Magnetic Raman continuum in single crystalline H$_3$LiIr$_2$O$_6$

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Recently H$_3$LiIr$_2$O$_6$ has been reported as a spin-orbital entangled quantum spin liquid (QSL) [K. Kitagawa et al., Nature 554, 341 (2018)], albeit its connection to Kitaev QSL has not been yet identified. To unveil the related Kitaev physics, we perform the first Raman spectroscopy studies on single crystalline H$_3$LiIr$_2$O$_6$ samples. We implement a soft chemical replacement of Li$^+$ with H$^+$ from α-Li$_2$IrO$_3$ single crystals to synthesize the single crystal samples of the iridate second generation H$_3$LiIr$_2$O$_6$. The Raman spectroscopy can be used to diagnose the QSL state since the magnetic Raman continuum arises from a process involving pairs of fractionalized Majorana fermionic excitation in a pure Kitaev model. We observe a broad dome-shaped magnetic continuum in H$_3$LiIr$_2$O$_6$, in line with theoretical expectations for the two-spin process in the Kitaev QSL. Our results establish the close connection to the Kitaev QSL physics in H$_3$LiIr$_2$O$_6$.

Introduction. – The search for quantum spin liquid (QSL) state has been a currently active and challenging topic in the condensed matter physics [1–12]. The spin degree of freedom in QSL does not freeze to display any magnetic order even at zero temperature, but highly entangles with each other [13–18]. In the early theoretical studies, the exact solvable Kitaev honeycomb spin model [13] built confidence about the existence of QSL in a simple spin interacting system; furthermore, it has been currently initializing the materialization of the Kitaev QSL in the experiments [19–21]. With the help of the intertwining between magnetism, spin-orbital coupling, and crystal field, Ir$^{4+}$ oxides and a Ru$^{4+}$ chloride with a $d^5$ electronic configuration are promising to materialize the Kitaev model, e.g., α-A$_2$IrO$_3$ (A=Na, Li) [22–24] and α-RuCl$_3$ [25].

Due to other non-Kitaev interactions, magnetic orders appears in α-A$_2$IrO$_3$ (A=Na, Li) and α-RuCl$_3$ at low temperatures [22, 26, 27]. The suppression of magnetic ordering in α-A$_2$IrO$_3$ (A=Na, Li) and α-RuCl$_3$ has been attempted by applying magnetic field [28, 29], high pressure [30–32], and chemical modification [12, 33]. For the chemical modification of α-Li$_2$IrO$_3$, a QSL state ground was recently established in the second generation of two-dimensional honeycomb iridates H$_3$LiIr$_2$O$_6$ [12, 33]. No sign of magnetic order, but signatures of local low-energy excitations are observed in H$_3$LiIr$_2$O$_6$, down to low temperatures in the magnetic susceptibility, specific heat, and NMR measurements [12]. H$_3$LiIr$_2$O$_6$ has immediately caught lots of theoretical investigation to explore the connection to the Kitaev QSL physics [34–38], and the roniness of H positions was also discussed as playing an important role in stabilizing the QSL state [35, 36]. currently, however, no spectroscopic information exists regarding the spin excitations and the possibility of spin fractionalization in H$_3$LiIr$_2$O$_6$.

In this Letter, we report our attempts to diagnose the spin liquid signature in the single crystalline H$_3$LiIr$_2$O$_6$ using the Raman spectroscopy methods. Single crystals of α-Li$_2$IrO$_3$ are soaked in 4 mol/L H$_2$SO$_4$ aqueous solution for the soft chemical replacement of Li$^+$ with H$^+$. As well as single crystals of the target second generation of iridate H$_3$LiIr$_2$O$_6$, we obtain the third iridate generation with the hypothesized formula H$_3$LiIr$_2$O$_6$. We carry out the X-ray photoelectron spectroscopy (XPS) measurements, and confirm that H$_3$LiIr$_2$O$_6$ has the same Ir$^{4+}$ oxidation state as α-Li$_2$IrO$_3$, while H$_3$LiIr$_2$O$_6$ has lower oxidation state Ir$^{3+}$. Submillimetre-size crystals are available for the Raman spectroscopy, that is capable of detecting magnetic excitations [39–41], even the spin fractionalizations signaled by the magnetic Raman continuum in the Kitaev-type compounds[31, 32, 42–44]. We observe a broad two-spin process continuum in the dynamical Raman susceptibility for H$_3$LiIr$_2$O$_6$, in a good agreement with the theoretically expected scattering from a pure Kitaev model [45]. Our results demonstrate Raman spectroscopic signatures of the fractionalized excitation for the Kiteav QSL state in H$_3$LiIr$_2$O$_6$.

