Pressure-tuning of α-RuCl$_3$ towards the ideal Kitaev-limit

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We report the discovery of an intriguing pressure-driven phase transformation in the layered Kitaev-material α-RuCl$_3$. By analyzing both the Bragg scattering as well as the diffuse scattering of high-quality single crystals, we reveal a collective reorganization of the layer stacking throughout the crystal. Importantly, this transformation also affects the structure of the RuCl$_3$ honeycomb layers, which acquire a high trigonal symmetry with a single Ru–Ru distance of 3.41 Å and a single Ru–Cl–Ru bond angle of 92.8°. Hydrostatic pressure therefore allows to tune the structure of α-RuCl$_3$ much closer to the ideal Kitaev-limit. The high-symmetry phase can also be stabilized by biaxial stress, which can explain conflicting results reported earlier and, more importantly, makes the high-symmetry phase accessible to a variety of experiments.

INTRODUCTION

Quantum spin liquids (QSLs) are fascinating states of matter in which competing interactions between magnetic moments prevent static magnetic order down to even zero temperature. Instead a massive quantum entanglement of spins dominates. QSLs can therefore not be identified by broken symmetries, nor do they correspond to a trivial disordered spin system. Instead, QSLs exhibit non-trivial topological properties, many-body quantum entanglement and emergent fractionalized quasiparticles.

A specific and very famous example is the so-called Kitaev-QSL, where the constituent spins can fractionalize into mobile Majorana fermions coupled to conserved $Z_2$-fluxes. Applying a magnetic field even results in a non-abelian QSL, which may in fact be a key ingredient for topological quantum computing and certainly is one reason for the large interest in these systems. As far as specific materials are concerned, a number of candidates could already be identified, including Na$_2$IrO$_3$, different polytypes of Li$_2$IrO$_3$, H$_3$LiIr$_2$O$_6$ and α-RuCl$_3$. Among these, as a matter of fact, α-RuCl$_3$ turned out to be particularly promising, because earlier indications of a field-induced QSL appear to be supported by signatures of a quantized thermal Hall conductance.

α-RuCl$_3$ is a spin-orbit assisted Mott-insulator with honeycomb layers formed by edge-sharing RuCl$_3$ octahedra, as illustrated in Fig. 1(a). The low-energy magnetism of the honeycomb layers can be described in terms of $j_{\text{eff}} = 1/2$ pseudo-spins of Ru $4d^5$. However, α-RuCl$_3$ is not a pure Kitaev-system. Besides the Kitaev-interactions, there are also other magnetic couplings beyond the ideal Kitaev-model, such as the Heisenberg exchange and the off-diagonal symmetric exchange. Due to these additional interactions, α-RuCl$_3$ does not display a Kitaev-QSL at ambient pressure and low temperature, but instead antiferromagnetic zigzag-order below $T_N = 7$ K. It has been realized early on that the magnetic order of α-RuCl$_3$ is affected by the stacking order of the RuCl$_3$ layers: A single and well-defined $T_N = 7$ K was found to require a well-defined layer-stacking, while disordered stacking broadens the magnetic transition significantly and can even introduce a second magnetic transition at 14 K.

In general, layered transition metal trihalides are well-known for their polytypism, meaning in particular that different stackings of the strongly covalent layers can occur. The polytypism facilitates modification of the stacking via external parameters, which in turn can provide a handle to manipulate magnetic properties. This is a strong motivation for exploring the relevance of polytypism to magnetism in the Kitaev-material α-RuCl$_3$.

One way to trigger different polytypes of α-RuCl$_3$ via an external parameter is to apply hydrostatic pressure. Previous studies of α-RuCl$_3$ already established that α-RuCl$_3$ in fact stabilizes a broken-symmetry state with ordered Ru–Ru dimers, i.e., a valence bond crystal, see Fig. 1(b). Here we study the transition from the ambient pressure monoclinic phase into this dimerized phase at room temperature in more detail. By means of x-ray diffraction (XRD) we discover that applying pressure at constant temperature $T$ stabilizes a rhombohedral phase of α-RuCl$_3$ with short-range stacking order, located in between the ambient and the dimerized phase in the $pT$ phase diagram. Importantly, the RuCl$_3$ layers in this rhombohedral phase acquire a high-symmetry configuration, bringing their geometry much closer to the ideal Kitaev-limit where all the Ru–Cl–Ru bond angles are 90°.
FIG. 1. Structure and layer stacking in α-RuCl₃ as functions of temperature and pressure. (a) Illustration of the three-dimensional monoclinic C2/m structure of α-RuCl₃ at ambient conditions. (b) Pressure-temperature phase diagram of α-RuCl₃. The red triangles and diamonds indicate points where full single-crystal diffraction data sets have been recorded at ambient and at increased pressure, respectively. The red crosses indicate points where overview scans have been collected (further explanations in the text). The C2/m symmetry with cubic close packed Cl is preserved in stress-free samples down to 3 K, as illustrated by the green region. Yellow indicates the region where the phase with hexagonal close packed Cl is stable. With further increasing pressure, a nonmagnetic dimer state is reached. The solid and open black circles, taken from Ref. 19, mark the reduction of the magnetic susceptibility upon cooling and warming at constant p, respectively.

