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Anisotropic susceptibilities in the honeycomb Kitaev system α -RuCl₃

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The magnetic insulator α -RuCl₃ is a promising candidate to realize Kitaev interactions on a quasi-2D honeycomb lattice. We perform extensive susceptibility measurements on single crystals of α -RuCl₃, including angle-dependence of the in-plane longitudinal and transverse susceptibilities, which reveal a unidirectional anisotropy within the honeycomb plane. By comparing the experimental results to a high-temperature expansion of a Kitaev-Heisenberg- Γ spin Hamiltonian with bond-anisotropy, we find excellent agreement with the observed phase shift and periodicity of the angle-resolved susceptibilities. Within this model, we show that the pronounced difference between in-plane and out-of-plane susceptibilities as well as the finite transverse susceptibility are rooted in strong symmetric off-diagonal Γ spin exchange. The Γ couplings and relationships between other terms in the model Hamiltonian are quantified by extracting relevant Curie-Weiss intercepts from the experimental data.

Introduction. Quantum spin liquids are exotic states of matter in which the formation of conventional long-range order is avoided down to the lowest temperatures due to strong quantum fluctuations [1, 2]. A number of frustrated magnets are promising candidates to host quantum spin liquid ground states [3], however both the theoretical prediction and the experimental observation of such spin liquids are notoriously difficult, since clear identifying signatures are uncommon in the absence of any order. A notable exception is the Kitaev honeycomb model, a spin Hamiltonian with an exactly solvable spin liquid ground state [4]. The exact solvability of the model allows for the extraction of insights and details which can be very difficult to determine for more generic systems [5].

Consequently, there has been considerable effort over the past several years to identify materials which realize Kitaev spin exchange [5–11]. Potential manifestations of the 2D Kitaev model are found in the layered honeycomb magnetic insulators A₂IrO₃ (A=Na, Li, Cu) [6, 12–14] and α -RuCl₃ [15–18]. Kitaev interactions in these systems are accompanied by more conventional spin exchange, leading to long-range magnetic order at low temperatures [19–25] with the exception of Cu₂IrO₃ which exhibits a short-range magnetic order [14]. Despite the rapidly increasing interest in these materials, the effective spin Hamiltonian that best captures the experimental results remains controversial - see discussion in [26] and references therein.

A marked anisotropy between the magnetic suscepti-

bilities measured with a magnetic field applied parallel $\chi_{||}$ or perpendicular χ_{\perp} to the honeycomb plane has been reported in α -RuCl₃ [21, 27, 28] and A₂IrO₃ [29, 30]. However, a systematic explanation for this phenomenon in terms of microscopic exchange couplings has not yet been given. Moreover, experimental results which involve a magnetic field applied parallel to the honeycomb plane depend on the in-plane angle of the applied field [31–33]. Motivated by these observations, we perform extensive susceptibility measurements on single crystals of α -RuCl₃. The longitudinal and transverse susceptibilities as a function of angle within the honeycomb plane are compared to a high-temperature expansion of the magnetic susceptibility tensor for a bond-anisotropic Kitaev-Heisenberg- Γ model. Given the excellent agreement between the model and experimental results, we suggest mechanisms for the observed anisotropies and extract quantitative relationships between terms in the model Hamiltonian.

Experimental details. Single crystals of α -RuCl₃ were prepared using a vapor transport technique [18], and crystallographic directions were identified prior to susceptibility measurements via Laue diffraction. Angle-resolved longitudinal and transverse magnetic susceptibilities within the honeycomb plane, $\chi_{||}(\phi)$ and $\chi_{\perp}^T(\phi)$ respectively, were measured using commercial SQUID magnetometers (Quantum Design) [34]. See Fig. 1 for a definition of the in-plane angle ϕ and details of the experimental setup. The raw transverse SQUID voltage was corrected for uncompensated longitudinal moment,

