Electronically highly cubic conditions for Ru in α-RuCl₃

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We studied the local Ru 4d electronic structure of α-RuCl₃ by means of polarization dependent x-ray absorption spectroscopy at the Ru-L₂,₃ edges. We observed a vanishingly small linear dichroism indicating that electronically the Ru 4d local symmetry is highly cubic. Using full multiplet cluster calculations we were able to reproduce the spectra excellently and to extract that the trigonal splitting of the t₂g orbitals is −12 ± 10 meV, i.e. negligible as compared to the Ru 4d spin-orbit coupling constant. Consistent with our magnetic circular dichroism measurements, we found that the ratio of the orbital and spin moments is 2.0, the value expected for a J$_{\text{eff}}$ = 1/2 ground state. We have thus shown that as far as the Ru 4d local properties are concerned, α-RuCl₃ is an ideal candidate for the realization of Kitaev physics.

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Geometrically frustrated quantum spin systems are important owing to the fact that frustration often results in a suppression of conventional mean field ground states in favor of more exotic phases of matter. Current research focuses on the effect of spin-orbit coupling (SOC) and the role it plays in the realization of different exotic phases such as unconventional superconductivity or quantum spin liquids [1–3]. Especially, quantum spin liquids can result in topological states with fractional excitations [1–3].

The search for fractionalized excitations and the identification of a Kitaev spin liquid phase has been experimentally quite difficult. Increased attention has been focused on the honeycomb iridates [4,5], starting from the assumption that large spin-orbit coupling is the leading interaction within the Kitaev model frustrates the spin arrangements, the bond-dependent spin interactions as Ir$_4$Cl$_8$ ions in the iridates. The SOC, despite being modest (∼150 meV), is still thought to be the leading energy scale and able to generate a J$_{\text{eff}}$ = 1/2 ground state.

Recently, α-RuCl₃ has been suggested as a promising candidate material for the realization of the Kitaev model [10] and excitations observed via Raman [11,12] and inelastic neutron scattering [13] have been presented as evidence that α-RuCl₃ may be close to a quantum spin liquid ground state. In the last two years a number of publications discussing the realization of the Kitaev physics in α-RuCl₃ has appeared in literature [5,11,13,20,35]. α-RuCl₃ has a monoclinic structure, where the Ru atoms are arranged in nearly regular honeycomb planes with a Ru–Cl–Ru bond close to 90°, the latter being one of the conditions for the realization of Kitaev magnetism. The Ru$^{3+}$ ions in α-RuCl₃ (hereafter RuCl₃) have the same t$_{2g}^2$ configuration as Ir$^{4+}$ ions in the iridates. The SOC, despite being modest (∼150 meV), is still thought to be the leading energy scale and able to generate a J$_{\text{eff}}$ = 1/2 ground state.

Unfortunately, a precise determination of the atomic positions of the Cl ions by x-ray diffraction (XRD) is quite difficult with conflicting reports about the crystallographic structure of RuCl₃ [5,13,14,36] in literature due to the broad mosaicity arising from the weak V–W bonds existing between the layers. The intensity of Bragg peaks in XRD is strongly affected by the diffuse scattering produced by twins and stacking faults. We will refer in the following to the last diffraction study [3], which was performed on unwinned RuCl₃ single crystals with moderate stacking faults. According to this investigation, the local structure is close to cubic despite the low symmetry of the point group of the Ru site, and the dominant distortion of the RuCl₃ octahedra is trigonal with the trigonal axis normal to the ab plane. Additional tetragonal distortions are present but negligible [3].

Notwithstanding the moderate trigonal distortion, quantum chemistry calculations using the structure given by Ref. [3] proposed a complete lifting of the degeneracy of the t$_{2g}$ orbitals by a trigonal splitting of D$_{:\text{trig}}$ = 70 meV.
Experimentally, a splitting of the order of the SOC was estimated from the large anisotropy shown by high field magnetization measurements \[15\]. Raman scattering spectroscopy observed a single peak instead of the two-peak structure characteristic for trigonal distortion, which might indicate a nearly cubic local symmetry but could also be explained with the zero-intensity of one peak for symmetry reasons (e.g. selection rules) \[21\]. Considering the critical importance of the local symmetry for the realization of the Kitaev physics, there is a clear need to establish in a quantitative way the magnitude of the trigonal distortion and its effect on the magnetic ground state of RuCl$_3$. Theoretical studies in the literature have shown that the analysis of the ground state of RuCl$_3$ heavily relies on the trigonal field strength relative to the SOC \[22\-23\].