EXPERIMENTAL DETAILS

α-RuCl₃ single crystals were grown from phase-pure commercial α-RuCl₃ powder via a high-temperature vapor transport technique and carefully characterized as described previously [19]. We confirmed the monoclinic C2/m structure at ambient conditions for a disorder-free crystal (crystal 1) by means of single crystal XRD (for details see Appendix). The obtained crystallographic parameters are fully consistent with previously published results [19].

High-pressure XRD studies were carried out at beamlines ID15B and ID27 of the European Synchrotron Radiation Facility (ESRF) in Grenoble. To provide nearly hydrostatic pressure conditions the membrane-driven diamond anvil cell (DAC) was loaded with helium as pressure transmitting medium. The pressure inside the DAC was monitored in-situ using the R₁₂₂ fluorescence of Cr centers in ruby spheres placed next to the sample. The high-pressure XRD was done in transmission geometry with the DAC mounted on a single-axis goniometer with the rotation axis (ω) perpendicular to the scattering plane. The diffracted radiation was recorded with a MAR555 flat panel detector at ID15B and a MAR-CCD detector at ID27 installed perpendicular to the primary beam.

RESULTS

Fully consistent with previous reports, our diffraction patterns taken at ambient conditions can be indexed by a monoclinic unit cell (space group C2/m) with lattice parameters aₘₐₜ=5.9875(6) Å, bₘₐₜ=10.3529(3) Å, cₘₐₜ=6.0456(6) Å and β=108.777(9), see Fig.1(a). However, the crystal studied as a function of p at room temperature (crystal 2) showed, apart from sharp Bragg reflections, a set of one-dimensional diffuse scattering rods and all the Ru–Ru as well Ru–Cl distances are identical.

Single crystal XRD data at room temperature were collected at ID15B, using a monochromatic radiation of 30 keV (λ=0.4113 Å) and a spot size of 10x10 µm² [red diamonds in Fig.1(b)]. Diffraction data were recorded in steps of approximately 0.2 GPa up to 2 GPa. Each data set contains 120 frames with 0.5° scan width and an exposure time of 1 s per frame over a sample rotation of 60° (-30° ≤ ω ≤ 30°). Using a very similar experimental setup at beamline ID27, the structural pressure-temperature phase diagram of α-RuCl₃ was mapped out further at lower temperatures as well, using a continuous He-flow cryostat [red crosses in Fig.1(b)]. In this experiment, the single crystalline sample was exposed to a monochromatic 3x3 µm² x-ray beam with a photon energy of 33 keV (λ=0.3738 Å), while continuously recording the diffracted intensity on the detector during an ω-movement of 60° (-30° ≤ ω ≤ 30°).
FIG. 2. Evolution of the XRD pattern during the pressure-driven phase transition. Reciprocal space maps parallel to the 03l-plane (a)-(f), the -15l-plane (g)-(l) and the 04l-plane (m)-(r) (integration thickness perpendicular to the plane: Δh = 0.04) in the pressure range 0.2 GPa to 1.26 GPa at 300 K. The indexing corresponds to the hexagonal setting (cf. Fig.3). The diffuse stripes along the l-direction observable in (h)-(j) and (m)-(r) are a hallmark of stacking faults. The intensity shift along the l-direction in (g)-(l) is representative for all reflections with h−k = 3n (n integer and h, k ≠ 3n) and reveals the rearrangement of the Cl–Ru–Cl sandwich layers from a cubic to a hexagonal closed chlorine packing. While, the diffuse stripes along the l-direction fulfilling the condition h−k = 3n ± 1 (with n integer) as depicted in (m)-(r) signal the disordered stacking of the Ru honeycomb nets over the entire pressure range.

at zero pressure, cf. Fig. 2 These rods are oriented parallel to c∗ m, thus revealing a disordered stacking of the Cl–Ru–Cl trilayers along the c m direction, which can be attributed to stacking faults, characterized by bn/3 shifts between adjacent layers [22].

