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Inelastic light scattering measurements of a pressure-induced quantum liquid in KCuF$_3$

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Pressure-dependent, low temperature inelastic light (Raman) scattering measurements of KCuF$_3$ show that applied pressure above $P^* \sim 7$ kbar suppresses a previously observed structural phase transition temperature to zero temperature in KCuF$_3$, resulting in the development of a $\omega \sim 0$ fluctuational (quasielastic) response near $T \sim 0$ K. This pressure-induced fluctuational response which we associate with slow fluctuations of the CuF$_6$ octahedral orientation — is temperature independent and exhibits a characteristic fluctuation rate that is much larger than the temperature, consistent with quantum fluctuations of the CuF$_6$ octahedra. A model of pseudospin-phonon coupling provides a qualitative description of both the temperature- and pressure-dependent evolution of the Raman spectra of KCuF$_3$.

Frustrated magnetic systems in which conventional magnetic order is suppressed down to $T = 0$ K are currently of great interest, because these systems can exhibit exotic phenomena, e.g., off-diagonal long range order,[1] and novel “liquid-like” ground states — such as orbital [2] and spin liquids [3] — that quantum mechanically fluctuate even at $T = 0$ K. Unfortunately, there are only a few examples of real materials in which such fluctuating ground states have been reported.[2,3]

In this paper, we report the first spectroscopic evidence for a pressure-tuned quantum melting transition in KCuF$_3$ between a static structural phase to a phase in which fluctuations persist even at $T \sim 0$ K. While often considered a model system for orbital-ordering behavior,[4] the 3d$^9$ perovskite KCuF$_3$ is known to exhibit a number of unusual properties that are still not well understood,[5–16] including a highly anisotropic exchange coupling ($J_e/J_a \sim -100$) [5] that results in 1D antiferromagnetic Heisenberg spin dynamics above 40 K,[6–8] and a large disparity between the orbital ordering temperature ($T_{o\infty} \sim 800$ K [9]) and the Néel ordering temperature ($T_N \sim 40$ K [5,8]) that cannot be explained by conventional superexchange models.[10] Pressure-dependent, low temperature inelastic light (Raman) scattering measurements reported here show that applied pressure above $P^* \sim 7$ kbar suppresses a previously observed structural phase transition temperature [15, 16] in KCuF$_3$ down to the lowest temperatures measured ($T = 3$ K), resulting in the development of a quasielastic response that is indicative of fluctuational dynamics near $T \sim 0$ K. This pressure-induced fluctuational response — which we associate with slow fluctuations of the CuF$_6$ octahedra between discrete orientations — is temperature independent and exhibits a characteristic fluctuation rate that is much larger than the temperature, similar to the behavior observed in “quantum paraelectric” phases in SrTiO$_3$ and KNaO$_3$.[1] A model of pseudospin-phonon coupling [17] — where the pseudospin is identified with different CuF$_6$ octahedral rotational configurations — is qualitatively consistent with our results on KCuF$_3$ and shows that KCuF$_3$ can be systematically tuned with pressure and temperature between the characteristic “soft-phonon” and “diffusive mode” regimes predicted for strongly pseudospin-phonon coupled systems.[17]

Single crystal samples of KCuF$_3$ were grown by an aqueous solution precipitation method described previously.[18] Samples were characterized with magnetic susceptibility and X-ray diffraction measurements, and the results obtained are in good agreement with previous results.[6,7,19] Low temperature, pressure-dependent Raman scattering measurements — using liquid argon as the quasiisohydrostatic pressure medium — were performed using the 6471 Å line from a krypton laser and a SiC- or diamond-anvil cell that fits in a flow-through helium cryostat, allowing simultaneous in situ control of the sample temperature ($T > 3$ K) and pressure ($P < 100$ kbar).

