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Structural Transition and Magnetic Anisotropy in α-$RuCl_3$

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We report X-ray diffraction and magnetic susceptibility studies of the structural phase transition in α-$RuCl_3$. By utilizing a single crystal sample with predominantly single twin domain, we show that α-$RuCl_3$ goes from high-temperature C2/m structure to a rhombohedral structure with $R\bar{3}$ symmetry at low temperature. While the defining feature of the structural transition is changing the stacking direction from the monoclinic a-axis to the b-axis, bond-length anisotropy disappears when the structural change occurs, indicating that the local C_3 symmetry is restored within the honeycomb layer. The symmetry change is corroborated by the vanishing magnetic anisotropy in the low-temperature structure. Our study demonstrates that magnetic interaction is extremely sensitive to structural details in α-$RuCl_3$, which could explain the sample dependence found in this material.

In recent years, α-$RuCl_3$ has emerged as the prime candidate for realizing a Kitaev quantum spin liquid phase [1–25]. In α-$RuCl_3$, strong spin-orbit coupling (SOC) and the honeycomb network formed by edge-sharing $RuCl_6$ octahedra (see Fig. 1) provides a platform to realize a bond-dependent anisotropic interaction called Kitaev interaction (K), an essential ingredient for realizing Kitaev's honeycomb model [22–24, 26, 27]. Although α-$RuCl_3$ magnetically orders below 7K, this order can be fully suppressed via applying magnetic field [7, 8, 11–15]. The explosion of interest in this material was spurred by the discovery of a half-quantized thermal Hall effect in this phase, suggesting that this field-induced phase is a quantum spin liquid with Majorana fermions as heat carriers [16]. However, subsequent experimental reports seem to suggest that the half-quantized thermal Hall effect is highly sample dependent [20, 21, 28]. Theoretical studies found that in addition to the Kitaev interaction, off-diagonal symmetric exchange interaction Γ as well as isotropic Heisenberg interaction J are important for describing the physics of α-$RuCl_3$ [18, 29–36]. In addition, further neighbor interactions or additional off-diagonal terms due to trigonal distortion are often considered in the study of α-$RuCl_3$ [22, 36–40]. Due to the complexity of the model, there is no consensus on the size (and sometimes even signs) of these interaction terms.

Another defining characteristic of α-$RuCl_3$ is that it belongs to a family of magnetic van der Waals materials with an easily cleavable layered structure. While this opens up the exciting possibility of using α-$RuCl_3$ in van der Waals heterostructures, it also means that this material is susceptible to the proliferation of stacking faults. It is now widely accepted that high-quality samples with a minimal number of stacking faults are in the monoclinic C2/m structure at room temperature [9, 10, 41]. These samples are characterized by a single magnetic transition around $T_N = 7$ K, while samples with many stacking faults tend to show multiple transitions in the range of 10 K to 14 K [3, 8, 25]. It turns out that even the high-quality samples show small differences in T_N, ranging from 6.5 K to 8 K [42, 43]. This additional sample variability is closely associated with the first-order structural phase transition around 150 K, which changes the stacking structure at low temperatures [8, 41, 43–45]. The twinning of the low-temperature structure could introduce a large number of stacking faults even for a high-quality (at room temperature) sample, which also makes it difficult to determine the low-temperature crystal structure unambiguously [43, 45]. As a result, both rhombohedral [41, 44, 45] and monoclinic [9, 10] low-temperature structures have been used in many theoretical and experimental studies.

While one might question whether the stacking sequence matters for two-dimensional Kitaev physics in α-$RuCl_3$, the experimentally observed sample dependence of the half-quantized thermal Hall effect suggests it does [16, 20, 21, 28]. An interesting question is whether the structural difference implies a difference in the underlying magnetic Hamiltonian, which would be unaffected if the structural difference is strictly due to the stacking sequence of honeycomb layers. To answer this question, one should pay attention to the local symmetry that governs magnetic interactions, rather than the global structural symmetry, which is determined from stacking arrangements.