To describe such stacking faults and the polytypism in α-RuCl3, it is convenient to use a hexagonal set of basis vectors a h, b h and c h, with a h and b h parallel to the Cl–Ru–Cl layer and the c h-axis normal to it (cf. Fig.3). In doing so, we neglect that the hexagonal symmetry is broken by a small monoclinic distortion in some regions of the phase diagram. However, this approximation enables us to draw upon the theoretical framework for XRD of transition metal trihalides with stacking faults developed by Ulrich Müller and Elke Conradi [23].

Rearrangement of Cl–Ru–Cl trilayers

In Fig. 2 we show the evolution of the x-ray intensity distribution in reciprocal space during the pressure induced rearrangement of the Cl–Ru–Cl trilayers at room temperature. Here and throughout the following, the indexing of the reflections refers to the approximate hexagonal cell introduced in the previous paragraph. In order to reveal changes in the layer stacking along c h, the intensities within a slice with −0.02 ≤ Δh ≤ 0.02 were projected onto the kl-plane.

The reflections in these reciprocal space maps can be divided into three families, depending on h and k:

Family 1: h = 3n and k = 3m (with n, m integers). This family is represented by the 03l-streak shown in Figs. 2(a)-(f), where it can be observed that these reflections appear at integer l positions and stay sharp along

\[ l \equiv \frac{3n}{3} = n \]

where n is an integer. This condition is satisfied when h = 3n and k = 3m, leading to a series of reflections at integer l positions along the k l family.

Family 2: h = 3n ± 1 and k = 3m ± 1 (with n, m integers). This family is characterized by diffraction spots at l positions that are shifted by 1/3 along the l-direction. These reflections appear at l = 3n ± 1 and k = 3m ± 1, corresponding to a disordered stacking of the Cl–Ru–Cl trilayers along the c h-axis.

Family 3: h = 3n ± 2 and k = 3m ± 2 (with n, m integers). These reflections represent the disordered stacking of the Ru honeycomb nets over the entire pressure range, characterized by diffuse stripes along the l-direction fulfilling the condition h−k = 3n ± 1 (with n integer) as depicted in (m)-(r).
the $l$-direction over the entire pressure range shown.

Family 2: $h - k = 3n$ with $n$ integer and $h,k \neq 3n$. These peaks are represented by the -11l-streak in Figs. 2 (g)–(l). At 0.2 GPa these reflections are sharp and centered at $l = 1/3 + n$. According to Ref. [27], the position of this family of reflections provides information about the Cl packing. Specifically, reflections located at $l = 1/3 + n$ indicate a cubic close packing of Cl, which indeed corresponds precisely to the monoclinic $C2/m$ crystal structure of $\alpha$-RuCl$_3$ at ambient conditions. However, above 0.2 GPa, a very pronounced broadening of the peaks is observable and intensity starts to spread along the $l$-direction, as can be seen in Figs. 2 (h)–(j). This signals the loss of long-range order of the Cl-sites in the out-of-plane direction. Note that the intensity maximum shifts towards integer $l$ values between 0.40 GPa and 0.81 GPa. Surprisingly, upon increasing $p$ further, the peaks again become sharper and sharper, until they are again resolution limited at 1.26 GPa. The new long-range ordered state at this pressure is characterized by the reflection condition $l = n$ (with $n$ integer) and peak widths comparable with the width of the 1st family. This reveals a rearrangement of the Cl–Ru–Cl trilayers, resulting in a transition from a cubic to a hexagonal chlorine close packing [23]. Interestingly, this $p$-driven transition between the two long-ranged ordered phases requires collective sliding of the Cl–Ru–Cl trilayers by about 2 Å.

Family 3: $h - k = 3n \pm 1$ with $n$ integer. This family is represented in Figs. 2(m)–(r), which shows the intensity distribution along the 04l-streak. The intensity of these reflections is very broad and diffuse along $l$ already at 0.2 GPa, but a maximum at $l = n$ is still recognizable. Referring again to Ref. [24], this implies that the stacking of the Ru honeycomb layers along $c_h$ is disordered already at 0.2 GPa, which, in fact, is also the case at ambient pressure for this sample (crystal 2). Notwithstanding, the maxima at $l = n$ at ambient pressure show that this sample exhibits the expected $C2/m$-structure at ambient pressure, although with stacking faults. Note that, even though the stacking of the Ru honeycomb layers is always disordered in this crystal, the stacking of the Cl-layers at ambient pressure and at $p = 1.26$ GPa is fully ordered in all spatial directions. This is due to the fact that for fixed Cl-positions the Ru-layers, which are sandwiched between the Cl-layers, can still assume different positions. Upon increasing pressure, the intensity distribution initially becomes completely smeared out along $l$, but then, with further increasing pressure, it accumulates in broad maxima at $l = n + 1/3$ and $l = n + 2/3$. Further representative intensity distributions for the 3$^\text{rd}$ family of reflections at 1.26 GPa are given in Fig. 4 (a)–(c), where the diffuse maxima for different $h-k = 3n \pm 1$ are shown.