Fig. 1 summarizes the temperature-dependence ($P = 0$) of some of the key phonon modes in KCuF$_3$,[20] showing evidence for a structural phase transition in KCuF$_3$ at $T = 50$ K. In particular, Figs. 1 (a) and (b) show that the $B_{1g}$-symmetry phonon near 72 cm$^{-1}$ exhibits a roughly 10-fold decrease in linewidth (FWHM) and a 20% decrease in energy (“softening”) with decreasing temperature (Fig. 1), consistent with previous evidence for thermally driven structural fluctuations that persist over a broad range of temperatures between $T_N (=40$ K) and 300 K.[11–14,16] Fig. 1(b) also shows that the $B_{1g}$ phonon frequency stabilizes at temperatures below $\sim 50$ K, concomitant with a splitting of the doubly degenerate 260 cm$^{-1}E_g$ mode into two singly degenerate modes at 260 cm$^{-1}$ and 265 cm$^{-1}$ (Figs 1 (c) and (d)); this result provides evidence that the thermally driven structural fluctuations in KCuF$_3$ are arrested by a tetragonal-orthorhombic structural distortion that locks the CuF$_6$ octahedral tilt orientations into a...
static, ‘glassy’ configuration at \( T = 50 \) K. [16]

Evidence that CuF\(_6\) octahedral fluctuations in KCuF\(_3\) extend down to very low temperatures (\( \sim 50 \) K) — and are interrupted only by a tetragonal-to-orthorhombic distortion — suggests that KCuF\(_3\) is close to a quantum critical point (QCP) at which the fluctuational regime extends down to \( T = 0 \) K. Hydrostatic pressure has been shown to reduce octahedral distortions in perovskite materials such as (La,Ba)\(_2\)CuO\(_4\), [21] Ca\(_2\)RuO\(_4\), [22] Ca\(_3\)Ru\(_2\)O\(_7\), [23] and LaMnO\(_3\); [24] therefore, pressure tuning offers a means of suppressing to \( T = 0 \) K the low-temperature tetragonal-to-orthorhombic distortion in KCuF\(_3\) that locks in CuF\(_6\) octahedral rotations below \( T = 50 \) K (and \( P = 0 \)). For this reason, we performed low-temperature, pressure-dependent Raman scattering measurements on KCuF\(_3\) in an effort to induce and study “quantum melting” between \( T \sim 0 \) static and fluctuational regimes in KCuF\(_3\).

Fig. 2 shows the pressure-dependent Raman spectra of KCuF\(_3\). The insets of Fig. 2 (a) and (b) show that the splitting of the \( \sim 260 \) cm\(^{-1}\) \( E_g \) phonon mode disappears above \( P^* \sim 7 \) kbar, revealing a pressure induced orthorhombic-to-tetragonal transition. Figs. 2 (a) and (b) also show that the pressure-induced structural transition near \( P^* \sim 7 \) kbar (at \( T = 3 \) K) is followed by the development with increasing pressure of a broad quasielastic response centered at \( \omega = 0 \); this quasielastic scattering response is indicative of fluctuational behavior at low temperatures and high pressures (\( P > 7 \) kbar) in KCuF\(_3\), and can be qualitatively described by a simple relaxation response function \( \chi''(\omega) \sim \frac{\omega \gamma}{(\omega_0^2 + \omega^2)^2} \) [25] which has a maximum value at the characteristic fluctuation rate \( \gamma \). Because the maximum value in the quasielastic scattering (i.e., \( \gamma \)) doesn’t change appreciably with
pressure (see Fig. 2(a)), the increasing quasielastic scattering with pressure in Fig. 2(b) is believed to primarily reflect an increase in the overall amplitude of the quasielastic scattering response, for example due to a systematic increase in the volume of fluctuating regions. Similar fluctuational responses — albeit with very different characteristic fluctuation rates — have been observed to result from slow relaxational structural fluctuations in SrTiO$_3$ [26], LaAlO$_3$ [27] and KMnF$_3$ [28]. In particular, a fluctuational (diffusive) neutron scattering response in isostructural KMnF$_3$ was also attributed to dynamic rotations of MnF$_6$ octahedra; these octahedral fluctuations were shown to be highly correlated — via the shared F ion — within the planes, but were shown to fluctuate in an uncorrelated fashion between adjacent planes. [28] Additionally, previous x-ray diffraction studies of KCuF$_3$ [16] show that in-plane correlations between CuF$_6$ octahedra extend no further than ~ 100 unit cells. Consequently, the fluctuational response we observe could involve interplane octahedral fluctuations and/or in-plane fluctuations between correlated regions of order ~ 1000 Å. Pressure-dependent x-ray diffraction measurements are needed to distinguish between these possibilities.