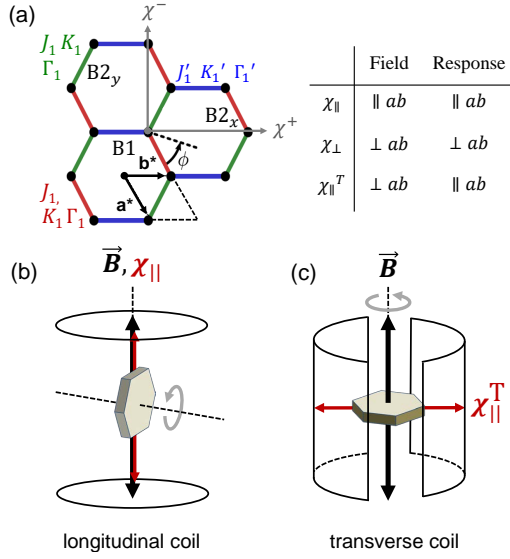


FIG. 1. (a) Definition of the in-plane angle ϕ , the three Ru-Ru bonds B1, B2_x, and B2_y, and notation for various measurement configurations. For simplicity we adopt a trigonal notation, in which the bonds are parallel to the (0,1,0), (1,0,0), and ($\bar{1}$,1,0) reciprocal lattice vectors, respectively. ϕ is the angle between the measurement direction and (1,0,0). Sketch of the geometry for in-plane angle-resolved susceptibility measurements in (b) longitudinal SQUID coils and (c) transverse SQUID coils. The axes along which the magnetic field \vec{B} is applied (black arrow) and the susceptibility is measured (red arrow) are indicated. The angle dependence is mapped out as the sample is rotated 360° about a fixed axis perpendicular or parallel to \vec{B} , respectively, yielding $\chi_{||}(\phi)$ and $\chi_{||}^T(\phi)$. The diagonal elements $\chi^{\mu\mu}$ of the susceptibility tensor are determined in a standard longitudinal SQUID measurement while the off-diagonal elements $\chi^{\mu\mu'}$ are accessed in the transverse geometry.

arising due to displacement from the precise center of rotation, before fitting to an appropriate response function to extract the transverse moment at each condition [34, 35].

Oscillating susceptibility. Figure 2(a) shows the longitudinal susceptibility of an α -RuCl₃ single crystal as the direction of the magnetic field varies within the ab plane (see Fig. 1b). Clear oscillations in the magnitude of the in-plane susceptibility $\chi_{||}(\phi)$ with π -periodicity are observed both below and above the zigzag magnetic ordering transition at $T_N \simeq 7$ K, suggesting that the appearance of in-plane magnetic anisotropy is not tied to long-range order. The maxima (minima) of $\chi_{||}$ occur at $\phi = 60^\circ$ and 240° ($\phi = 150^\circ$ and 330°), corresponding to magnetic field parallel (perpendicular) to one of the Ru-Ru bond directions. This inequivalent bond is referred to hereafter as B1 (Fig. 1a). Oscillations in $\chi_{||}$ with π -periodicity persist for $T \gg T_N$ even as the mean value χ_m decays with the overall susceptibility at high temperatures.

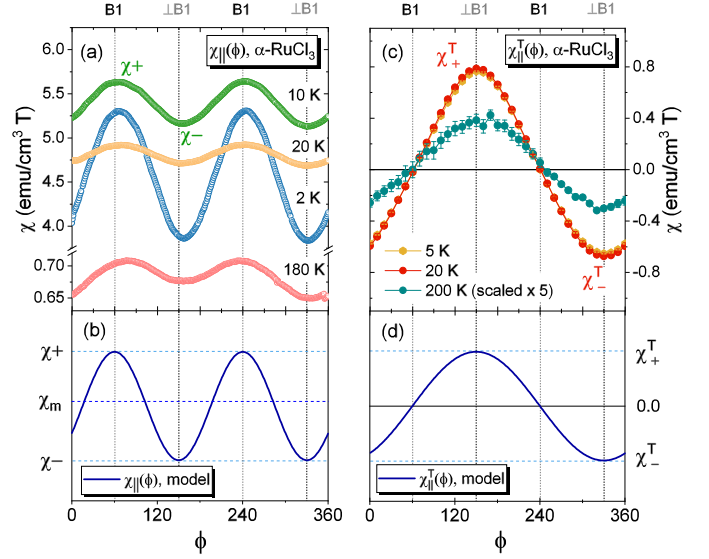


FIG. 2. (a) Angle-resolved longitudinal susceptibility $\chi_{||}(\phi)$ of a single crystal of α -RuCl₃ as the direction of magnetic field ($B = 0.1$ T) is varied within the honeycomb plane shown at 2 K (blue), 10 K (green), 20 K (yellow) and 180 K (pink). ϕ is the in-plane angle between \mathbf{a}^* and the measurement direction. A diamagnetic contribution from the rotation stage is subtracted from the presented data. (b) Theoretical oscillation of $\chi_{||}(\phi)$ predicted for a bond-anisotropic Kitaev-Heisenberg- Γ model, see Eq. (4). (c) Angle-resolved transverse susceptibility $\chi_{||}^T(\phi)$ of a single crystal of α -RuCl₃ as a function of the in-plane angle ϕ with $B = 1$ T applied perpendicular to the ab plane. The 200 K data are scaled by a factor of 5 to facilitate viewing on the same axes. (d) Theoretical oscillation of $\chi_{||}^T(\phi)$ resulting from Eq. (5). The location of the anisotropic bond (B1) is marked on the upper horizontal axis.