Single crystal synthesis and experimental setup. – We implement the soft chemical replacement of of Li$^+$ with H$^+$ in the iridate first generation α-Li$_2$IrO$_3$ single crystals. We obtain single crystals of different generations of honeycomb iridate oxides, depending the growth condition, especially reaction (soaking) time. For the growth:
of \(\alpha\)-Li\(_2\)Ir\(_3\)O\(_6\) single crystal, we adopted the similar setup as described in Ref. [46] with iridium metal (powder, 99.99\%) and lithium (granule, 99.99\%) used as starting materials. The whole setup was placed in a preheated furnace of 200 °C heated to 1020 °C and dwelled for 10 days. For cation exchange, \(\alpha\)-Li\(_2\)Ir\(_3\)O\(_6\) single crystals were added into in a 25 ml Teflon-lined steel autoclave with 20 ml H\(_2\)SO\(_4\) aqueous solution (4 mol/L).

The XPS investigations were carried out on Thermo Fisher ESCALAB 250Xi using monochromated Al K\(\alpha\) radiation at room temperature, and the electron flood gun was turned on to eliminate electric charging effect in our insulating samples. The binding energy in XPS was calibrated by 1s spectra of carbon. XRD measurements were conducted on Rigaku Smartlab 9KW using Cu K\(\alpha\) radiation at room temperature, and the electron flood gun was kept low enough (about 100 \(\mu\)W) to prevent the samples from heating and damaging samples. We use 1200 grooves/mm grating to get the high resolution, and the radiation for three generations of the iridate oxides. The binding energy in XPS was calibrated by 1s spectra of carbon. XRD measurements were conducted on Rigaku Smartlab 9KW using Cu K\(\alpha\) radiation at room temperature.

The Raman spectra were measured in the quasi-back-scattering geometry, with light polarized in the basal plane. The experiments were performed on our home-built system using a HORIBA iHR550 spectrometer and the 632.8 nm excitation line of a He-Ne laser. The power of the laser was kept low enough (about 100 \(\mu\)W) to prevent from heating and damaging samples. We use 1200 grooves/mm grating to get the high resolution. Since the light scattering intensity is weak, we set the integral time to 1800 s. The samples were placed in a He-flow cryostat which evacuated to 2 \(\times\) 10\(^{-5}\) Torr. The samples temperatures were calibrated according to the in-He-flow cryostat which evacuated to 2 \(\times\) 10\(^{-5}\) Torr. The samples were placed in a He-flow cryostat which evacuated to 2 \(\times\) 10\(^{-5}\) Torr. The samples were placed in a He-flow cryostat which evacuated to 2 \(\times\) 10\(^{-5}\) Torr.

**Sample characterizations.** Single crystals of \(\alpha\)-Li\(_2\)Ir\(_3\)O\(_6\) have different appearances, e.g., the flake and pyramid shapes, probably due to different stacking patterns of LiIr\(_2\)O\(_6\) layers. We find that the pyramid-shaped \(\alpha\)-Li\(_2\)Ir\(_3\)O\(_6\) have more ordered stacking pattern, however, the flake-shaped crystals are easily accessible for the soft chemical replacement as the present study in this work. Fig. 1 (a) is the image for typical single crystals of three generations of the iridate oxides. The parent generation \(\alpha\)-Li\(_2\)Ir\(_3\)O\(_6\) (the flake crystral) displays the black appearance. The second generation (H\(_3\)LiIr\(_2\)O\(_6\)) has the reddish black color, and the third generation (hy-pothesized formula H\(_2\)LiIr\(_2\)O\(_6\)) has the lustrous red appearance. During the soft-chemical-ion-exchange reaction (about 70 min), the interlayer Li\(^+\) will be replaced by H\(^+\), and we can get the target iridate second generation H\(_3\)LiIr\(_2\)O\(_6\). With longer soaking time (about 3 hours), more Hydrogen atoms intercalate into the inter-layers of [LiIr\(_2\)O\(_6\)] layers, and we get the crystals of the third generation H\(_2\)LiIr\(_2\)O\(_6\). While \(\alpha\)-Li\(_2\)Ir\(_3\)O\(_6\) and H\(_2\)LiIr\(_2\)O\(_6\) is very stable, H\(_3\)LiIr\(_2\)O\(_6\) may react with the vapour in the air.