Taken together, the data presented in Fig. 2 thus uncovers a pressure-induced rearrangement of the Cl–Ru–Cl trilayers, which results in an ordered hexagonal close packing of chlorine atoms, but lacks a long-range ordered stacking of the Ru honeycomb layers along $c_h$.

Structure of the Cl–Ru–Cl trilayers

In order to determine the structure of the Cl–Ru–Cl trilayers, we analyze both the sharp Bragg reflections and diffuse scattering. In Fig. 3(a) the locations of the different reflection families are illustrated. The first step is to determine the averaged structure of a single Cl–Ru–Cl layer at room temperature and $p = 1.26$ GPa from the sharp Bragg peaks alone (family 1 and 2). This intensity distribution can be modeled in terms of the averaged RuCl$_3$-layer shown in Fig. 3(b), which corresponds to a projection of all atomic sites along $c_h$-direction onto a single layer. Note that the Ru-sites in this average layer do not form a honeycomb net and that all Ru-sites possess a site occupation factor of 2/3.

These layers are then stacked on top of each other along $c_h$ to form an averaged three dimensional structure. Analysing the positions of the sharp Bragg peaks only, we find that the three dimensional averaged structure is described by a trigonal cell with lattice parameters $a_h$, $b'_h$, and $c_h$. This allows for a structural model of the Cl–Ru–Cl trilayers. The positions of the sharp Bragg reflections are then explained in terms of the averaged structure. The diffuse scattering is then interpreted in terms of the stacking faults between the Cl–Ru–Cl trilayers.
a_l = b_l = 3.4080(4) Å and c_l = 5.562(10) Å. While no systematic extinction condition was found, the analysis of the intensities is consistent with the trigonal Laue class 3m1. The averaged structure was then solved and refined in the space group P3m1 as described in detail in the Appendix. On account of the small atomic displacements and possible strong parameter correlations in fact no split positions but merely averaged atomic positions are obtained by our crystallographic refinements.

The structural parameters determined from XRD for both the monoclinic phase at ambient pressure and the high-symmetry phase at \( p = 1.26 \) GPa are summarized in Table I. In order to further substantiate our experimental findings, we performed a structural optimization within density functional theory and the generalized gradient approximation (GGA) of the exchange-correlation potential using the QUANTUM-ESPRESSO software package [25][27]. The Kohn-Sham orbitals were expanded in a plane-wave basis set with a kinetic-energy cutoff of 100 Ry. The Brillouin zone was sampled on a grid of \( 24 \times 24 \times 24 \) k-points and integrated with the optimized tetrahedron method [28]. For the structural optimization, the lattice constants and the space group were kept fixed (C2/m at ambient pressure and R3 at 1.26 GPa), while the total energy and internal forces were optimized as a function of the allowed fractional coordinates. The results of these calculations are also included in Table I where they can be compared directly to the experimental values. We find excellent agreement between DFT and experiment, which confirms the experimentally de-


|          | 0 GPa - $C2/m$       |         | 1.26 GPa - $p31m$       |         |
|----------|----------------------|---------|-------------------------|---------|
|          | Experiment          | DFT     | Experiment              | DFT     |
| Ru       | $x$  | 0                  | 0       | $2/3$                   | $2/3$   |
|          | $y$  | 0.16651(2)         | 0.16635 | $1/3$                   | $1/3$   |
|          | $z$  | 1/2                | 1/2     | 1/2                     | 1/2     |
| Cl$_1$   | $x$  | 0.22680(13)        | 0.22692 | 0.3435(17)              | 0.34291 |
|          | $y$  | 0                  | 0       | 0.7400(20)              | 0.74045 |
|          | $z$  | 0.73488(12)        | 0.73488 | 0.7404(20)              | 0.74045 |
| Cl$_2$   | $x$  | 0.25058(10)        | 0.25059 | 0.17407                 | 0.17411 |
|          | $y$  | 0.17411(4)         | 0.17407 | 0.17407                 | 0.17407 |
|          | $z$  | 0.26761(9)         | 0.26769 | 0.26769                 | 0.26769 |

TABLE I. Structural parameters as determined from the single crystal data and structural optimization calculations as a function of pressure at 300 K.