Oscillations are also observed in the in-plane transverse susceptibility $\chi_{||}^T$, where the magnetic field is applied along (0,0,1). Figure 2(c) shows the ϕ -dependence of $\chi_{||}^T$ as the crystal was rotated about a vertical axis coinciding with the field direction. Both below and above T_N , the susceptibility shows a well-defined oscillation about zero with a 2π period. The absolute maxima (nodes) of the oscillation occur perpendicular (parallel) to the inequivalent B1 bond at $\phi = 150^\circ$ and 330° ($\phi = 60^\circ$ and 240°).

A number of space groups, distinguished primarily by the stacking sequence of van der Waals-coupled honeycomb layers, have been proposed for α -RuCl₃ [36]. Most recently, a structural transition from high-temperature monoclinic $C2/m$ to trigonal $R\bar{3}$ was reported at $T \simeq 150$ K [37]. Our analysis below relies on a high-temperature model expansion, and thus a quantitative comparison to the model is made within the monoclinic phase. The monoclinic structure of the sample for which data is presented in Figs. 2-4 was confirmed directly by single crystal neutron diffraction at $T > 150$ K using the HB-3A beamline at the High Flux Isotope Reactor, Oak

Ridge National Laboratory (see Supplementary Information (SI) [38]). The small inequivalence in one of the Ru-Ru bond lengths [22] provides a natural explanation for the observation of a unique magnetically easy direction. We note that the π -period oscillation observed at all temperatures in this work, as well as in-plane anisotropy reported in a recent THz study [32], appear to be incompatible with a low-temperature trigonal point group. These results suggest a deviation from an ideal $R\bar{3}$ structure, which may be related to strain induced at the structural transition.

Model and high-temperature expansion. To model the observed behavior we consider a variant of an anisotropic Kitaev-Heisenberg- Γ Hamiltonian with nearest neighbor Heisenberg exchange (J_1), Kitaev interactions (K_1), and nearest neighbor symmetric off-diagonal spin exchange (Γ_1). Inequivalent interactions J'_1 , K'_1 , and Γ'_1 are assigned to the bond direction B1 giving a Hamiltonian of the form $H = H_{B1} + H_{B2_x} + H_{B2_y}$, where

$$H_{B1} = \sum_{\text{B1-bonds (ij)}} J'_1 \mathbf{S}_i \mathbf{S}_j + K'_1 S_i^z S_j^z + \Gamma'_1 (S_i^x S_j^y + S_i^y S_j^x), \quad (1)$$

$$H_{B2_x} = \sum_{\text{B2}_x\text{-bonds (ij)}} J_1 \mathbf{S}_i \mathbf{S}_j + K_1 S_i^x S_j^x + \Gamma_1 (S_i^y S_j^z + S_i^z S_j^y), \quad (2)$$

and H_{B2_y} follows from H_{B2_x} by replacing $x \leftrightarrow y$ [39]. Note that the B1 bond is symmetry-inequivalent to the two $B2_\alpha$ bonds while H_{B2_x} and H_{B2_y} are related by a spin rotation. Additional further neighbor couplings can be straightforwardly included (which also applies to the J_3 coupling which has been proposed to be sizeable [40]), however here we restrict the analysis to nearest neighbor couplings for simplicity of notation [41].

A high-temperature expansion of the full zero-field susceptibility tensor $\chi^{\mu\mu'}$ ($\mu, \mu' = x, y, z$) of this model up to terms $\sim T^{-2}$ yields

$$\begin{aligned} \chi^{\mu\mu'}(T) &= \frac{\mu_B^2 N}{4k_B T} \begin{pmatrix} g_x^2 & 0 & 0 \\ 0 & g_x^2 & 0 \\ 0 & 0 & g_z^2 \end{pmatrix} - \frac{\mu_B^2 N}{(4k_B T)^2} \times \\ &\times \begin{pmatrix} g_x^2(2J_1 + J'_1 + K_1) & g_x^2 \Gamma'_1 & g_x g_z \Gamma_1 \\ g_x^2 \Gamma'_1 & g_x^2(2J_1 + J'_1 + K_1) & g_x g_z \Gamma_1 \\ g_x g_z \Gamma_1 & g_x g_z \Gamma_1 & g_z^2(2J_1 + J'_1 + K'_1) \end{pmatrix} \\ &+ \mathcal{O}(T^{-3}), \end{aligned} \quad (3)$$

