insight could mark a breakthrough in comprehending the debated issue of sample dependence.

We also performed various magnetic property measurements on $\alpha$–RuCl$_3$ with rhombohedral structure. The observed zigzag magnetic structure and its angular dependency in our low-temperature crystal structure are explained well with the minimal Hamiltonian model of $J - K - \Gamma$. In particular, our angular-dependent magnetization measurements reveal a distinctive 6-fold symmetry of the critical field ($H_c$). This symmetry defies the conventional explanation by $XY$, or Heisenberg antiferromagnets in spin lattices with an isotropic hexagonal structure, as found in $R3$. Within the hexagonal lattice symmetry with spin $J_{HF} = 1/2$, the conventional Ising spin model is not allowed, and rather it most likely corresponds to the $\alpha$-symmetry of the Ising-like Kitaev spin. Furthermore, the observed critical exponent, $\beta = 0.11(1)$, near the $T_N$ closely resembles the predictions of the universality class of the 2D Ising model where the Kitaev spins break the $\alpha$ symmetry through thermal order by disorder, selecting the moment orientation [39, 51]. These results provide insights into the underlying nature of bond-dependent Kitaev spins through the investigation of the zigzag antiferromagnetic order as functions of temperature, angle, and field in $\alpha$–RuCl$_3$.

Data availability statement

The data cannot be made publicly available upon publication because no suitable repository exists for hosting data in this field of study. The data that support the findings of this study are available upon reasonable request from the authors.

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Appendix A. Reciprocal lattice vector transformation

In order to obtain the reciprocal lattice vector transformation between a monoclinic and a hexagonal structure, we make the corresponding unit cell vector transformation between two structures,
The monoclinic reflection indices follow, and unit cells can be written as related to the hexagonal one as shown in Figure A1. The monoclinic unit cell volume \( V_m \) is related to the hexagonal one \( V_h \) with \( 3V_m = 2V_h \).

The reciprocal lattice vectors of monoclinic and hexagonal unit cells can be written as

\[
\begin{align*}
\mathbf{a}_m^* &= \frac{\mathbf{a}_h \times \mathbf{c}_h}{V_m} \quad \text{and} \quad \mathbf{b}_m^* = \frac{\mathbf{c}_h \times \mathbf{a}_h}{V_m} \\
\mathbf{c}_m^* &= \frac{\mathbf{a}_h \times \mathbf{b}_h}{V_m}
\end{align*}
\]

and \( \mathbf{a}_m^* \)'s are expressed with \( \mathbf{a}_m^* \) using equation (A.1), as follows:

\[
\mathbf{c}_m^* = \frac{\mathbf{a}_h \times \mathbf{b}_h}{V_m} = \frac{\mathbf{a}_h \times (\mathbf{a}_h + 2\mathbf{b}_h)}{V_m} = 3\frac{\mathbf{c}_h \times \mathbf{a}_h}{V_h} = 3\mathbf{c}_h^*.
\] (A.3)

The monoclinic reflection indices \((h,k,l)_m\) are transformed to the hexagonal \((h,k,l)_h\) by

\[
\begin{align*}
h_m\mathbf{a}_m + k_m\mathbf{b}_m + l_m\mathbf{c}_m^* &= h_m(\mathbf{a}_m^* - \mathbf{b}_h^*/2 + \mathbf{c}_h^*) + k_m(\mathbf{b}_h^*/2) + l_m(3\mathbf{c}_h^*) \\
&= h_m\mathbf{a}_m^* + (h_m/2 + k_m/2)\mathbf{b}_h^* + 3l_m\mathbf{c}_h^* \\
&= h_m\mathbf{a}_m^* + h_0\mathbf{b}_h^* + l_0\mathbf{c}_h^*.
\end{align*}
\] (A.4)

and expressed as a matrix form,

\[
\begin{pmatrix}
h_m \\
k_m \\
l_m
\end{pmatrix}
= \begin{pmatrix}
1 & 0 & 0 \\
1 & 2 & 0 \\
-1/3 & 0 & 1/3
\end{pmatrix}
\begin{pmatrix}
h_h \\
k_h \\
l_h
\end{pmatrix}.
\] (A.5)

---

**Figure A1.** (a) schematic diagrams of hexagonal unit cell vectors \( \mathbf{a}_h^* \)'s and monoclinic ones \( \mathbf{a}_m^* \)'s. The hexagonal and monoclinic unit cells are represented by solid and dashed lines, respectively. (b)–(c), The projection of both unit cells to (b) ac- and (c) ab-plane.

---

**Figure B1.** dc magnetic susceptibility of sample \( \gamma_2 \), measured with magnetic fields along (a) \((2,1,0)\) and (b) \((0,1,0)\). Inset of (a) shows the first derivative of \( \chi \) measured at \( H = 0.1 \text{ T} \). The arrow indicates the transition temperature at \( T_N = 6.2 \text{ K} \).

**Appendix B. DC Magnetic susceptibility**

Figure B1 shows dc magnetic susceptibility, \( \chi_{dc}(T) \), measured with applied magnetic fields along \((2,1,0)\) and \((0,1,0)\). The \( \chi_{dc} \) curve for \( H\parallel(2,1,0) \) exhibits a drop at 6.2 K and 0.1 T due to the zigzag antiferromagnetic transition. This transition temperature gradually decreases with increasing magnetic field and disappears beyond 6 T, indicating the appearance of a polarized ferromagnetic phase. In contrast, \( \chi_{dc} \) measured with \( H\parallel(0,1,0) \) at 0.1 T shows a similar drop at 6.2 K in the antiferromagnetic order. However, it increases at 2 T and then decreases with higher magnetic fields, revealing distinct field responses for the two different directions. This discrepancy reflects the response to the spin direction of the zigzag AFM with the 120° twinned domain for two orthogonal magnetic field directions [43, 55].
Appendix C. Sample dependence with transition temperatures

Figure C1 shows the zero-field specific heat measurements for the samples used for experiments. A sharp $\lambda$-transitions for $T_N$ are shown in between 6 K and 6.6 K.

ORCID iDs

Sang-Youn Park https://orcid.org/0000-0002-1500-4384
Seung-Hwan Do https://orcid.org/0000-0001-8212-7803
D Jang https://orcid.org/0000-0003-3875-7802
J S Gardner https://orcid.org/0000-0002-7823-4072

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