In this Letter, we report our detailed investigation of structural and magnetic properties of a high-quality single crystal α-$RuCl_3$ across the structural phase transition. This is made possible by studying a low-temperature-twin-free single crystal sample. We find that the low-temperature structure has a rhombohedral $R\bar{3}$ symmetry, in agreement of several recent reports [41, 45]. Crucially, this low-temperature structure recovers the C_3 rotational symmetry of the honeycomb plane, which is broken in the room-temperature C2/m structure. This symmetry change is corroborated by our bond-length data as well as magnetic susceptibility data. The implication is that the magnetic Hamiltonian of α-$RuCl_3$

must have C_3 symmetry, although this symmetry might be fragile against structural stacking disorder, such as the coexistence of C2/m and R$\bar{3}$ stacking due to incomplete structural transformation.

Experimental details: Single crystal α-$RuCl_3$ crystals were grown using chemical vapor transport methods as described in Ref. [25]. Carefully selected crystals show a sharp single magnetic transition at T_N=7.2 K with a sharp mosaic width along L of less than 0.1 degrees. Magnetic susceptibility was measured using Quantum Design Magnetic Property Measurement System (MPMS) and specific heat was measured using Quantum Design Physical Property Measurement System (PPMS). Single crystal X-ray diffraction measurements were carried out at the BXDS-IVU beamline at Canadian Light Source (CLS) with 10 keV X-ray energy and also using the Rigaku Smartlab diffractometer at the University of Toronto. The reciprocal space maps were obtained at the QM2 beamline at Cornell High Energy Synchrotron Source (CHESS) using 20 keV X-ray energy in transmission geometry. The lateral size of the sample was about 4 mm × 3.5 mm and the beam size was about 0.5 mm× 0.2 mm. The sample mosaicity remained fairly uniform across the sample, indicating that the structural data presented below is representative data of the whole sample.

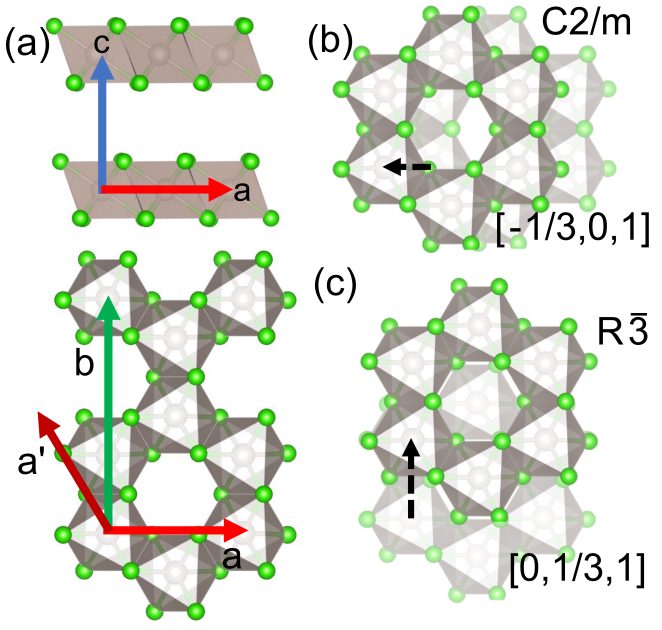


FIG. 1. Crystal structure of α-$RuCl_3$. (a) Orthorhombic axes used in this Letter. (b) Structure of α-$RuCl_3$ above the structural transition temperature. Monoclinic C2/m structure has neighbouring honeycomb layers that are shifted along [-1/3,0,1]. (c) Structure of α-$RuCl_3$ below the structural transition temperature. Rhombohedral R$\bar{3}$ structure has neighbouring honeycomb layers that are shifted along [0,1/3,1].