where N denotes the total number of spins (see SI Section II for the derivation of the expansion). Here we allow for a g -factor anisotropy of the form $g_x = g_y \neq g_z$ due to symmetry considerations. Projecting Eq. (3) onto an in-plane direction yields an expression for the longitudinal

in-plane susceptibility $\chi_{\parallel}(\phi)$,

$$\begin{aligned} \chi_{\parallel}(\phi) &= \frac{1}{6} \left[4\chi^{xx} + 2\chi^{zz} - 2\chi^{xy} - 4\chi^{xz} \right. \\ &\left. + (\chi^{xx} - \chi^{zz} - 2\chi^{xy} + 2\chi^{xz})(-\cos(2\phi) + \sqrt{3}\sin(2\phi)) \right]. \end{aligned} \quad (4)$$

The harmonic oscillation described by the term $-\cos(2\phi) + \sqrt{3}\sin(2\phi)$ is illustrated in Fig. 2(b), which reproduces the experimentally observed periodicity of $\chi_{\parallel}(\phi)$. Furthermore, the location of the extrema parallel and perpendicular to a Ru-Ru bond direction is in agreement with the measured susceptibility.

The susceptibility tensor $\chi^{\mu\mu'}$ can likewise be projected to yield an expression for the transverse in-plane susceptibility $\chi_{\parallel}^T(\phi)$,

$$\chi_{\parallel}^T(\phi) = \frac{1}{3\sqrt{2}} (-\chi^{xx} + \chi^{zz} - \chi^{xy} + \chi^{xz})(\sin(\phi) - \sqrt{3}\cos(\phi)), \quad (5)$$

where the term $\sin(\phi) - \sqrt{3}\cos(\phi)$ again reproduces the measured oscillations, showing maxima (minima) at $\phi = 150^\circ$ (330°) as well as zeros at 60° and 240° , see Fig. 2(c,d).

The results of Fig. 2 demonstrate that the anisotropic nature of the susceptibilities in α -RuCl₃ is captured well by the bond-inequivalent Kitaev-Heisenberg- Γ model described in Eqs. (1) and (2). Using the high-temperature expansion in Eq. (3) and assuming an isotropic g -factor $g_x = g_y = g_z$, which is close to the recently reported value $g_x = g_y = 1.1g_z$ [42], a simple interpretation of the observed oscillations and the in-plane/out-of-plane anisotropy arises: The amplitude $\chi_+ - \chi_-$ of the oscillation in $\chi_{\parallel}(\phi)$ (where χ_+ and χ_- are the maxima and minima of $\chi_{\parallel}(\phi)$) is proportional to the differences of the couplings on the B1 and $B2_\alpha$ -bonds,

$$\chi_+ - \chi_- \sim T^{-2} [K'_1 - K_1 + 2(\Gamma'_1 - \Gamma_1)]. \quad (6)$$

The oscillation of the in-plane susceptibility is expected to vanish in the absence of bond anisotropies. Furthermore, the difference $\chi_m - \chi_\perp$ (where $\chi_m = (\chi_+ + \chi_-)/2$ is the mean value of the in-plane oscillation) is proportional to the off-diagonal exchange couplings Γ_1 and Γ'_1 ,

$$\chi_m - \chi_\perp \sim T^{-2} (\Gamma'_1 + 2\Gamma_1). \quad (7)$$

That is, the observed anisotropy between in-plane and out-of-plane susceptibility originates from symmetric off-diagonal Γ spin exchange. As discussed below, a small g -factor anisotropy of the form $g_x = g_y \neq g_z$ generates additional terms in these dependencies, however the overall trends remain unchanged.