Here, we report on a Ru $L_{2,3}$ edge x-ray absorption spectroscopy (XAS) study of the local electronic and magnetic state of the Ru$^{3+}$ ion in RuCl$_3$, using both linear and circular polarized light. In combination with full-multiplet cluster simulations using parameters which are based on \textit{ab-initio} band structure calculations, we can extract values for the trigonal crystal field splitting as well as the ratio between the orbital and spin contributions to the local magnetic moment, thereby evaluating to what extent the local $J_{\text{eff}} = 1/2$ ground state is realized for the Ru ion.

Starting from polycrystalline RuCl$_3$ (Chempur) the crystals were obtained by chemical transport reaction with chlorine between 730 to 660 °C. The crystals were annealed for five months at 440°C under vacuum. A full characterization of the crystals is provided in Ref.\[16\]. The linear polarized XAS at the Ru-$L_{2,3}$ edges (2800-3000 eV) was measured at the 16A1 tender x-ray beamline of the NSRRC in Taiwan. The spectra were collected at room temperature in the total electron yield (TEY) mode. The degree of linear polarization of the incident light was close to 100% and the energy resolution was set to 0.6 eV. The x-ray magnetic circular dichroism (XMCD) experiments at the Ru-$L_{2,3}$ edges were performed at the BL29 Boreas beamline of the ALBA synchrotron radiation facility in Barcelona. The energy resolution was 1.4 eV and the degree of circular polarization delivered by the Apple II-type elliptical undulator was set to 70%. The spectra were recorded in the TEY method at $T = 2$ K and $B = 6$ T. The RuCl$_3$ crystals were cleaved \textit{in situ} to obtain a clean sample surface normal to the (001) direction. Density functional theory (DFT) based calculations were carried out using the full-potential local-orbital code FPLO \[37\], including both SOC and electron correlation ($U$) effects for the simplest ferromagnetic spin configuration \[38\].

In Fig. 1 we report the Ru-$L_{2,3}$ XAS measured on RuCl$_3$ at room temperature for linearly polarized light coming in with the electric field vector $E$ normal and parallel to the $ab$-plane. The chosen geometry has the incoming light polarization parallel and normal to the trigonal axis [111] of the local $D_{3d}$ symmetry. The Ru 2$p$ core-hole spin-orbit coupling splits the spectrum roughly in two parts, namely the $L_3$ (at $h\nu \approx 2840$ eV) and the $L_2$ (at $h\nu \approx 2969$ eV) white line regions. Additional features appearing in the low energy part of the spectrum are related to the Cl-$K$ edge at $h\nu \approx 2822$ eV.

We first focus on the Cl-$K$ edge features, which can be explained in terms of dipole allowed transitions from the Cl 1$s$ core level to the unoccupied Cl 3$p$ states. Fig. 2 displays the Cl 3$p$ and Ru 3$d$ partial density of states (DOS) from the DFT calculations, which reveal the pres-
ence of two sharp features above the Fermi level, namely at ~0.5 eV and ~2.4 eV. These are given by the unoccupied Ru 4d \( t_{2g} \) and \( e_g \) states, respectively, hybridizing with the Cl 3p. Comparing these unoccupied Cl states with the experimental Cl-K edge features, we can observe a very satisfactory agreement, especially when we include a broadening for the calculated curves in order to take the experimental resolution into account. Also the weak but clear polarization dependence in the experimental spectra is well explained by the DFT calculations.

For a better view of the multiplet and polarization dependence in the Ru-L\(_{2,3}\) spectra we show in Fig. 3 a close-up of the spectra. Notably there is hardly any linear dichroism (LD) visible at the low energy peak (at 2838 eV) of the L\(_3\) edge, which corresponds to the signal of the \( t_{2g} \) orbitals. The absence of LD is a very sensitive signal for how close to cubic the local symmetry is. For example, a trigonal elongation (compression) of the RuCl\(_6\) octahedron will cause a splitting of the \( t_{2g} \) orbitals in to \( a_{1g} \) and \( e_g \) orbitals, with the \( a_{1g} \) orbital lying higher (lower) in energy and, hence, having more (less) holes. Such an uneven hole distribution will then produce a difference in the spectral weight between \( E \) normal and parallel to the [111] axis. The experimental result that the LD is vanishingly small gives a clear and direct indication that the trigonal distortion of the RuCl\(_6\) octahedra is electronically negligible.