Structural Transition: The crystal structure of α-$RuCl_3$ is shown in Fig. 1. We find it convenient to describe both monoclinic and rhombohedral structures using an orthorhombic coordinate system shown in Fig. 1(a). The in-plane unit vectors $\vec{a}_o$ and $\vec{b}_o$ are two distinct high-symmetry vectors, same as in the C2/m structure, but $\vec{c}_o$ now refers to the vector perpendicular to the honeycomb plane with the length equal to the layer separation. Note that $\vec{c}_o$ is not a lattice translation vector in either structure and one should be careful when comparing h, k, l in different structures. See Supplemental Material for reciprocal space comparisons. We will drop the subscript in the following discussions. The defining feature of the structural transition is the change in how the top layer is stacked against the bottom layer. As we will show below, the neighboring layer on top is shifted along the $\vec{a}$ direction in the high-temperature structure, while the shift direction changes to $\vec{b}_o$ below the structural transition temperature. The stacking sequence in the high-temperature C2/m structure can be restated as the lattice translation vector $-\frac{1}{3}\vec{a}+\vec{c}$ in the three-layer periodic structure. The stacking sequence in the R$\bar{3}$ structure is $\pm\frac{1}{3}\vec{b}+\vec{c}$. Note that there are two equivalent translation vectors in the R$\bar{3}$ structure. The C2/m and R$\bar{3}$ structures can be distinguished easily in a diffraction experiment. For the C2/m structure with $-\frac{1}{3}\vec{a}+\vec{c}$ translation, we expect Bragg peaks to occur at $(h, k, l + h/3)$ where h, k, l are integers with even $h + k$. Now, for the lattice translation vector $\pm\frac{1}{3}\vec{b}+\vec{c}$, Bragg peaks will be found at $(h, k, l \mp k/3)$.

Figure 2 shows x-ray diffraction reciprocal space maps and line scans at two different temperatures above and well below the structural transition temperature. In Fig. 2(a)(b), the reciprocal space maps at 200K are shown. Clear sharp Bragg peaks with little diffuse scattering is observed, which confirms the high crystalline quality with minimum stacking faults at high temperature. As expected from the structure factor introduced above, Bragg peaks are observed at all integer L values in the $(0, K, L)$ plane, while they are observed at non-integer L values in the $(H, 0, L)$ plane. Figure 2(c)(d) shows reciprocal space maps at 20 K, showing the shift of the Bragg peak position below the transition temperature. To see this clearly, in Fig. 2(e)(f), the intensity in the rectangular boxes is plotted as a function of L for both $(0, 2, L)$ and $(2, 0, L)$ directions. The $(0, 2, l)$ Bragg peaks shift to $(0, 2, l-2/3)$ – equivalently $(0, 2, l+1/3)$ – and the $(2, 0, l+2/3)$ Bragg peaks shift to $(2, 0, l)$, respectively. This change in the Bragg peak positions is precisely what is expected from a transition from the monoclinic C2/m structure to the rhombohedral R$\bar{3}$ structure. In addition, this shift can be explained with a single translation vector $\frac{1}{3}\vec{b}+\vec{c}$, associated with only one type of twin domain. In fact, one can observe small peaks at $(0, 2, l + 2/3)$ in Fig. 2(e), which is due to contributions from the minority twin domain. We estimate more than

