Pico-scale Distortions in Encapsulated Monolayer $\alpha$-RuCl$_3$ Characterized with 3D Electron Diffraction

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Two dimensional (2D) $\alpha$-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 $\alpha$-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 $\alpha$-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 $\alpha$-RuCl$_3$ that readily degrades with oxygen exposure. By encapsulating an exfoliated $\alpha$-RuCl$_3$ monolayer between single layer graphenes, we realize a protected monolayer $\alpha$-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 $\lambda_{\text{Cl}}$, and Ru atoms may buckle out-of-plane as denoted by $\Delta\zeta_{\text{Ru}}$ (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 $\lambda_{\text{Cl}}$.

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 $+35^\circ$ to $-35^\circ$ in $1^\circ$ 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, $\Delta\zeta_{\text{Ru}}$. Simultaneous curve fitting of the kinematic model to the $\{10\overline{1}0\}, \{11\overline{2}0\}, \{30\overline{3}0\}$ peaks of α-RuCl$_3$ gives $\lambda_{\text{Cl}} = 1.3101 \pm 0.0257\text{Å}$ and $\Delta\zeta_{\text{Ru}} = 0.30 \pm 0.15\text{Å}$. 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:


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
function of $k_z$ (scatter points) fitted with kinematic model (solid lines) of monolayer $\alpha$-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.