To obtain a quantitative estimate of how close to cubic the system is from an electronic point of view, we have simulated the Ru-L\(_{2,3}\) XAS spectrum using the configuration-interaction cluster model \[39\], \[40\]. This model includes the full atomic multiplet theory and takes into account the intra-atomic 4d–4d and 2p–4d Coulomb interactions, the atomic 2p and 4d spin-orbit couplings, the Cl-3p with Ru-4d hybridization, and the local crystal field parameters. In the simulations we considered a RuCl\(_6\) cluster with a D\(_{3d}\) symmetry as further distortions of the octahedra beyond the trigonal symmetry can be safely neglected \[3\], \[14\]. The cubic crystal field splitting between the Ru \( t_{2g} \) and \( e_g \) orbitals was estimated from the difference in energy position between the maximum in the XAS spectrum, corresponding to the signal from the unoccupied \( e_g \) levels, and the maximum of the XMCD signal (see below), which is due to the \( t_{2g} \) orbitals. The hybridization parameters and the crystal field acting on the chlorine ligands were extracted \textit{ab-initio} by DFT calculations. The calculations of the XAS spectra were performed using the XTLS 8.3 code \[41\] and the input parameters are given in Ref.\[42\].

The calculated Ru-L\(_{2,3}\) XAS spectra are plotted in Fig. 3(a). They nicely reproduce the experiment. In order to show how the trigonal distortion affects LD, we have plotted in Fig. 3(b) the experimental difference spectrum (\( E_{\perp ab} - E_{/ab} \)) together with the calculations for different trigonal crystal field splitting \( D_{trig} = E(e_g) - E(a_{1g}) \). As one can see, the LD is very sensitive to the magnitude and sign of the trigonal splitting. For positive \( D_{trig} \), the calculated LD has the opposite sign compared to the experimental one. On the other hand, a negative \( D_{trig} = -24 \) meV produces a LD signal with the correct sign but is already twice as large compared to the experiment. Hence, our experimental LD signal provides strong limits for the trigonal splitting of the \( t_{2g} \) orbitals. The best fit to the experimental data is obtained for \( D_{trig} = -12 \) meV. The accuracy of our method is actually limited by the presence of the Cl K-edge EXAFS oscillations which occur in the same region as the Ru-L\(_{2,3}\) edges. Part of these EXAFS oscillations show up as a slow varying background outside the Ru L-edge white line region (Fig. 3(b) ) and is as small as the small LD in the Ru-L\(_{2,3}\). Thus, our estimates result in a \( D_{trig} = -12 \pm 10 \) meV. This is an important finding since we now can conclude that the trigonal crystal field splitting is at least ten times smaller than the spin-orbit coupling constant (~150 meV), implying that the Ru \( d^5 \) ion may indeed be in the \( J_{eff} = 1/2 \) ground state.

Having established the crystal field situation, we now investigate the magnetic ground state of the Ru ions by performing Ru-L\(_{2,3}\) x-ray absorption measurements us-
ing circular polarized light with the photon spin aligned parallel ($\sigma^+$) and antiparallel ($\sigma^-$) to the magnetic field. A sketch of the experimental geometry is shown in Fig. 4. The difference or XMCD spectrum ($\sigma^+ - \sigma^-$) and the sum spectrum ($\sigma^+ + \sigma^-$) are reported in Fig. 5. The spectra were collected at $T = 2$ K in grazing incidence with the magnetic field ($B = 6$ T) lying in the ac plane ($xz$ plane in local D$_{3d}$ symmetry) and forming an angle of $20^\circ$ with the (100) axis (x-axis in local symmetry). The grazing geometry allowed to maximize the magnetic signal according to the easy-plane magnetic anisotropy of RuCl$_3$ reported in literature [15, 16].

The Ru-$L_{2,3}$ XMCD spectrum as obtained from our full-multiplet calculations is also presented in Fig. 5. In our model we have used the same parameters as for the simulation of the LD data, with $D_{\text{trig}} = -12$ meV. The lineshape of the calculated XMCD spectrum is in nice agreement with the experimental one, further validating our calculations. Here, we have used an exchange field of about $H_{\text{ex}} = 10$ meV in order to reproduce the magnitude of the experimental XMCD spectrum. If we would have used zero exchange field, the calculated XMCD signal in an applied field of 6 Tesla is much larger than the measured one, i.e. the magnitude of the XMCD is very sensitive to the size of the exchange field (see supplemental information). This in fact can be understood as RuCl$_3$ exhibits a zig-zag modulated antiferromagnetic order below $T_N = 8$ K and the XMCD signal is given only by the canting of the moments induced by the applied field. The exchange field we have applied is directed along the Ru spins, which form an angle of $\phi = 35^\circ$ with the $ab$ plane [3] (blue arrows in Fig. 3). We would like to note that the XMCD alone is rather unsuitable to determine accurately the magnitude of the trigonal crystal field splitting (see supplemental information).

