doi:10.1017/S1431927622007711
Microsc. Microanal. 28 (Suppl 1), 2022

Pico-scale Distortions in Encapsulated Monolayer α-$RuCl_3$ Characterized with 3D Electron Diffraction

Yin Min Goh[1], Suk Hyun Sung[2], Bowen Yang[3,4], Gaihua Ye[5], Sananda Biswas[6], David A. S. Kaib[6], Ramesh Dhakal[7], Shaohua Yan[8], Chenghe Li[8], Shengwei Jiang[9,10], Fangchu Chen[3,4], Hechang Lei[8], Rui He[5], Roser Valenti[6], Stephen M. Winter[7], Adam W. Tsen[3,11], Robert Hovden[2,12]

[1.] Department of Physics, University of Michigan, Ann Arbor, MI, USA.

[2.] Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI, USA.

[3.] Institute for Quantum Computing, University of Waterloo, Waterloo, ON, Canada.

[4.] Department of Physics and Astronomy, University of Waterloo, Waterloo, ON, Canada.

[5.] Department of Electrical and Computer Engineering, Texas Tech University, Lubbock, TX, USA.

[6.] Institut für Theoretische Physik, Goethe-Universität Frankfurt, Max-von-Laue-Strasse 1, Frankfurt am Main, Germany.

[7.] Department of Physics and Center for Functional Materials, Wake Forest University, Winston-Salem, NC, USA.

[8.] Department of Physics and Beijing Key Laboratory of Opto-electronic Functional Materials & Micro-nano Devices, Renmin University of China, Beijing, China.

[9.] Department of Physics, Cornell University, Ithaca, NY, USA.

[10.] Key Laboratory of Artificial Structures and Quantum Control (Ministry of Education), School of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai, China.

[11.] Department of Chemistry, University of Waterloo, Waterloo, ON, Canada.

[12.] Applied Physics Program, University of Michigan, Ann Arbor, MI, USA.

Two dimensional (2D) α-$RuCl_3$ is a promising candidate for realizing the Kitaev quantum spin liquid (QSL)—an exactly solvable spin model on a 2D honeycomb lattice [1]. QSL have strong magnetic frustration and competing magnetic ground states, which collectively leads to long-range quantum entanglement that is ideal for quantum computing [2]. Due to the highly two-dimensional (2D) nature of α-$RuCl_3$, stacking faults and interlayer spacing could play a role in the magnetic response of the system [3]. More generally, magnetic materials are sensitive to bond coordination and small structural distortions of the lattice. Monolayer α-$RuCl_3$ can have energy and properties different from its bulk counterpart, and pico-scale distortions that increases the material's proximity to QSL [4]. However, observations of the magnetic excitations and associated atomic configuration are challenging, especially in a single layer of α-$RuCl_3$ that readily degrades with oxygen exposure. By encapsulating an exfoliated α-$RuCl_3$ monolayer between single layer graphenes, we realize a protected monolayer α-$RuCl_3$ sample in the true 2D limit. However, encapsulation poses an additional challenge: real-space imaging methods such as AFM or HAADF-STEM are incapable or poorly suited for structural characterization of encapsulated samples. We employ 3D electron diffraction that probes the out of plane structure to extract the thickness and pico-scale distortions of encapsulated materials.

Here, we characterize the crystal structure and pico-scale distortions of an encapsulated 2D magnetic system—monolayer α-$RuCl_3$—using 3D electron diffraction and a kinematic scattering model of the 3D reciprocal structure for 2D materials. The real space structure of monolayer α-$RuCl_3$ is a honeycomb lattice in projection (Fig. 1a). The spacing between Cl and Ru atomic planes is denoted by λ_{Cl}, and Ru atoms may buckle out-of-plane as denoted by $\Delta\zeta_{Ru}$ (Fig. 1b). Acquiring electron diffraction patterns at various tilt angles is akin to slicing through the reciprocal structure consisting of Bragg rods (Fig. 1c). The in-plane reciprocal lattice positions (h, k $\in \mathbb{Z}$) and continuous out-of-plane ($k_z \in \mathbb{R}$) oscillations of the Bragg rods encode information about the structural parameters (Fig. 1d). For α-$RuCl_3$, specific Bragg rods in reciprocal space advantageously decouple structural parameters that can be quantified by the Bragg intensity oscillations. The (h, k) = {1, 0} peaks are useful for quantifying the number of layers and the {1, 1} and {3, 0} peaks oscillate along k_z-direction with a direct dependence on λ_{Cl}.

