Pico-scale Distortions in Encapsulated Monolayer α-RuCl₃ Characterized with 3D Electron Diffraction

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Two dimensional (2D) α-RuCl₃ 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-RuCl₃, 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-RuCl₃ 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-RuCl₃ that readily degrades with oxygen exposure. By encapsulating an exfoliated α-RuCl₃ monolayer between single layer graphenes, we realize a protected monolayer α-RuCl₃ 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-RuCl₃—using 3D electron diffraction and a kinematic scattering model of the 3D reciprocal structure for 2D materials. The real space structure of monolayer α-RuCl₃ 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 Δς_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 ∈ ℤ) and continuous out-of-plane (k_z ∈ ℝ) oscillations of the Bragg rods encode information about the structural parameters (Fig. 1d). For α-RuCl₃, specific Bragg rods in reciprocal space advantageous 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-RuCl₃ 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-RuCl₃ (Fig. 2b–c, solid lines) thereby confirming the realization of α-RuCl₃ 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, Δς_Ru. Simultaneous curve fitting of the kinematic model to the {10̅10}, {11̅20}, {30̅30} peaks of α-RuCl₃ gives λ_Cl = 1.3101 ± 0.0257Å and Δς_Ru = 0.30 ± 0.15Å. These values are consistent with previously reported interatomic plane spacing and modes of distortion in monolayer α-RuCl₃ [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-RuCl₃ 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-RuCl₃. (a) A schematic of our monolayer α-RuCl₃ sample encapsulated in between graphene layers, and a plane view of the 2D honeycomb lattice. (b) Structural parameters indicated on α-RuCl₃ with and without Ru buckling. (c) Bragg rods occupy the reciprocal space of α-RuCl₃. 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 (kₚ) dependence.

Figure 2. Kinematic model fitting to α-RuCl₃ Bragg peaks of an electron diffraction tilt series. (a) Selected area electron diffraction (SAED) pattern of graphene-encapsulated α-RuCl₃. Twin diffraction peaks highlighted in gray are due to encapsulating graphene layers. Various orders of α-RuCl₃ 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.