Having obtained $D_{\text{trig}}$ from LD and $H_{\text{ex}}$ from XMCD we can now focus on the orbital moment of Ru in RuCl$_3$. Very interestingly, the XMCD signal has the same negative sign at both $L_3$ and $L_2$ edges. Usually, the XMCD has the opposite sign at the two edges, which is a consequence of the reduction of the orbital moment from its atomic value when the transition metal ion is placed in a solid. The fact that the XMCD does not change sign clearly indicates that the orbital moment of the Ru$^{3+}$ ion in RuCl$_3$ is large, possibly close to the atomic values. From our configuration-interaction calculations we obtain a ratio of $L_z/2S_z = 2.0$ for $H_{\text{ex}} = 10$ meV (2.1 if $H_{\text{ex}} = 0$ meV). This value is very close to the ratio between the orbital and the spin moments expected for a pure $J_{\text{eff}} = 1/2$ system [13].

From the Zeeman splitting of the energy levels in the presence of an applied magnetic field we can calculate the magnetic g factor to be $g_x = g_y = 2.27$ and $g_z = 2.05$ [14]. The fairly isotropic g factor ($g_x/g_z = 1.1$) indicates that the strong anisotropy shown by both susceptibility [15, 16] and high-field magnetization [14] can not be ascribed to single ion physics. Instead, hybridization with neighboring Ru ions needs to be considered explicitly, giving rise to various nearest neighbor and next nearest neighbor Heisenberg, Kitaev and off-diagonal couplings [22]. Our calculations also shows that the average $g = (2g_x + g_z)/3 = 2.2$ is larger than that (2.0) for a pure ionic $t^3_{2g}$ system. While covalency tends to de-
crease the value of the $g$ factor, the mixing-in of some $e_g$ character into the $t_{2g}$ manifold will quickly increase the $g$ factor value. This $e_g$-$t_{2g}$ mixing can take place locally on a one-electron level, for example by the presence of a trigonal crystal field, but also (and in fact, certainly) on a many-electron level due to the presence of atomic multiplet interactions (Slater $F^2$ and $F^4$ integrals) which are not at all small compared to the $e_g$-$t_{2g}$ crystal field splitting ($10Dq$).

To summarize, our X-ray absorption linear dichroism study demonstrates that the ground state of RuCl$_3$ is a doublet with a very close to perfect cubic local symmetry. Our excellent simulations of the experimental spectra give a ratio of 2.0 between the orbital and the spin contributions to the local Ru $4d$ magnetic moment, i.e. the value expected for a $J_{\text{eff}} = 1/2$ ground state. Further quantitative modeling is highly desired as to include not only the Ru $t_{2g}$ but also the $e_g$ orbitals.

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Electronically highly cubic conditions for Ru in $\alpha$-RuCl$_3$

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In Fig. S1 we report simulations for the Ru-$L_{2,3}$ XMCD spectra calculated for $T = 2$ K and $B = 6$ T using different values of the trigonal crystal field splitting $D_{\text{trig}}$ under the assumption that the exchange field $H_{\text{ex}}$ is absent. One can clearly observe that the simulated XMCD signal is always much larger than the measured one of RuCl$_3$, no matter what trigonal distortion is considered.

In Fig. S2 we show the simulations for the XMCD for different values of $H_{\text{ex}}$ with $D_{\text{trig}}$ fixed at -12 meV. The exchange field has a very strong influence on the magnitude of the XMCD signal. The experimental XMCD is best simulated for $H_{\text{ex}} = 10$ meV. We note that in the considered range, the exchange field has no significant effect on the lineshape of the XMCD spectrum but determines mainly the size of the XMCD signal.