Figure. 1 (b) is the powder X-ray diffraction (PXRD) result for three generations of iridate oxides. Apparently, they have very similar overall PXRD patterns since the acid treatment have caused a mild change in the constitution of the LiIr\(_2\)O\(_6\) layers, adn only the ions situated in-between the layers are changed. The intense basal reflection \(2\theta\) shifts up from \(\alpha\)-Li\(_2\)Ir\(_3\)O\(_6\) (18.36°) to H\(_3\)LiIr\(_2\)O\(_6\) (19.52°), and then down to H\(_2\)LiIr\(_2\)O\(_6\) (18.85°), corresponding to the interlayer distance 4.828 Å, 4.544 Å and 4.704 Å, respectively. Strong anisotropic broadening of the reflections in the XRD-pattern revealed heavy stacking faulting of the samples. Fig. 1 (c) is the typical Raman result for the three generations at a room temperature. The Raman intensity of of H\(_3\)LiIr\(_2\)O\(_6\) rescales by multiplying by 1/2. During the crystal synthesis, we use the Raman spectra to monitor the soaking process of our samples.

We implement XPS to verify the oxidation state of iridium ions in the three generations. As shown in Fig. 1 (d), three generations have very similar Ir 4\(f\) XPS spectra, indicating the similar local electronic environment of IrO\(_6\). The shift of the binding energy of Ir 4\(f\) implies the changes of oxidation state of Ir, and lower binding energy represents lower valance state. The mild change can be seen from \(\alpha\)-Li\(_2\)Ir\(_3\)O\(_6\) to H\(_3\)LiIr\(_2\)O\(_6\) by comparing the position of 4f\(_{5/2}\) and 4f\(_{7/2}\) energy level, indicating the same electronic configuration of Ir\(^{4+}\). H\(_3\)LiIr\(_2\)O\(_6\) has a significant lower binding energy (about 0.7 eV). According to Ir-based compounds in the database[47], Ir\(^{3+}\) and Ir\(^{4+}\) usually have a difference of the binding energy about 0.5 eV. Comparing Ir\(^{4+}\) in \(\alpha\)-Li\(_2\)Ir\(_3\)O\(_6\) and H\(_3\)LiIr\(_2\)O\(_6\), we have Ir\(^{3+}\) in IrO\(_6\) octahedron in H\(_3\)LiIr\(_2\)O\(_6\). Ir\(^{3+}\) has the 3\(d^6\) electronic configurations without partially occupied orbitals, and hence no magnetism. This explains the negligible magnetic Raman continuum in H\(_3\)LiIr\(_2\)O\(_6\).
as shown in Fig. 1 (c) and Fig. 3.

**Evolution of Raman spectra** – Figures. 2 is the evolution of Raman spectra of H₃LiIr₂O₆ at different temperatures. Comparing with our α-Li₂IrO₃ results [32], we can assign the sharp phonon modes by assuming that H₃LiIr₂O₆ has the same space group (#12, C2/m) as α-Li₂IrO₃. Three modes at 364.0 and 630.8 cm⁻¹ are assigned as A_g modes, the mode at 131.9 cm⁻¹ is assigned as B_g mode, and four modes at 189.6, 259.9, 490.0 and 541.0 cm⁻¹ are assigned as A_g + B_g modes which are nearly doubly degenerate. 131.9 and 189.6 cm⁻¹ modes are the Ir-Ir out-of-phase motions along the out-of-plane and in-plane directions, respectively. The 259.9 cm⁻¹ mode is the twist of Ir-O-Ir-O plane, the 364.0 cm⁻¹ mode is the relative twist of between the upper and lower oxygen triangles. The 490 cm⁻¹ mode is related to the Ir-O-Ir-O plane shearing, and the 541.0 cm⁻¹ mode is the breathing mode of Ir-O-Ir-O ring. The A_g mode at 630.8 cm⁻¹ can be assigned as the symmetrical breathing mode between the upper and lower oxygen layers. Several weak phonon peaks at around 155, 220, 325 and 600 cm⁻¹ become visible at low temperatures in H₃LiIr₂O₆, and these modes don’t appear in α-Li₂IrO₃ [32]. We notice that Raman phonon modes in H₃LiIr₂O₆ in this work and α-Li₂IrO₃ [32] are quite similar to those in other Kitaev materials, e.g. α-RuCl₃ [31, 42] and β- and γ-Li₂IrO₃ [43], suggestive of similar local crystal RuCl₆ and IrO₆ octahedral structures.