At ambient pressure, the lattice parameter are $a_m$=5.9875(6) Å, $b_m$=10.3529(3) Å, $c_m$=6.0456(6) Å and $\beta$=108.777(9) and the structure is described by the space group $C2/m$. At 1.26 GPa the lattice parameter are $a_h$=5.9028(4) Å and $c_h$=5.562(10) Å and the structure of a single Cl-Ru-Cl layer is described by the trigonal layer group $p\bar{3}1m$. We note that the fractional coordinate we obtain from structural optimization calculations for the chlorine atom very slightly deviates from the $p\bar{3}1m$ symmetry. Illustrations of the ambient and high pressure structural models are shown in Fig. 5 (a), (b) and Fig. 5 (c), (d) respectively.

termined structures and fractional coordinates.

Discussion and conclusion

The pressure-driven structural transformation discovered here is illustrated further in Fig. 5. As reported earlier, the structure of $\alpha$-RuCl$_3$ at ambient conditions deviates from the ideal honeycomb structure, as there are different Ru–Cl distances, different Ru–Ru distances and different Ru–Cl–Ru bond angles [Figs. 5(a),(b)]. Upon increasing the pressure to 1.26 GPa, these differences disappear: there is only one single Ru–Cl distance, one single Ru–Ru distance and one single Ru–Cl–Ru bond angle, as shown in Figs. 5(c),(d). The Cl–Ru–Cl trilayers of the pressure-induced $p31m$ phase form an undistorted Ru-honeycomb net with a Ru–Cl–Ru bond angle of 92.80° – very close to the ideal value of 90°. Comparing Fig. 5 (b) and (d), it is obvious that the applied pressure mostly affects the van der Waals spacing, while the thickness of a single layer remains almost the same. Consequently, no further trigonal distortion of the RuCl$_6$ octahedron occurs, leaving the $j_{eff}$ = 1/2 state stable. Application of hydrostatic pressure therefore drives the structure of the Cl–Ru–Cl trilayers closer to the ideal geometry for realizing the Kitaev-model.

According to the data shown in Fig. 2 the $p$-induced high-symmetry phase exhibits a well defined trigonal layer symmetry $p31m$, but also a significant amount of stacking disorder of the Ru-honeycomb layers [Figs. 2(m)–(r)]. The overall structure does therefore not correspond to an ordered $R\overline{3}$-structure, but rather consist of structural $R\overline{3}$-domains separated by stacking faults. We will therefore refer to this phase as high-symmetry phase with $p31m$ layer symmetry.

This high-symmetry polytype has been determined at

FIG. 5. The crystal structure of $\alpha$-RuCl$_3$ determined by analyzing the Bragg scattering as well as the diffuse scattering of high-quality single crystals at 0.0 GPa and 1.26 GPa. The local Cl-Ru-Cl layer geometry is depicted in (a),(c) and two successive honeycomb layers viewed normal to the stacking direction are shown in (b),(d) for the monoclinic $C2/m$ structure at 0.0 GPa and the high-symmetry structure with $p31m$ layer symmetry at 1.26 GPa, respectively. Equivalent nearest neighbor Ru-Ru links and Ru-Cl bond distances are encoded in the same colors in (a) and (b). For improved clarity only two nearest neighbor edge-sharing RuCl$_6$ octahedra are shown in (a).
RT, which immediately raises the question as to whether it also exists at low-temperature. To address this issue we performed low-temperature measurements with two differently mounted samples: Sample 1 was simply placed on a diamond anvil and not glued down, in order to avoid external stresses caused by the different thermal contractions of sample and holder during cooling. Sample 2 was instead firmly glued onto an Al-holder. At low $T$, the different thermal contractions of $\alpha$-RuCl$_3$ and Al do result in a biaxial stress parallel to the $ab$-plane of sample 2.

As can nicely be observed in Fig. 6, the peak positions of the stress-free sample 1 do not change upon cooling, indicating that this sample remains in the monoclinic $C2/m$ phase. For sample 2, however, we do observe additional strong reflections at integer $l$ at low temperature, which signals an almost complete transition from the monoclinic to the high-symmetry phase with $p31m$ layer symmetry. While our low-temperature data under biaxial stress does not allow for a detailed structure analysis, they are, however, fully consistent with the results published in Ref. [29] where a rhombohedral phase at low temperature has been determined, which corresponds to the high-symmetry phase determined here with a Ru–Cl–Ru bond angle of 93.73°. This is almost 1° larger than the Ru–Cl–Ru bond angle found at 1.26 GPa and room temperature, since $p$ indeed causes a reduction of Ru–Cl–Ru bond angle and brings it closer to the ideal value of 90°.