Fig. S3 displays the simulations for the XMCD as a function of $D_{\text{trig}}$ in order to investigate the sensitivity of the XMCD lineshape to $D_{\text{trig}}$. The calculations have been done for a fixed $H_{\text{ex}} = 10$ meV and the curves have been normalized to the XMCD peak height to highlight the lineshape of the spectra rather than the magnitude of the signal. The top panel shows the results for a large range of $D_{\text{trig}}$, i.e. between -500 and +500 meV, and the bottom panel presents the result for a narrower range with smaller steps, i.e. between -100 and +100 meV. From the figure we can observe that the spectral lineshape of XMCD is sensitive to the trigonal crystal field splitting, but only so if the $D_{\text{trig}}$ value is varied in a range that exceeds the spin-orbit coupling constant of about 150 meV. Varying $D_{\text{trig}}$ between -50 and +100 meV in fact does not change the lineshape visibly. In other words, XMCD alone is not a very sensitive method to determine $D_{\text{trig}}$ accurately. To establish whether the $J_{\text{eff}} = 1/2$ condition is fulfilled (or not) implies that one needs to determine whether $D_{\text{trig}}$ is negligible (or not negligible) compared to the spin-orbit constant. The more accurate method to resolve this issue is to measure the smallness of the linear dichroism in the XAS itself. XMCD is valuable to determine the magnitude of the exchange field and to serve as a strict consistency check of the simulations: the same set of parameters must provide excellent simulations for both the XAS and the XMCD spectra.

In literature the sum rules for XMCD developed by...
FIG. S3: (color online) Ru-L_{2,3} XMCD simulations (solid lines) calculated using different values of $D_{trig}$ with $H_{ex} = 10$ meV, together with the experimental XMCD spectrum of RuCl₃ (red circles). In the top panel $D_{trig}$ is varied between -500 and +500 meV, and in the bottom panel between -100 and +100 meV. For a better comparison of the line shapes, the simulated spectra are normalized to the XMCD peak height, with the normalization factor also indicated in the legend.

Thole and Carra et al. [1, 2] are often used to extract directly from the spectrum the ratio of orbital and spin moments. The sum rules can be summarized as:

$$
\frac{L_x}{2S_x + 7T_x} = \frac{2}{3} \cdot \frac{\int_{L_3} (\sigma^+ - \sigma^-) dE}{\int_{L_2} (\sigma^+ - \sigma^-) dE - 2 \int_{L_2} (\sigma^+ - \sigma^-) dE},
$$

(1)

where $S_x$ and $L_x$ are the spin and orbital contributions to the local magnetic moment, respectively, and $T_x$ is the intra-atomic magnetic dipole moment. The application of the sum rules to our experimental Ru L_{2,3} XMCD data gives $L_x/(2S_x + 7T_x) = 1.0(1)$, which confirms that the orbital moment of Ru^{3+} is relatively large. If we use the value of $T_x/2S_x = 0.15$ given by our configuration-interaction calculations, we obtain from the application of the sum rules the ratio $L_x/2S_x = 2.0(1)$, which is in very good agreement with the value given by our configuration interaction calculations for $D_{trig} = 5$ meV and $H_{ex} = 10$ meV. This demonstrates that the analysis using the sum rules is fully consistent with the analysis based on the simulations of the XAS and XMCD spectra, i.e. analyses based on the lineshape, as it should be.

Fig. S4 shows the calculated $L_x/(2S_x + 7T_x)$ ratio as a function of the trigonal crystal field splitting for a fixed exchange field of 10 meV. We can clearly observe that the sum rule quantity $L_x/(2S_x + 7T_x)$ is a slowly varying function of $D_{trig}$. The experimental XMCD data is given by the dashed line and the shadow area represents its error bar. Hence, the value obtained by applying the sum rules to the XMCD data can correspond to the wide range $-100 \leq D_{trig} \leq +100$ meV. In other words, our calculations reveal that the XMCD alone of RuCl₃ cannot, either through spectral lineshape analysis or through the application of the sum rules, provide a value of $D_{trig}$ with the required precision. A reliable and accurate determination of $D_{trig}$ can be best obtained from the linear dichroic signal in the polarization dependent XAS spectra as we have reported in the main text of the manuscript.

We would like to note that in our model we have taken into account the zig-zag modulated magnetic structure (shown in fig. 3) proposed by Cao et al. [3], by applying an exchange field of 10 meV along the direction of the Ru spins, which forms an angle of $\phi = 35^\circ$ with the $ab$ plane. If the alternative $\phi = -35^\circ$ zig-zag magnetic structure is considered then the exchange field has to be reduced to 3 meV in order to simulate the size of the experimental XMCD signal. The reason of the need of reducing the exchange field lies in the fact that in the case of the second magnetic structure the applied magnetic field would be close to the direction of the spins, which is a hard direction for the magnetization. With the present XCMD data we are not able to distinguish which of the two magnetic structure is correct. Yet, this does not affect the conclusions that we have made about the trigonal crystal field value and the $L_x/2S_x = 2.0$ for
RuCl$_3$, i.e. our finding that the Ru ground state fulfills the $J_{\text{eff}} = 1/2$ condition is robust.

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