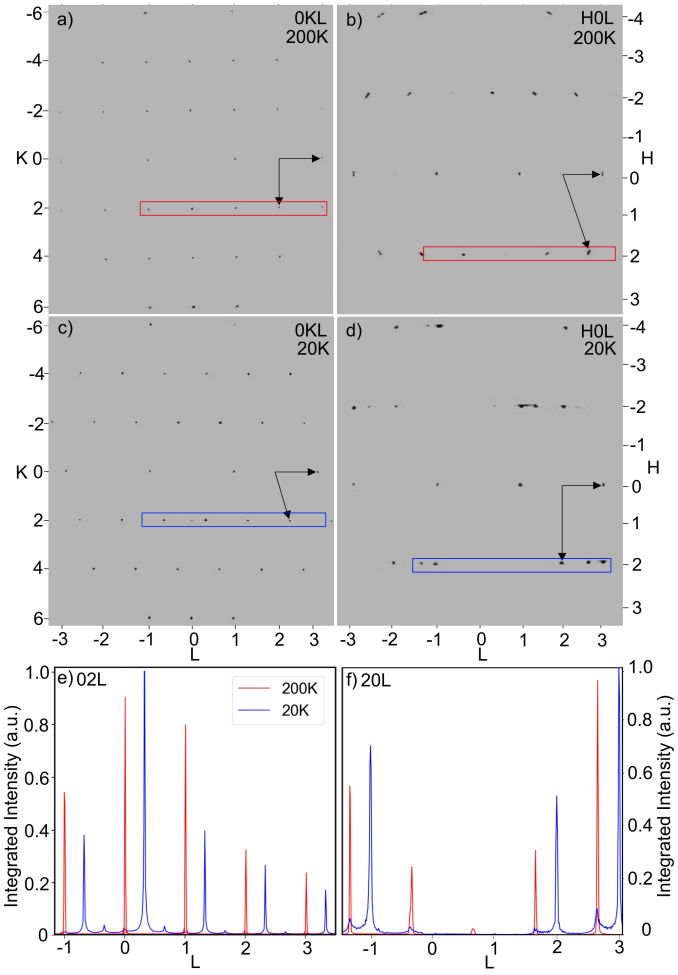


FIG. 2. (a)(b) X-ray diffraction reciprocal space map of (0,K,L) plane and (H,0,L) plane respectively above the structural transition of 200K. The peak positions can be well-explained using monoclinic structures which is shown in Fig.1(b). (c)(d) same reciprocal space map at 20K. The main peaks are well explained by the rhombohedral structure shown in Fig.1(c). (e)(f) shows L scan along (0,2,L) and (2,0,L) in the rectangular boxes shown in panels (a)-(d), demonstrating the change in Bragg peak positions across the structural transition.

95% of the crystal is in the majority twin domain. On the other hand, a more even mixture of the two twin domains is found in many other crystals we examined, as is the data shown in the recent study by Zhang et al. [43]. We also note that our data rules out the $P3_112$ stacking, which would show both $l \pm 1/3$ peaks. However, even for our sample, which consists of mostly single twin-domain, weak diffuse scattering develops at low temperatures, indicating the presence of stacking faults.

The $C2/m$ or $R\bar{3}$ crystal symmetry does not necessarily mean that the honeycomb layer must have the same local symmetry. An ideal honeycomb layer has local C_3 symmetry with the rotation axis out of the plane. However, monoclinic stacking of the honeycomb layers in the C2/m structure breaks global three-fold rotational symmetry. On the other hand, the stacking shift along the b-axis of the R$\bar{3}$ structure (Fig. 1(c)) preserves the C_3 symmetry. As shown below, we find evidence from our x-ray diffraction that the local symmetry also changes when the structural change occurs. That is, the structural transition is not just a stacking sequence change, but is accompanied by the in-plane bond-length change.

In Fig. 3(c,d), we compare 2θ scans of three equivalent peaks at two temperatures. The $(-2, 0, L)$, $(-1, -3, L)$, and $(-1, 3, L)$ Bragg peaks with common L would be symmetry equivalent in an ideal honeycomb structure. These peak positions are denoted with circles in the reciprocal space map shown in Fig. 3(b). This is the case in the low-temperature structure with a good agreement in 2θ values between the three peaks. In contrast, a clear difference in 2θ is observed at high temperatures, indicating the presence of inequivalent bonds. Note that we need to use $(2, 0, L)$ instead of $(-2, 0, L)$ in the $C2/m$ structure to find equivalent peaks (see Supplemental Material for further explanation). We find that the bonds along the stacking direction in the monoclinic structure are elongated as shown in Fig. 3. In other words, the bond-anisotropy present at high temperatures vanishes below the structural transition temperature, and the crystal recovers global as well as local C_3 symmetry at low temperatures. Our result, therefore, indicates that the structural distortion observed in the exfoliated monolayer sample [46] is not present in a bulk crystal.