Fitting of the Bragg rod structure to experimental diffraction intensities confirms the successful isolation of monolayer α-$RuCl_3$ in between single sheets of graphene. In 3D electron diffraction, we acquired selected area electron diffraction (SAED) patterns while tilting the sample from +35° to -35° in 1° increment and each Bragg peak intensity is mapped as a function of k_z [4]. The integrated diffraction intensities as a function of k_z (Fig. 2b–c, scatter points) matches closely with the kinematic model of a monolayer α-$RuCl_3$ (Fig. 2b–c, solid lines) thereby confirming the realization of α-$RuCl_3$ in 2D.

Small structural distortions away from the ideal crystal can also be measured by 3D electron diffraction. By fitting a more general reciprocal structure, distortions in the Ru-Cl interatomic distance and pico-scale buckling of Ru atoms are extracted for our encapsulated monolayer sample. In an undistorted structure, we expect the (h, k) = {1, 0} peaks to be symmetric and centered about $k_z = 0$ (Fig 2c: no buckling). However, experimental diffraction intensities exhibit a symmetry reduction (Fig. 2c) which correspond to out-of-plane buckling of the Ru atoms, $\Delta\zeta_{Ru}$. Simultaneous curve fitting of the kinematic model to the $\{10\bar{1}0\}, \{11\bar{2}0\}, \{30\bar{3}0\}$ peaks of α-$RuCl_3$ gives $\lambda_{Cl} = 1.3101 \pm 0.0257$Å and $\Delta\zeta_{Ru} = 0.30 \pm 0.15$Å. These values are consistent with previously reported interatomic plane spacing and modes of distortion in monolayer α-$RuCl_3$ [5, 6].

To extract the structural information of an encapsulated 2D magnet, we combined 3D electron diffraction with a kinematic model of the reciprocal space structure. Experimental diffraction intensities provide a representative average of the real-space structure of an encapsulated α-$RuCl_3$ sample—including its thickness, interatomic plane spacing, pico-scale Ru buckling out-of-plane. The technique proposed here provides precise atomic coordinates for *ab-initio* calculations and is applicable to other 2D materials that require encapsulation.

References:

[1] Kitaev, A. Anyons in an exactly solved model and beyond. *Ann. Phys. (N. Y).* **321**, 2–111 (2006).

[2] Takagi, H., Takayama, T., Jackeli, G., Khaliullin, G. & Nagler, S. E. Concept and realization of Kitaev quantum spin liquids. Nat. Rev. Phys. 2019 14 1, 264–280 (2019).

[3] A. Banerjee, et al., *Nature Materials* **15**, 733–740 (2016), doi: 10.1038/nmat4604.

[4] S. H. Sung, et al., *Phys. Rev. Materials* **3**, 064003 (2019), doi:10.1103/PhysRevMaterials.3.064003

[5] Z. Dai, et al., *2D Mater.* **7**, 035004 (2020), doi: 10.1088/2053-1583/ab7e0e.

https://doi.org/10.1017/S1431927622007711 Published online by Cambridge University Press

[6] H.-S. Kim and H.-Y. Kee, *Phys. Rev. B* **93**, 155143 (2016), doi:10.1103/PhysRevB.93.155143.