From the above we conclude that biaxial stress can induce a structural transition from $C2/m$ to the high-symmetry phase. On the one hand, this renders the high-symmetry phase with $p31m$ layer symmetry accessible to a variety of experiments. On the other hand, this also means that care must be taken when mounting $\alpha$-RuCl$_3$ for low $T$ measurements. The strain-dependence may in fact be the reason why some previous studies reported the occurrence of a first-order structural phase transition during cooling [30, 31].

It is remarkable that biaxial stress parallel to the Cl–Ru–Cl trilayers affects the stacking in the perpendicular direction. The underlying physical mechanism certainly deserves further study. It will also be very important to determine the difference between the $C2/m$ and the high-symmetry phase in terms of magnetic couplings. Recent studies indeed report the relevance of interlayer interactions for the magnetism of $\alpha$-RuCl$_3$ [11, 32]. A very recent neutron scattering study could in fact identify the rhombohedral phase with the transition at $T_N$=7 K (Ref. [13] and notes in Ref. [29]). The latter corresponds to the high-symmetry polytype described above. It is therefore not unlikely that the transition at $T_N$=14 K, which is observed in some samples, is related to the monoclinic $C2/m$-polytype.

To conclude, we showed that hydrostatic pressure $p$ as well as biaxial stress parallel to the $ab$-plane can drive the structure of $\alpha$-RuCl$_3$ closer towards the ideal Kitaev-geometry. An intricate interplay between the in-plane and out-of-plane structure in $\alpha$-RuCl$_3$ was observed, which not only modifies the magnetic interactions in the out-of-plane direction perpendicular to the Cl–Ru–Cl trilayers, but is likely to also affect the relative strength of the in-plane interactions and the magnetic ground state of this very promising Kitaev-candidate material. It will be extremely interesting to further explore this new aspect and its role for the QSL-behaviour in $\alpha$-RuCl$_3$ in future studies.

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APPENDIX

X-ray data analysis and structure refinement

The data collected at ambient conditions for crystal 1 was processed using Bruker’s Apex3 software (Ref. 33), the reflection intensities were integrated using SAINT (Ref. 34) and multi-scan absorption correction was applied using SADABS (Ref. 35). The subsequent structure solution and weighted fullmatrix least-squares refinement on F² were done with SHELXT-2014/5 (Ref. 36) and SHELXL-2018/3 (Ref. 37) as implemented in the WinGx 2018.3 program suite (Ref. 38). Key details of the data collection and the structural refinement are summarized in Table II. The atomic positions and isotropic displacement parameter based on the single-crystal x-ray diffraction data at ambient conditions are listed in Table IV.

To determine the averaged structure at 1.26 GPa and ambient temperature of crystal 2, the data was integrated and corrected for Lorentz, polarization and background effects using the CrysAlisPro software suite (version 171.39.46) [39]. Reflections, which were saturated due to overexposure or an overlap with diamond peaks, were omitted from the integration process. The separation of sharp and diffuse scattering requires no special treatment, as the Bragg peaks of family 1 and 2 are separated by a background intensity. The background intensity was as well determined line-by-line along l ing a background intensity. The background intensity was characterized in form of a right stochastic matrix containing the transition probabilities.

Extraction of the diffuse intensities

The diffuse intensity profiles were extracted from the diffraction data collected with a MAR555 flat panel detector at ID15B of the ESRF. The diffraction images were transformed into reciprocal space and |F₀²| maps were reconstructed by applying Lorentz and polarization factors using the CrysAlisPro software package [39]. For further data processing the Python packages numpy, matplotlib, and fabio were applied. The intensity profiles were estimated from the reconstructed layers for each pixel row and 30 independent reflections with Rint = 4.69 %. The averaged structure was then solved in the space group p3rn1 using the SHELXT-2014/5 (Ref. 36) and SHELXL-2018/3 (Ref. 37) as implemented in the WinGx 2018.3 program suite (Ref. 38). The final refinement converged at R₁ (all data) = 2.65 % and wR₂ (all data) = 5.31 %. The parameters characterizing the data collection and the structural refinement are summarized in Table III.