In-plane Magnetic Anisotropy: The local symmetry change is also corroborated by our magnetic susceptibility data. Figure 4 shows temperature dependent magnetic susceptibility $\chi(T)$ with a field applied in different high-symmetry directions in-plane: $\vec{a}$,$\vec{b}$ and $\vec{a}'$ as labelled in Fig. 1. As shown in Fig. 4(a), $\chi(T)$ is isotropic over a wide temperature range, except for two temperature regions. The inset of Fig. 4(a) shows the region near the magnetic transition temperature T_N=7.2K, determined from the peaks in $d\chi/dT$ as well as in specific heat $C_p(T)$. The susceptibility along a, $\chi_a(T)$, is the smallest below T_N as expected from the ordered moment along the a-axis (ignoring the tilt away from the honeycomb plane). The other region showing in-plane anisotropy is around the structural transition, which is shown in more detail in Fig. 4(b).

Figure 4(b) clearly shows that the magnetic susceptibility measured along the three directions is indistinguishable below 130 K but distinct above 160 K. The temperature hysteresis of the structural transition gives rise to somewhat complex behavior in between. The largest change in the susceptibility is observed for $\chi_a(T)$, while the change in the susceptibility is in the opposite sign for $\chi_b(T)$. $\chi_{a'}(T)$ remains almost unchanged through the transition. To gain further understanding, we plot $\chi^{-1}(T)$ in the inset of Fig. 4(b). We can see that the Curie constant, the slope of the inverse susceptibility,

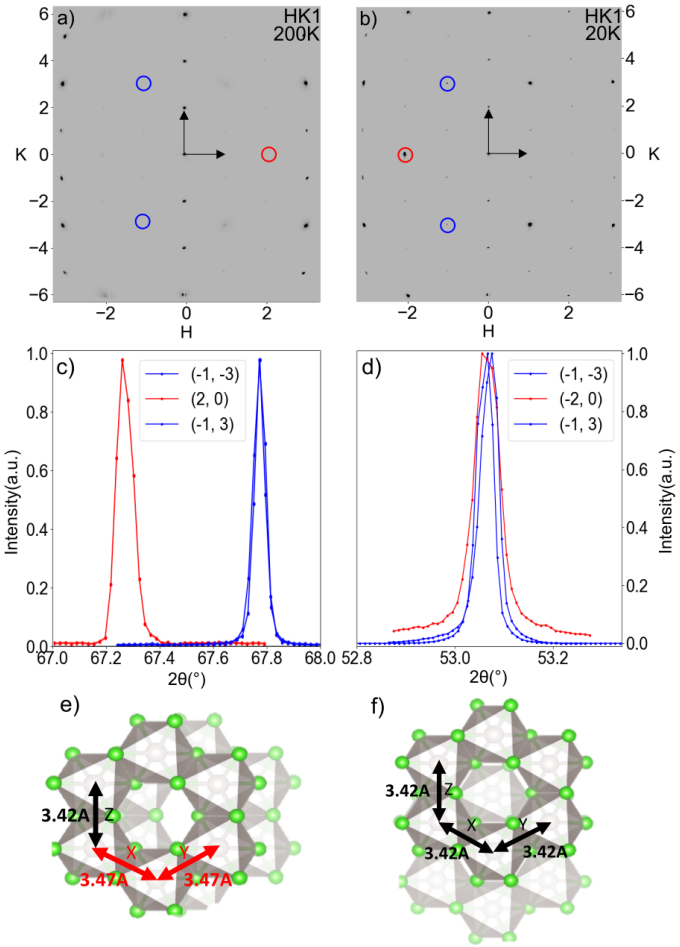


FIG. 3. (a)(b) X-ray diffraction reciprocal space map of the (H, K) plane with fixed $L = 1$, obtained at 200 K and 20 K, respectively. (c)(d) High-resolution 2θ scans of the peaks equivalent to the ones circled in panels (a) and (b), respectively. Note that $L = 3.67$ and $L = 5$ are chosen for panels (c) and (d), respectively, because of the shift of the Bragg peak discussed in Figure 2. A clear difference in the 2θ values is observed at 200 K, which disappears at 20 K. (e)(f) The structure with an in-plane lattice parameter above and below the structural transition.