Significantly, all the key spectroscopic features of our temperature- and pressure-dependent Raman results on KCuF$_3$ — which are summarized in Fig. 3 — can be qualitatively described by a coupled pseudospin-phonon model [17] in which the normal mode vibrations of a phonon are associated with a molecular group (i.e., the CuF$_6$ octahedra in KCuF$_3$) that fluctuates between discrete configurations and whose dynamics can be described using a pseudospin representation. This coupled pseudospin-phonon model provides a qualitative description of how fluctuations in CuF$_6$ octahedral orientation influence phonon modes (e.g., the $E_g$ and $B_{1g}$ phonons) associated with the fluorine ions in KCuF$_3$. [29] The Hamiltonian for the coupled pseudospin-phonon model is given by, [17]

$$H = \frac{1}{2} \sum_k \left\{ P(k) P^*(k) + \omega^2_o(k) Q(k) Q^*(k) \right\} - \frac{1}{2} \sum_{i,j} J_{ij} \sigma_i \sigma_j + \sum_{k,j} \frac{\omega_0(k)}{\sqrt{N}} g(k) Q(k) \sigma_j e^{ik \cdot r_j},$$

where $Q$ is the normal coordinate of the phonon, $P$ is the conjugate coordinate of $Q$, $\sigma_i$ is the pseudospin, $J_{ij}$ is the pair interaction between the $i$th and $j$th pseudospins, $g$ is the pseudospin-phonon coupling constant, and $\omega_o$ is the bare phonon frequency. The identification of the pseudospin with discrete CuF$_6$ octahedral configurations is supported by x-ray diffraction results on KCuF$_3$ showing that discrete CuF$_6$ octahedral orientations lock into a glassy configuration below the structural phase transition.[16] The coupled phonon response function associated with this Hamiltonian is:[17]

$$\Phi = \frac{2 \gamma k_B T \left( \frac{\sigma}{\Gamma} \right)^2}{[\omega^2 - \omega^2_o]^2 + \omega^2 \Gamma^2}$$  \hspace{1cm} (1)

where $\gamma$ is the pseudospin (CuF$_6$ octahedral orientation) fluctuation rate, $J' = k_B T - J$ is the renormalized exchange coupling, $\omega_o \left\{ = \omega_o \left[ 1 - (g^2/J') \right]^{1/2} \right\}$ is the renormalized phonon frequency, and $\Gamma_1 \left\{ = (\omega^2 - \omega^2_o) / \gamma J' \right\}$ is the phonon damping parameter.

The coupled pseudospin-phonon model predicts two regimes of behavior that are qualitatively consistent with the observed pressure- and temperature-dependent Raman results observed in KCuF$_3$:

"Soft phonon" regime, $\gamma \gg \omega_o$ — When the fluctuation rate ($\gamma$) of the pseudospin (CuF$_6$ octahedral orientation) is much faster than the phonon frequency ($\omega_o$), i.e., for $\gamma \gg \omega_o$, this model predicts phonon mode softening as the temperature decreases towards the structural phase transition ($T \to T_c$).[17] As illustrated in the inset

![FIG. 3. PT phase diagram for the CuF$_6$ octahedral fluctuations in KCuF$_3$. Horizontal axes represent the temperature and pressure. The contour plot on the horizontal plane represents the measured fluctuational response integrated intensity, with dark green = 2000 counts and white = 0 counts, based on temperature sweeps at the following pressures: $P = 0, 5, 13, 18.7, 27, 35, 42$ kbar. The vertical axis shows the mode frequency, with both the $\sim 79$ cm$^{-1}$ $B_{1g}$ and $\sim 261$ cm$^{-1}$ $E_g$ phonon frequencies shown as functions of temperature (filled red and green circles, respectively) and pressure (open red and green circles, respectively). Filled squares illustrate the characteristic energy $\Gamma$ of the fluctuational response. Diagrams on top depict (left) thermally activated hopping between CuF$_6$ configurations in the fast-fluctuating regime of KCuF$_3$, and (right) the quantum tunneling between CuF$_6$ configurations in the pressure-tuned slow fluctuating regime.]

of Fig. 1(b) for the case $\gamma = 10\omega_0$. This model prediction is qualitatively consistent with the temperature-dependent mode softening observed for the 50 cm$^{-1} E_g$ (not shown, see [16]) and 72 cm$^{-1} B_{1g}$ (see Figs. 1(a) and (b)) rotational F$^-$ phonon modes in KCuF$_3$, supporting the conclusion [12, 16] that there is a thermally driven fluctuational regime in KCuF$_3$ in which thermal fluctuations of the CuF$_6$ octahedra occur on a faster timescale than the $E_g$ and $B_{1g}$ phonon frequencies to which they are coupled.