Modelling of the diffuse scattering

First, a single layer was built up by expanding the hexagonal unit cell to a 20x20x1 supercell. For the simulation 1000 of these layers were stacked along c. There are various possibilities to stack the individual layers, while preserving a hexagonal or cubic closed packing of the Cl-atoms. Altogether, there are 9 possibilities for the orientation of two adjacent layers that meet these requirements. The configuration of a single layer is specified by the position A1, A2, ..., C3 of the octahedral voids within the hexagonal cell, as illustrated in Fig. 7. In order to depict the stacking of the layers a stacking vector Tₛ is implemented, which connects the octahedral voids in successive layers. The stacking vector Tₛ with S=A1,A2,...C3 points from the octahedral void A1 in the initial layer to an octahedral void S in the successive layer. In the event of a hexagonal closed packing of the Cl-atoms the arrangement options for two consecutive layers is reduced to three. We define these three kinds of stacking as eclipsed (e), forward (f) and backward (b), that correspond to the stacking vectors Tₐ₁ = [0,0,1], Tₐ₂ = [2/3,1/3,1] and Tₐ₃ = [1/3,2/3,1] respectively. However, our analysis showed that the measured XRD-data is very well reproduced by the exclusive use of f and b stacks. In order to probe the short-range order in the pressurized α-RuCl₃ samples, the sequence of f and b stacks in our simulation is generated by a first-order Markov process. To resemble the experimental found stacking disorder two independent transition probabilities pₕₙ and pₘₙ must be defined. Here, pₕₙ corresponds to the probability that a layer be f stacked on a preceding f stack, and accordingly pₘₙ is the probability of continuing in a backward stacking sequence. Therefore the probabilities for the presence of a stacking fault are pₘ₁ₙ=1-pₙₖ and pₘ₁=1-pₙₖ, respectively. The process is characterized in form of a right stochastic matrix P containing the transition probabilities.

\[
P = \begin{pmatrix}
    p_{ff} & p_{fb} \\
    p_{bf} & p_{bb}
\end{pmatrix}
\]

Using this approach DISCUS creates a list of layer positions. The scattering intensity of the layered model crystal is finally calculated as the product of the individual Fourier transform of the layer positions and the single layer. All in all we created 676 different disorder models by adjusting the transition probabilities pₕₙ and pₘₙ in steps of 0.04. For each model we calculated the intensity profiles along 12l, 1-3l and 1-4l over the range -2 ≤ l ≤ +2. Obviously the model crystal contain far fewer layers than do real crystals and consequently the number of stacking fault events is small. To reduce the statistical noise and thus produce a smooth intensity distribution along l the line profiles for each set of transition
TABLE II. Details on data collection and structure refinement of α-RuCl$_3$ as determined from single-crystal X-ray diffraction at ambient conditions.

| Crystal data | Data collection | Refinement | Intensity profiles. We estimate the uncertainties of the optimized values $p_{ff} = 0.60$ and $p_{bb} = 0.72$ to be ±0.02. In contrast, the relative intensities with a period $l = n + 1$ along the streaks are mainly dependent on the $x$ coordinate of the Cl-atom, which is particularly evident for the intensity maxima located at $l = n + 1/3$ and $l = n + 2/3$. The simulation was carried out for several Cl-positions $\Delta x$ displaced in 3 pm steps parallel to $\alpha_h$ from the average position $x_{Cl} = 1/3 (\Delta x = 0 \text{ pm})$ deduced from the sharp reflections. The results are shown in Fig. 4 (a)-(c) by solid lines. Note that only the position of the Cl-atom is changed for the simulated profiles shown in Fig. 4 (a)-(c), while the stacking fault probabilities remain unaltered.

[1] C. Broholm, R. J. Cava, S. A. Kivelson, D. G. Nocera, M. R. Norman, and T. Senthil, Science 367, eaay0668 (2020).
[2] H. Takagi, T. Takayama, G. Jackeli, G. Khaliullin, and S. E. Nagler, Nature Reviews Physics 1, 264 (2019).
[3] L. Balents, Nature 464, 199 (2010).
[4] A. Kitaev, Annals of Physics 321, 2 (2006).
[5] C. Nayak, S. H. Simon, A. Stern, M. Freedman, and S. Das Sarma, Rev. Mod. Phys. 80, 1083 (2008).
[6] S.-H. Baek, S.-H. Do, K.-Y. Choi, Y. S. Kwon, A. U. B. Wolter, L. T. Corredor, L. Janssen, K. Nenkov, S. Schönecker, S.-H. Do, K.-Y. Choi, R. Albrecht, J. Hunger, T. Doert, M. Vojta, and B. Büchner, Phys. Rev. Lett. 119, 037201 (2017).
[7] A. U. B. Wolter, L. T. Corredor, L. Janssen, K. Nenkov, S. Schönecker, S.-H. Do, K.-Y. Choi, R. Albrecht, J. Hunger, T. Doert, M. Vojta, and B. Büchner, Phys. Rev. B 96, 041405 (2017).
[8] T. Yokoi, S. Ma, Y. Kasahara, S. Kasahara, T. Shibauchi, N. Kurita, H. Tanaka, J. Nsuy, Y. Motome, C. Hickey.
FIG. 7. Schematic illustration Plane view of one Cl–Ru–Cl layer with in-plane basis vectors $a_h$ and $b_h$, and illustrated Ru honeycomb net. The A1, A2, ..., C3 notation is used to specify the nine different possibilities of stacking two adjacent layers on top of each other according to the position of the octahedral voids within a single layer.