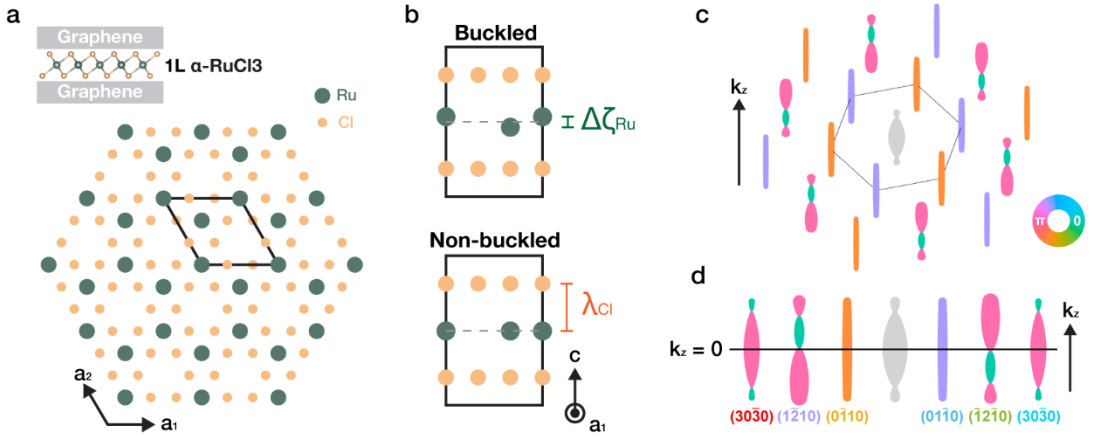

Figure 1. Real and reciprocal space structure of monolayer α-$RuCl_3$. (a) A schematic of our monolayer α-$RuCl_3$ sample encapsulated in between graphene layers, and a plane view of the 2D honeycomb lattice. **(b)** Structural parameters indicated on α-$RuCl_3$ with and without Ru buckling. **(c)** Bragg rods occupy the reciprocal space of α-$RuCl_3$. The thickness and color of rods represent their complex amplitude and phase of oscillation. **(d)** Side view of the Bragg rods showing out-of-plane momentum (k_z) dependence.

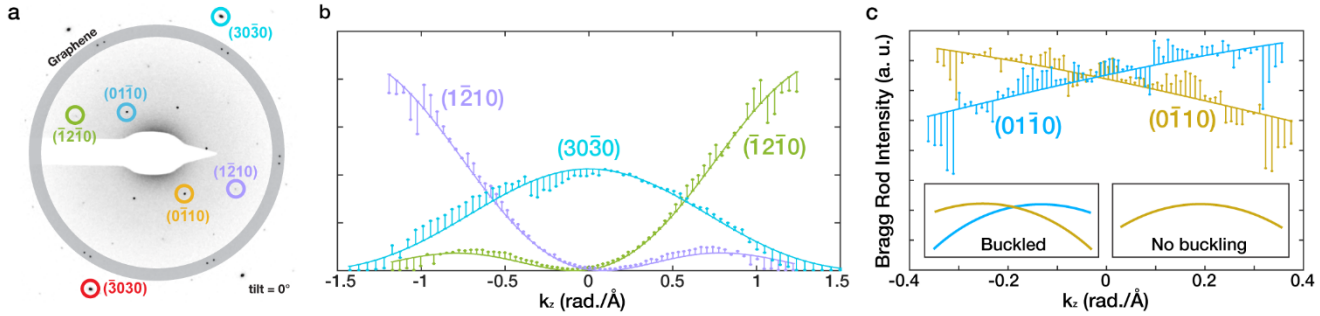

Figure 2. Kinematic model fitting to α-$RuCl_3$ Bragg peaks of an electron diffraction tilt series. (a) Selected area electron diffraction (SAED) pattern of graphene-encapsulated α-$RuCl_3$. Twin diffraction peaks highlighted in gray are due to encapsulating graphene layers. Various orders of α-$RuCl_3$ diffraction peaks (circled) are used in model fitting. **(b, c)** Experimental diffraction intensities as a

https://doi.org/10.1017/S1431927622007711 Published online by Cambridge University Press

function of k_z (scatter points) fitted with kinematic model (solid lines) of monolayer α-$RuCl_3$. Color and indices of data correspond to circled peaks in (a). In (c), symmetry-breaking of $(01\bar{1}0)$ and $(0\bar{1}10)$ Bragg rod intensities signifies out-of-plane buckling of Ru atoms.

https://doi.org/10.1017/S1431927622007711 Published online by Cambridge University Press