As shown in Fig. 2, the experimentally observed oscillations of χ as a function of ϕ , and the locations of their extrema, persist over large temperature ranges. Figure

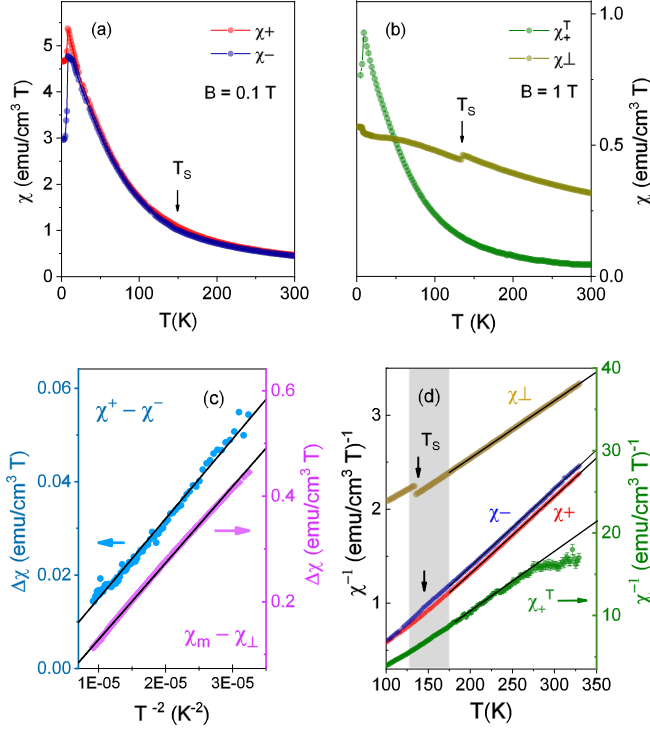


FIG. 3. Temperature-dependent susceptibilities at fixed angle, corrected for core diamagnetism [43]. (a) In-plane maximum and minimum longitudinal susceptibilities χ_+ and χ_- . (b) Out-of-plane longitudinal susceptibility χ_\perp and maximum transverse in-plane susceptibility χ_+^T . χ_+ , χ_- , and χ_+^T are measured in the same crystal for which angle-resolved data are shown. χ_\perp is measured on a second sample with greater thickness in the c direction. (c) Differences $\chi_+ - \chi_-$ (blue axis, left) and $\chi_m - \chi_\perp$ (purple axis, right), where χ_m is the mean longitudinal in-plane susceptibility, shown in the range $T = 150 - 330$ K. Solid lines are a linear fit. (d) Inverse of the temperature-dependent susceptibilities. χ_+^T is plotted on a different scale for clarity (green axis, right). Solid lines are a fit to the Curie-Weiss law above the structural transition T_S (grey region). The extraction of the small transverse signal at high temperature leads to large systematic error $\gtrsim 250$ K (see text).

3(a),(b) shows the temperature dependence of the longitudinal susceptibility measured perpendicular to the plane $\chi_\perp(T)$ and at the locations of the in-plane extrema $\chi_+(T)$ and $\chi_-(T)$, as well as the maximum transverse in-plane susceptibility $\chi_+^T(T)$. The temperature-dependent data were collected at fixed angle using standard, low-background sample holders to avoid diamagnetic contributions from the sample rotation stage. To confirm the validity of the high-temperature model, the differences $\chi_+ - \chi_-$ and $\chi_m - \chi_\perp$ are shown in Fig. 3(c). The data plotted against T^{-2} show reasonable correspondence with the linear behavior predicted by Eqn. (6) and (7).

Curie-Weiss analysis and model parameters. The good agreement between the ϕ -dependence of the ex-

perimentally measured susceptibility and the high-temperature expansion suggests a route to quantify the relationships between various model parameters. Due to symmetry considerations, the susceptibility tensor $\chi^{\mu\mu'}$ in Eq. (3) has four independent components χ^{xx} , χ^{zz} , χ^{xy} , χ^{xz} , which allows the same number of exchange couplings to be determined. Since a bond-isotropic Kitaev model does not break the cubic symmetry of the interactions in spin space, it is generally impossible from susceptibility alone to distinguish between Heisenberg interactions J_1 and Kitaev exchange K_1 when fitting our experimental data to the high-temperature expansion. A possible set of linearly independent model parameters that can be determined in a fitting procedure is given by $\tilde{J}_1 \equiv 2J_1 + J'_1 + K_1$, $\Delta K_1 \equiv K_1 - K'_1$, Γ_1 , Γ'_1 .