Besides the phonon modes, we observe a strong continuum background with increasing intensity as increasing temperatures particularly for low Raman frequencies (Fig. 2). We attribute such a continuum background as the magnetic Raman scattering as observed in α-RuCl₃ [42] and β- and γ-Li₂IrO₃ [43] due to spin fractionized excitations. H₃LiIr₂O₆ is a layered material and there are heavily stacking faults which may lead to broad phonon modes that could explain the continuum. However, the static structural disorder cannot produce the significant temperature dependence. Furthermore, the damped phonon scenario couldn’t account for the Raman continuum according to the polarization dependence of the Raman spectra in H₃LiIr₂O₆ as shown in Fig. 3 (a). As a matter of fact, the weak polarization dependence of Raman spectra in H₃LiIr₂O₆ agrees well with theoretical calculations for the isotropic Kitaev model [48].

As a control experiment, Fig. 3 (b) is the evolution of Raman spectra in H₃LiIr₂O₆ at different temperatures. Actually, H₃LiIr₂O₆ would have similar stacking faults to H₃LiIr₂O₆ since they main difference in their synthesis is the soaking time of the soft chemical reaction. With increasing temperature, all phonon peaks in H₃LiIr₂O₆ change very mild, and there is not any continuum background at all at the whole temperature range, which is in contrast to the spectra of H₃LiIr₂O₆ in Fig. 2. On one hand, as a control experiment, the Raman spectra of H₃LiIr₂O₆ in Fig. 3 (b) implies that the continuum background of H₃LiIr₂O₆ in Fig. 2 is not due to the stacking faults, but has the magnetic origin. On the other hand, even if some regions of H₃LiIr₂O₆ (Ir⁴⁺) turn into H₃LiIr₂O₆ (Ir³⁺) due to the over soaking in the acid, they behave as handful impurities and do not contribute to the magnetic Raman continuum.

According to the fluctuation-dissipation theorem, the Raman intensity I(ω) is proportional to the dynamical Raman susceptibility as I(ω) = [1 + n(ω)]χ''(ω). Here n(ω) is the boson factor, and χ''(ω) is the imaginary part of the correlation functions of Raman tensor τ(r, t), χ(ω) = ∫₀ʳ dτ'[τ(0, 0), τ(r, t)]=e⁻⁻⁺⁻τ.

To examine the the magnetic Raman susceptibility χ''(ω) in H₃LiIr₂O₆ more explicitly, we remove phonon modes using the Gaussian-type line-shape. As a consequence, the obtained magnetic Raman susceptibility in H₃LiIr₂O₆
We extract the integrated Raman susceptibility $\chi_R$ in accordance with the Kramers-Kronig relation $\chi_R = \frac{2}{\pi} \int \frac{\chi''(\omega)}{\omega} d\omega$. To do the integration, we extrapolate the Raman conductivity $\chi''(\omega)$ in H$_3$LiIr$_2$O$_6$ to 0 cm$^{-1}$. The temperature dependent $\chi_R$ in H$_3$LiIr$_2$O$_6$ is plotted in Fig. 5, in which the integration is carried out from 0 cm$^{-1}$ to 410 cm$^{-1}$, taking into account the fact that the magnetic Raman continuum with the frequency between 410 cm$^{-1}$ and 710 cm$^{-1}$ is weakly temperature dependent. The integrated Raman susceptibility $\chi_R$ in H$_3$LiIr$_2$O$_6$ essentially decreases monotonically as lowering the temperatures at least above 50 K, very different from that in $\alpha$-Li$_2$IrO$_3$[32], where $\chi_R$ increases monotonically with temperature decreasing. It is worthy to mention that the temperature dependence of $\chi_R$ in H$_3$LiIr$_2$O$_6$ is similar to that in $\beta$- and $\gamma$-Li$_2$IrO$_3$[43]. The integrated Raman susceptibility $\chi_R$ of $\alpha$-Li$_2$IrO$_3$ has a very similar temperature dependence behavior to $\alpha$-RuCl$_3$, i.e., increasing monotonically with temperature decreasing [32, 44]. More specifically, the inelastic light scattering in H$_3$LiIr$_2$O$_6$ and $\beta$- and $\gamma$-Li$_2$IrO$_3$ has different form from that in $\alpha$-RuCl$_3$ and $\alpha$-Li$_2$IrO$_3$, which deserves further detailed investigations.