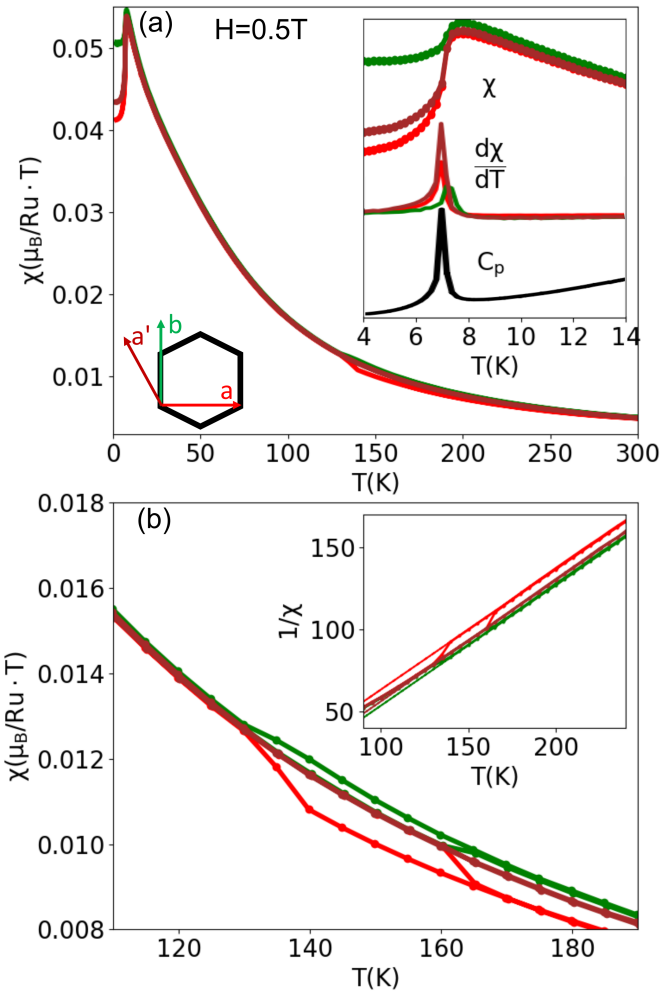


FIG. 4. (a) Temperature-dependent magnetic susceptibility with different in-plane field direction $\vec{a}$,$\vec{a'}$, and $\vec{b}$ where the directions are shown in Fig. 1(a). Inset of (a) focuses on the magnetic transition. (b) Magnetic susceptibility close to the structural transition. The arrows denote heating and cooling directions. An identical range of hysteresis loops of 30K is observed for different high symmetry directions. However, the hysteresis behaviour is anisotropic. The susceptibility decreases in $\vec{a}$ while it increases in $\vec{b}$ and no change is seen in $\vec{a'}$. The inset shows the inverse susceptibility.

remains the same in all three directions at all temperatures (corresponding to a moment size of $2.46(6)\mu_B$). Therefore, the observed anisotropy can be attributed to different Weiss temperatures, shown as the vertical shifts in the plot. Since Curie constants are often associated with g-factors while Weiss temperatures depend strongly on the exchange interactions, we can conclude that the magnetic anisotropy in the high-temperature phase is caused by different magnetic interaction parameters.

