Inelastic Light Scattering Measurements of a Pressure-Induced Quantum Liquid in KCuF_{3}

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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 materals 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 ($J_c/J_a \sim -100$) [5] that results in 1D antiferromagnetic Heisenberg spin dynamics above 40 K,[6–8] and a large disparity between the orbital ordering temperature ($T_{oo} \sim 800$ 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 quasihydrostatic pressure medium — were performed using the 6471 $\mathring{A}$ 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 $KCuF_3$,[16,20] 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 ~ 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

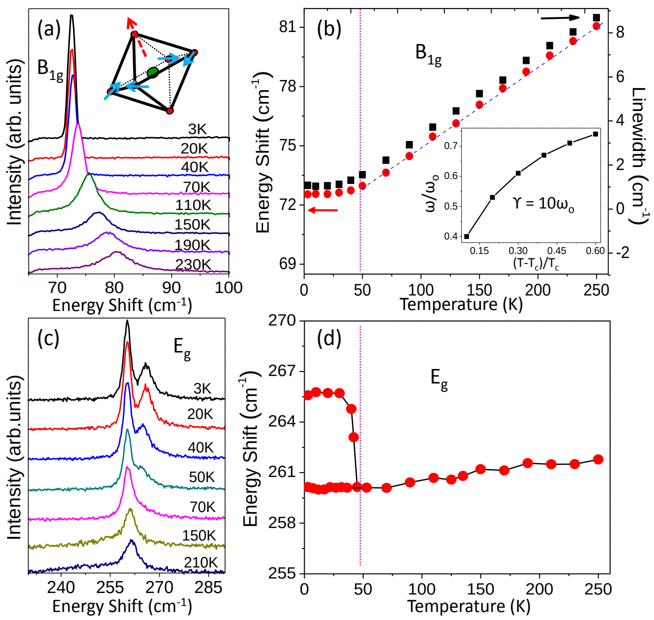

FIG. 1. (a) Temperature dependence of the B_{1g} symmetry phonon mode in $KCuF_3$. All spectra have the same y-axis scale and have been offset in the y-axis direction for clarity. Inset shows B_{1g} phonon normal mode vibration of F^- ions (blue arrows), and dashed red arrow depicts octahedral orientation (pseudospin). (b) Summary of the temperature dependence of the peak energy (circles) and linewidth (squares) of the B_{1g} phonon mode. The inset shows the calculated temperature dependence of the normalized peak frequencies, ω/ω_o, using Eq. 1 for the case $\gamma = 10\omega_o$, from [17]. (c) Temperature dependence of the E_g symmetry phonon mode in $KCuF_3$. All spectra have the same y-axis scale and have been offset in the y-axis direction for clarity. (d) Summary of the temperature dependence of the peak energy of the E_g phonon mode, showing a splitting of the mode at the tetragonal-to-orthorhombic structural transition at $T = 50$ K.