**Discussions and conclusions** – With the help of strong spin-orbit coupling, crystal field splitting and electronic correlation, the Kitaev materials have the effective spin-1/2 moment [19, 21]. The magnetic Raman tensor $\tau(r)$ in these systems can be expanded in powers of the effective spin-1/2 operators, $\tau^{\alpha\beta}(r) = \tau_0^{\alpha\beta}(r) + \sum_{\mu} K_{\mu}^{\alpha\beta} S_{\mu}^{r}(r) + \sum_{\delta} \sum_{\mu\nu} M_{\mu\nu}^{\alpha\beta}(r, \delta) S_{\mu}^{r} S_{\nu}^{r} + \ldots$. The first term corresponds to Rayleigh scattering, the second and third terms correspond to the one-spin and two-spin process, respectively [39–41]. The complex tensors $K_{\mu}^{\alpha\beta}$ and $M_{\mu\nu}^{\alpha\beta}$ are determined by the strength of the spin-orbit couplings and the sublattice coupling form of light to the spin system. If the one-spin process dominates the inelastic light scattering, the integrated Raman susceptibility $\chi_R$ is associated with the thermodynamic magnetic susceptibility $\chi$, as demonstrated in $\alpha$-RuCl$_3$ [44] and $\alpha$-Li$_2$IrO$_3$ [32]. In $\beta$- and $\gamma$-Li$_2$IrO$_3$, the integrated Raman susceptibility $\chi_R$ is associated with the magnetic-specific heat $C_m$ multiplied by the temperature $T$, i.e., $C_mT$ [43], indicating that the two-spin process dominates the magnetic Raman scattering.

The temperature dependence behavior of H$_3$LiIr$_2$O$_6$ is similar to that in $\beta$- and $\gamma$-Li$_2$IrO$_3$, therefore, two-spin process dominates in the magnetic Raman continuum in Fig. 4. In the putative Kitaev QSL, the magnetic Raman scattering of two-spin process directly probes the pairs of the Majorana fermions which are characterization of the elusive spin fractionalizations [48, 49]. Particularly, Knolle et. al. have calculated the magnetic Raman scattering for the two-spin process, and our dome-shaped magnetic Raman continuum agrees very well with the simulated Raman response [48]. Therefore, our results

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**Figures:**

**Fig. 4.** Temperature dependent evolution of magnetic Raman continuum in the dynamical Raman susceptibility $\chi''(\omega)$ in H$_3$LiIr$_2$O$_6$.

**Fig. 5.** Temperature dependent magnetic Raman susceptibility $\chi_R(T)$ in H$_3$LiIr$_2$O$_6$.
demonstrate the emergence of spin fractionalization, and establish a Kitaev QSL in H$_3$LiIr$_2$O$_6$. The theoretical simulated Raman response has a maximum at 1.5 $J_k$ (where $J_k$ is the Kitaev interaction for the effective spin-1/2 operators) [48]. Equating 1.5 $J_k$ with the experimental maximum of continuum scattering of 40 meV yields $J_k = 26$ meV, in a good consistent with DFT estimations [35–37].

H$_3$LiIr$_2$O$_6$ have heavily stacking faults [12, 33], and theoretical investigations of have discussed the important role of the randomness to stabilize the Kitaev QSL [34–38]. However, Raman scattering is not sensitive to the local randomness, and our results didn’t address the issue about the physics of disorder in quantum spin liquids. Knolle et al. predicted a $\delta$-function peak reflecting the local two-particle density of states of Majorana fermions in the presence of four vison fluxes [48]. Such a vison peak is not resolved in our Raman data due to the severely bad resolution at small wave numbers.

In conclusion, we perform the Raman spectroscopy studies of single-crystal H$_3$LiIr$_2$O$_6$ samples and observe a dome-shaped magnetic Raman continuum. Our results demonstrate the spin fractionalization in H$_3$LiIr$_2$O$_6$, which is a defining feature of the Kitaev quantum spin liquid state.

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