S. Trebst, and Y. Matsuda, Science 373, 568 (2021).

[9] K. W. Plumb, J. P. Clancy, L. J. Sandilands, V. V. Shankar, Y. F. Hu, K. S. Burch, H.-Y. Kee, and Y.-J. Kim, Physical Review B 90 (2014), 10.1103/physrevb.90.041112.

[10] R. Yadav, N. A. Bogdanov, V. M. Katukuri, S. Nishimoto, J. van den Brink, and L. Hozoi, Physical Review B 97 (2018), 10.1103/physrevb.97.241108.

[20] G. Bastien, G. Garbarino, R. Yadav, F. J. Martinez-Casado, R. Beltrán Rodríguez, Q. Stahl, M. Kusch, S. P. Limandri, R. Ray, P. Lampen-Kelley, D. G. Mandrus, S. E. Nagler, M. Roslova, A. Isaeva, T. Doert, L. Hozoi, A. U. B. Wolter, B. Büchner, J. Georg, and J. van den Brink, Physical Review B 97 (2018), 10.1103/physrevb.97.241108.

[21] T. Biesner, S. Biswas, W. Li, Y. Saito, A. Pustogow, M. Altmeyer, A. U. Wolter, B. Büchner, M. Roslova, T. Doert, et al., Physical Review B 97, 220401 (2018).

[22] R. D. Johnson, S. C. Williams, A. A. Haghighirad, J. Singleton, V. Zapf, P. Manuel, I. I. Mazin, Y. Li, H. O. Jeschke, R. Valentí, and R. Coldea, Phys. Rev. B 92, 235119 (2015).

[23] U. Müller and E. Conradi, Zeitschrift für Kristallographie - Crystalline Materials 176, 233 (1986).

[24] Zeitschrift für Kristallographie - Crystalline Materials 210, 650 (1995).

[25] J. F. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

[26] P. Giannozzi, O. Andreussi, T. Brumme, O. Bnau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carmineo, A. D. Corso, S. de Gironcoli, P. Delugas, R. A. DiStasio, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.-Y. Ko, A. Kokalj, E. Küçükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H.-V. Nguyen, A. O. de-la Roza, L. Paulatto, S. Poncé, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, and S. Baroni, Journal of Physics: Condensed Matter 29, 465901 (2017).

[27] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Scardoni, A. Smogunov, P. Umari, and R. M. Wentzcovitch, Journal of Physics: Condensed Matter 21, 395502 (2009).

[28] M. Kawamura, Y. Gohda, and S. Tsuchiyuki, Physical Review B 89, 094515 (2014).

[29] S. Mu, K. D. Dixit, X. Wang, D. L. Abernathy, H. Cao, S. E. Nagler, J. Yan, P. Lampen-Kelley, D. Mandrus, C. A. Polanco, et al., Physical Review Research 4, 013067 (2022).

[30] S. Reschke, F. Mayr, S. Widmann, H.-A. K. Von Nidda, V. Tsukanov, M. V. Eremin, S.-H. Do, K.-Y. Choi, Z. Wang, and A. Loidl, Journal of Physics: Condensed Matter 30, 475604 (2018).

[31] S. Gass, P. M. Consoli, V. Koczis, L. Corredor, P. Lampen-Kelley, D. Mandrus, S. Nagler, L. Janssen, M. Vojta, B. Büchner, et al., Physical Review B 101, 245158 (2020).

[32] C. Balz, L. Janssen, P. Lampen-Kelley, A. Banerjee, Y. Liu, J.-Q. Yan, D. Mandrus, M. Vojta, and S. E. Nagler, Physical Review B 103, 174417 (2021).

[33] Bruker AXS Inc.,  “ Apex3 v2018.1-0,” (2017).

[34] Bruker AXS Inc., “Saint(v8.30a),” (2017).
[35] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, and D. Stalke, *Journal of Applied Crystallography* **48**, 3 (2015).

[36] G. M. Sheldrick, *Acta Crystallographica Section A Foundations and Advances* **71**, 3 (2015).

[37] G. M. Sheldrick, *Acta Crystallographica Section C Structural Chemistry* **71**, 3 (2015).

[38] L. J. Farrugia, *Journal of Applied Crystallography* **45**, 849 (2012).

[39] Rigaku Oxford Diffraction, “CrysAlisPro Software system version 1.171.39.46,” (2018).