Using the expansion in Eq. (3), the inverse of the four susceptibility datasets shown in Fig. 3(a),(b) can be brought into the form $\chi^{-1}(T) \sim T - T_{CW} + \mathcal{O}(T^{-1})$ yielding four Curie-Weiss temperatures $T_{CW\perp}$, T_{CW+} , T_{CW-} , and T_{CW+}^T . These Curie-Weiss temperatures can be expressed as linear combinations of the model parameters. Defining the vectors $\mathcal{T}_{CW} = (T_{CW\perp}, T_{CW+}, T_{CW-}, T_{CW+}^T)$ and $\mathcal{J} = (\tilde{J}_1, \Delta K_1, \Gamma_1, \Gamma'_1)$ one finds $\mathcal{J} = k_B \mathcal{M} \mathcal{T}_{CW}$, where \mathcal{M} is a matrix which depends on the ratio g_x/g_z (see SI Section II).

The components of \mathcal{T}_{CW} were determined by fitting a linear Curie-Weiss behavior to the high-temperature inverse susceptibilities χ_\perp^{-1} , χ_+^{-1} , χ_-^{-1} , and χ_+^{T-1} (Fig. 3d). The analysis is restricted to the high-temperature region $175 \text{ K} \leq T \leq 330 \text{ K}$ away from the structural transition at $T_S \simeq 150 \text{ K}$ [37] that produces kinks in the susceptibility curves. Fitting the longitudinal susceptibilities yields $T_{CW\perp} = -216.4(3) \text{ K}$, $T_{CW+} = 39.6(2) \text{ K}$, and $T_{CW-} = 32.6(3) \text{ K}$. At high temperatures, longitudinal contamination in the transverse SQUID coils is comparable to the intrinsic transverse signal, so that separating the two components introduces large errors (Fig. 3b,d). Therefore the Curie-Weiss fitting is performed over a narrower temperature range of $175 \text{ K} \leq T \leq 275 \text{ K}$ to determine the intercept, $T_{CW+}^T = 50(2) \text{ K}$. Based on these Curie-Weiss temperatures and the reported g -factor anisotropy of $g_x/g_z = 1.1$ [42] we obtain the model parameters $(\tilde{J}_1, \Delta K_1, \Gamma_1, \Gamma'_1) = (14.3, -7.7, 29.8, 27.9) \text{ meV}$.

Inelastic neutron scattering [18, 44–47] and most calculations [26] place the magnetic exchange couplings for $\alpha\text{-RuCl}_3$ on the order of $\sim 5 - 10 \text{ meV}$, although K_1 as high as 16 meV [48] and recently 30 meV [49] have also been proposed. The discrepancy in energy scale between lower estimates and the couplings of up to 30 meV in the model parameters determined above might be due to the limited temperature ranges in which our Curie-Weiss fits are performed. Despite the fact that our inverse susceptibility data are well described by a linear behavior within our fitting range (see Fig. 3), shifting the temperature intervals upwards might still improve the re-

sults. Indeed, it has been argued for a Kitaev-Heisenberg model that depending on the precise fitting range, experimentally determined Curie-Weiss temperatures need to be rescaled by factors of 2 or larger to obtain the true Curie-Weiss intercepts [50]. We speculate that such a rescaling (which in the simplest case would apply to all interactions in the same way) would lead to exchange couplings with an overall size more consistent with other methods. Independent of such considerations, we conclude that off-diagonal exchange Γ and Γ' plays a large role in the susceptibility of α -RuCl₃, in line with growing theoretical recognition of the importance of the Γ term in the behavior of the system [23, 26], including the recent prediction of a quantum spin liquid ground state in a Kitaev- Γ model [51, 52]. Moreover, assuming the aforementioned model parameters and mapping out the classical phase diagram within Luttinger-Tisza as a function of the remaining free parameters J1 and K1, we indeed find the experimentally observed zigzag antiferromagnetic ground state in a large region of parameter space (see [38] Section III and Fig. S2). We point out that no longer-ranged interactions are necessary to stabilize the zigzag ground state in the presence of the bond anisotropies manifested in the measured oscillations of the longitudinal susceptibility.

Conclusion. The mapping out of the susceptibility tensor in single crystals of α -RuCl₃ yields new insight into possibilities for the correct Hamiltonian describing the system. The phase shifts and periodicity of the observed in-plane oscillations can be understood within a bond-anisotropic spin Hamiltonian with substantial Γ exchange. The agreement between the high-temperature expansion of the theoretical model and the measured oscillating susceptibilities χ_{\parallel} and χ^T is remarkable, and indicates that the amplitude of the oscillations of susceptibility are proportional to the bond anisotropies in the Kitaev and Γ terms. Our analysis further reveals that the marked easy-plane anisotropy in the system is a consequence of significant symmetric off-diagonal Γ exchange.

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