Anisotropic magnetic susceptibility was investigated previously by Lampen-Kelley and coworkers, who observed that the in-plane magnetic susceptibility exhibits C_2 rotational symmetry, similar to the high-temperature data reported here [17]. The observed angle-dependence was explained using the high-temperature series expansion of the anisotropic $J-K-\Gamma$ model, allowing different interaction strengths between bonds along and perpendicular to the a-axis (i.e., zigzag direction). Our data could be quantitatively accounted for by using the same high-temperature expansion formula used in Ref. [17] as shown in Supplemental Materials, although the Weiss temperatures are smaller than those obtained in Ref. [17]. Of course, a major difference is the disappearance of the anisotropy in the low-temperature structure in our data, which presumably is due to the fact that our sample is mostly made up of a single twin domain of R$\bar{3}$. Our observation is consistent with the 6-fold symmetric angular

dependence of specific heat reported in Yokoi et. al. [19].

Discussion: Let's first discuss the implication of the observed change in the in-plane magnetic anisotropy as a function of temperature. Both high- and low-temperature structures have inversion symmetry with respect to the center of the bond, which means that the $J-K-\Gamma$ model is still the minimal Hamiltonian for this material at low temperatures. We also note that additional small terms required to stabilize the zigzag ground state, such as the third-nearest neighbor interaction or the Γ' interaction due to trigonal crystal field, do not give rise to the magnetic anisotropy observed at high temperatures[17]. Therefore, observations of magnetic anisotropy can be only explained by the crystal structure explicitly breaking the local C_3 symmetry. Then, the magnetic anisotropy at low temperatures, reported in the literature, requires the presence of $C2/m$ structure. In fact, a small fraction (a few percent) of $C2/m$ is also found in our structural (see Fig.2e) as well as magnetic data, as indicated by the difference in the susceptibility along the $\vec{a}$ and $\vec{a'}$ directions below T_N in Fig. 4(a).

This would be possible if the structural phase transition is incomplete and the high-temperature $C2/m$ structure coexists with the low temperature $R\bar{3}$ structure below the structural transition temperature [43]. Recent studies using torque magnetometry [47] and diffuse X-ray scattering [48] further sheds light on the coexistence of the $C2/m$ and the $R\bar{3}$ structure in α-$RuCl_3$ crystals. We found that the small in-plane anisotropy below T_N is strongly sample-dependent, suggesting that the anisotropy arises from magnetic domains. While it is expected that the $R\bar{3}$ structure will have three equally populated zigzag magnetic domains, this ideal population distribution does not seem to be realized even in our mostly single-twin sample. However, our result seems to indicate that the best sample is the one with minimal structural twinning and exhibiting the smallest in-plane anisotropy in the zigzag phase.

The origin of the persistent C2/m fraction is unclear, but may be due to the strain caused by gluing the sample and/or strain during the cooling process as discussed in detail in Ref. [47]. Another possibility is that the $C2/m$ phase remains in the structural domain boundary region. Note that to go from $C2/m$ to $R\bar{3}$ structure, the upper layer should slide along the $-\frac{1}{3}\vec{a}+\frac{1}{3}\vec{b}+\vec{c}$ direction or the $-\frac{1}{3}\vec{a}-\frac{1}{3}\vec{b}+\vec{c}$ direction, resulting in the two twin domains discussed above. It is reasonable to assume that the twin domain boundary will remain in the $C2/m$ structure, and therefore heavily-twinned samples will show more of the residual $C2/m$ phase.

Conclusions: We report our x-ray diffraction study of a structural phase transition in the high-quality (almost) twin-free α-$RuCl_3$ crystals. α-$RuCl_3$ goes through the structural transition from C2/m to R$\bar{3}$ structure, associated with the change in the stacking direction from the monoclinic a-axis to b-axis. We confirm that the bond-length anisotropy disappears in the R$\bar{3}$ phase, suggesting that the local symmetry of the honeycomb layer follows the global crystal symmetry. This is also supported by our observation of vanishing in-plane magnetic anisotropy in the low-temperature structure. Our study provides an unambiguous answer to the long-standing question about the low-temperature crystal structure of α-$RuCl_3$, arguably the most promising candidate material for a Kitaev quantum spin liquid.

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