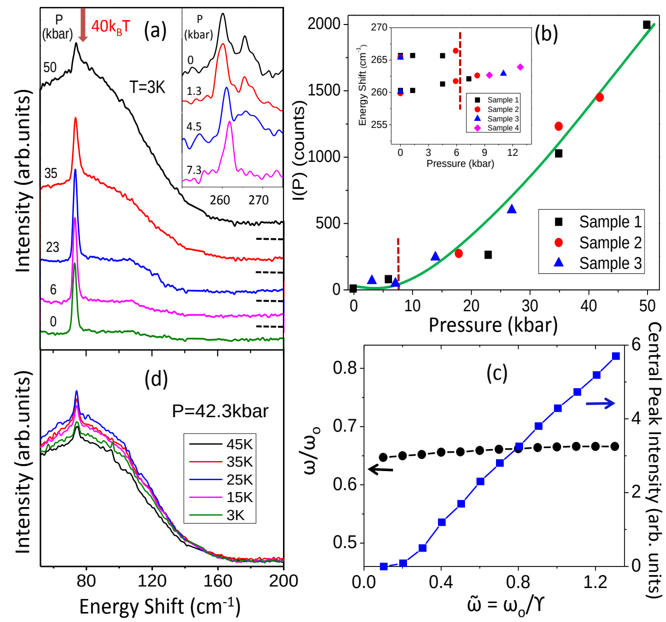

FIG. 2. (a) Pressure dependence of Raman spectra of $KCuF_3$ at $T = 3$ K. The arrow indicates a frequency corresponding to 40 k_BT. All spectra have the same y-axis scale and have been offset in the y-axis direction for clarity. Dashed lines indicate the common baseline for all the spectra. The inset illustrates the pressure dependence of the E_g phonon mode at $T = 3$ K. (b) Pressure dependence of the integrated quasielastic scattering response intensity, $I(P)$, at $T = 3$ K for three different samples of $KCuF_3$. The inset shows the pressure dependence of the peak energies of the E_g phonon mode at 3 K for four different samples, showing evidence for an orthorhombic-to-tetragonal transition near $P^* = 7$ kbar. (c) Calculated normalized phonon frequency, ω/ω_o, (black circles) and quasielastic scattering response integrated intensity (blue squares) as a function of ω_o/γ, using Eq. 1 from [17]. (d) Temperature dependence of quasielastic scattering response of $KCuF_3$ at $P = 42.3$ kbar. All spectra have the same y-axis scale and all spectra have been shifted by the same amount in the -y direction to emphasize the quasielastic contribution to the spectra. The low energy (55 cm^{-1}) cutoff in Figs. (a) and (d) reflects the low energy limit of the spectral window defined by our spectrometer.

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 $(La,Ba)_2CuO_4$,[21] Ca_2RuO_4,[22] $Ca_3Ru_2O_7$,[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 ω=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 relaxational response function $\chi''(\omega) \sim \frac{\omega\gamma}{\omega^2+\gamma^2}$,[25] which has a maximum value at the characteristic fluctuation rate γ. Because the maximum value in the quasielastic scattering (i.e., γ) 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 ions — 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]

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

where Q is the normal coordinate of the phonon, P is the conjugate coordinate of Q, σ_i is the pseudospin, J_{ij} is the pair interaction between the ith and jth pseudospins, g is the pseudospin-phonon coupling constant, and ω_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]

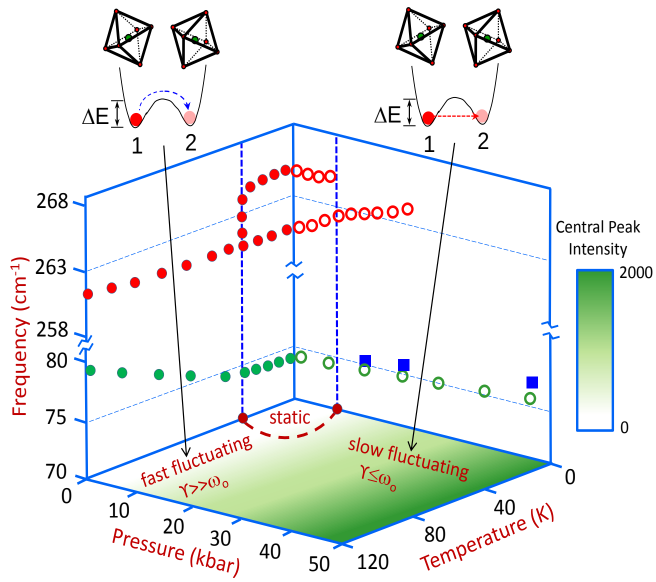

FIG. 3. PT phase diagram for the CuF_6 octahedral fluctuations in $KCuF_3$. Horizontal axes represent the temperature and pressure. The contour plot on the horizontal plane represents the measured fluctuational response integrated intensity, with dark green = 2000 counts and white = 0 counts, based on 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 ~ 79 cm^{-1} B_{1g} and ~ 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 Γ 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.

$$\Phi = \frac{2\gamma k_B T\left(\frac{g}{\gamma J'}\right)^2}{\left[\omega^2 - \overline{\omega}_o^2\right]^2 + \omega^2\Gamma_1^2} \tag{1}$$

where γ is the pseudospin (CuF_6 octahedral orientation) fluctuation rate, $J' = k_B T - J$ is the renormalized exchange coupling, $\overline{\omega}_o \left\{= \omega_o\left[1 - \left(g^2/J'\right)\right]^{1/2}\right\}$ is the renormalized phonon frequency, and $\Gamma_1\left\{= \left(\omega^2 - \omega_o^2\right)/\gamma J'\right\}$ 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 (γ) of the pseudospin (CuF_6 octahedral orientation) is much faster than the phonon frequency (ω_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

of Fig. 1(b) for the case $\gamma = 10\omega_o$. 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, $\gamma \leq \omega_o$ — By contrast, when the fluctuation rate (γ) of the pseudospin (CuF_6 octahedral orientation) is comparable to or slower than the phonon frequency (ω_o), 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_2PO_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 ($\gamma \gg \omega_o$) 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.

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