"Diffusive mode" regime, $\gamma \leq \omega_0$ — By contrast, when the fluctuation rate ($\gamma$) of the pseudospin (CuF$_6$ octahedral orientation) is comparable to or slower than the phonon frequency ($\omega_0$), the coupled pseudospin-phonon model (Eq. 1) [17] predicts a “diffusive mode” regime, i.e., the development of a $\omega = 0$ fluctuational response (squares, Fig. 2(c)), and reduced phonon softening (filled circles, Fig. 2(c)). This prediction matches the observed pressure-induced quasielastic response (Fig. 2(a)) and pressure-independent $B_{1g}$ mode frequency (Fig. 2(a) and open green circles, Fig. 3) observed in KCuF$_3$. Thus, the pressure-dependent development of a quasielastic fluctuational response at low temperatures in KCuF$_3$ is consistent with the onset of slow fluctuations (compared to phonon frequencies) of the CuF$_6$ octahedra, which result when the pressure-induced octahedral-to-tetragonal distortion “unlocks” the glassy arrangement of CuF$_6$ octahedral tilts.

The pressure results presented here offer evidence for a pressure-tuned “quantum melting” transition near $T \sim 0$ in KCuF$_3$ between a static configuration of the CuF$_6$ octahedra to a phase in which the CuF$_6$ octahedra are slowly fluctuating on a timescale that is comparable to or slower than the $E_g$ and $B_{1g}$ phonon frequencies. Because the characteristic rate associated with these CuF$_6$ fluctuations, $\gamma \sim 80$ cm$^{-1}$ (10 meV), is temperature independent and more than an order-of-magnitude larger than the thermal energies, $\gamma \sim 40k_BT$ (arrow in Fig. 2(a)), we propose that these low temperature, pressure-induced fluctuations are primarily driven by zero-point fluctuations (i.e., quantum tunneling) between different wells in the free energy landscape (top right diagram in Fig. 3). This interpretation suggests that the pressure-induced “quantum melting” transition in KCuF$_3$ is similar to the “rotational melting” transitions [1] to quantum paraelectric phases in SrTiO$_3$ and KTaO$_3$ at low temperatures,[31] and in KH$_2$PO$_4$ (KDP) at high pressures.[32]

One outstanding issue concerns the role these octahedral fluctuations play in disrupting magnetic order in KCuF$_3$. A connection between quantum structural (octahedral) fluctuations and the spin and/or orbital degree of freedom might indicate that a pressure-induced orbital/spin liquid state accompanies quantum fluctuations of the octahedral orientations in KCuF$_3$. To study this important issue, pressure dependent magnetic measurements are needed to test whether the pressure-tuned onset of octahedral fluctuations is coupled with a suppression of Néel order. Uniaxial pressure measurements would also provide an interesting comparison to these hydrostatic pressure studies,[1] by stabilizing the lower symmetry, static configuration of KCuF$_3$ and thereby favoring the onset of magnetic/orbital order.

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[25] The simple relaxational response function assumes a frequency-independent relaxational response between two discrete levels. Neither of these assumptions likely applied to the fluctuational response in KCuF$_3$, and therefore detailed fits of this response to the observed
data would not provide useful information. While we can’t completely rule out the possibility that the response observed in KCuF$_3$ is associated with a standard inelastic Lorentzian response, such a response would imply a strongly overdamped ($\gamma \gg \omega_0$) response, and hence the presence of strong fluctuations of the CuF$_6$ octahedra in this pressure and temperature regime. Note also that the thermal Bose factor $(1+n(\omega)) \sim 1$ over the temperature and frequency range studied in this paper, so there is a negligible Bose factor contribution in the Raman spectra presented in Figs. 1 and 2.


[29] Indeed, neutron scattering studies of isostructural KMnF$_3$ show that the diffuse neutron scattering associated with fluctuations of the MnF$_6$ octahedra are connected with mode softening observed for rotational F modes; see ref. 28.

