Inelastic Light Scattering Measurements of a Pressure-Induced Quantum Liquid in $\mathrm{KCuF_3}$

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Pressure-dependent, low-temperature inelastic light (Raman) scattering measurements of $\mathrm{KCuF_3}$ show that applied pressure above $P^* \sim 7$ kbar suppresses a previously observed structural phase transition temperature to zero temperature in $\mathrm{KCuF_3}$, resulting in the development of a fluctuational (quasielastic) response near $T \sim 0$ K. This pressure-induced fluctuational response—which we associate with slow fluctuations of the $\mathrm{CuF_6}$ octahedral orientation—is temperature independent and exhibits a characteristic fluctuation rate that is much larger than the temperature, consistent with quantum fluctuations of the $\mathrm{CuF_6}$ octahedra. A model of pseudospin-phonon coupling provides a qualitative description of both the temperature- and pressure-dependent evolution of the Raman spectra of $\mathrm{KCuF_3}$.

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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 Letter, we report the first spectroscopic evidence for a pressure-tuned quantum melting transition in $\mathrm{KCuF_3}$ from 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 $\mathrm{KCuF_3}$ 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 ($T_{\mathrm{oo}} \sim 800$ 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 $\mathrm{KCuF_3}$ 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 $\mathrm{CuF_6}$ 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 $\mathrm{SrTiO_3}$ and $\mathrm{KNaO_3}$ [1]. A model of pseudospin-phonon coupling [17]—where the pseudospin represents distinct $\mathrm{CuF_6}$ octahedral orientations—is qualitatively consistent with our results on $\mathrm{KCuF_3}$ and shows that $\mathrm{KCuF_3}$ 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 $\mathrm{KCuF_3}$ 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 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).

Figure 1 summarizes the temperature dependence ($P = 0$) of some of the key phonon modes in $\mathrm{KCuF_3}$ [16,20], showing evidence for a structural phase transition in $\mathrm{KCuF_3}$ at $T = 50$ K. In particular, Figs. 1(a) and 1(b) show that the B_{1g}-symmetry phonon near 72 $\mathrm{cm^{-1}}$ exhibits a roughly tenfold 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]. Figure 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 $\mathrm{cm^{-1}}$ E_g mode into two singly degenerate modes at 260 and 265 $\mathrm{cm^{-1}}$ [Figs. 1(c) and 1(d)]; this result provides evidence that the thermally driven structural fluctuations in $\mathrm{KCuF_3}$ are arrested by a tetragonal-orthorhombic structural distortion that locks the $\mathrm{CuF_6}$ octahedral tilt orientations into a static, "glassy" configuration at $T = 50$ K [16].

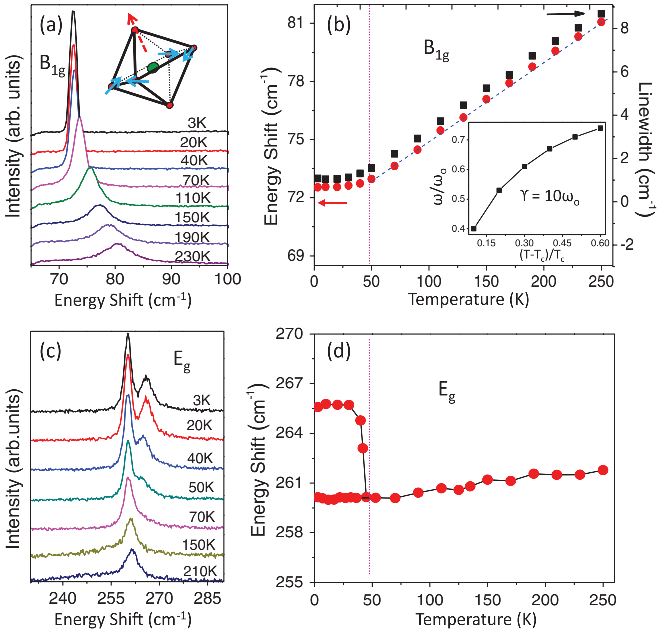

FIG. 1 (color). (a) Temperature dependence of the B_{1g}-symmetry phonon mode in $KCuF_3$. All spectra have the same y-axis scale and have been offset in the y-axis direction for clarity. Inset shows B_{1g} phonon normal mode vibration of F^- ions (blue arrows), and dashed red arrow depicts octahedral 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_0, using Eq. (1) for the case $\gamma = 10\omega_0$, from Ref. [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.

Evidence that CuF_6 octahedral fluctuations in $KCuF_3$ extend down to very low temperatures (~ 50 K)—and are interrupted only by a tetragonal-to-orthorhombic distortion—suggests that $KCuF_3$ is close to a quantum critical point 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 $KCuF_3$.

Figure 2 shows the pressure-dependent Raman spectra of $KCuF_3$. The insets of Figs. 2(a) and 2(b) show that the splitting of the ~ 260 cm^{-1} E_g phonon mode disappears

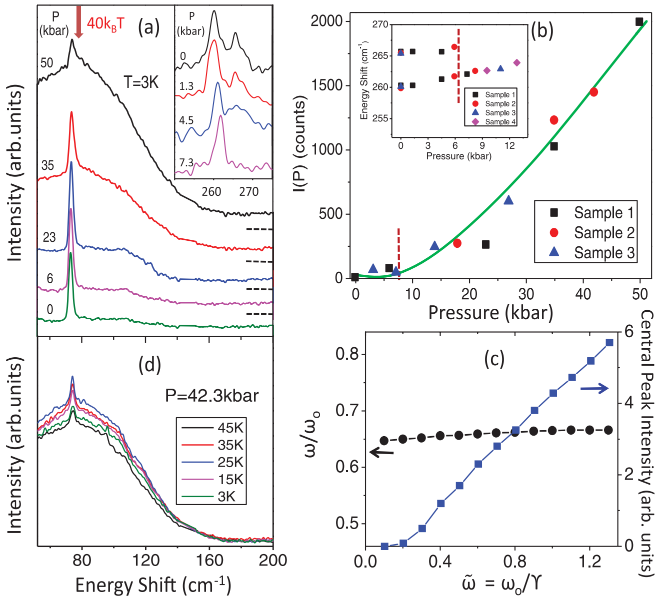

FIG. 2 (color). (a) Pressure dependence of Raman spectra of $KCuF_3$ at $T = 3$ K. The arrow indicates a frequency corresponding to $40k_BT$. All spectra have the same y-axis scale and have been offset in the y-axis direction for clarity. Dashed lines indicate the common baseline for all the spectra. 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_0 (black circles) and quasielastic scattering response integrated intensity (blue squares) as a function of ω_0/γ, using Eq. (1) from Ref. [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 (a) and (d) reflects the low energy limit of the spectral window defined by our spectrometer.

above $P^* \sim 7$ kbar, revealing a pressure-induced orthorhombic-to-tetragonal transition. Figures 2(a) and 2(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 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) does not 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, likely indicating 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 of 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]

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

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_0 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 the CuF_6 octahedra lock into a finite number of distinct orientational configurations below the structural phase transition [16]. The coupled phonon response function associated with this Hamiltonian is [17]

$$\Phi = \frac{2\gamma k_B T(\frac{g}{\gamma J'})^2}{[\omega^2 - \bar{\omega}_0^2]^2 + \omega^2\Gamma_1^2}. \qquad (1)$$

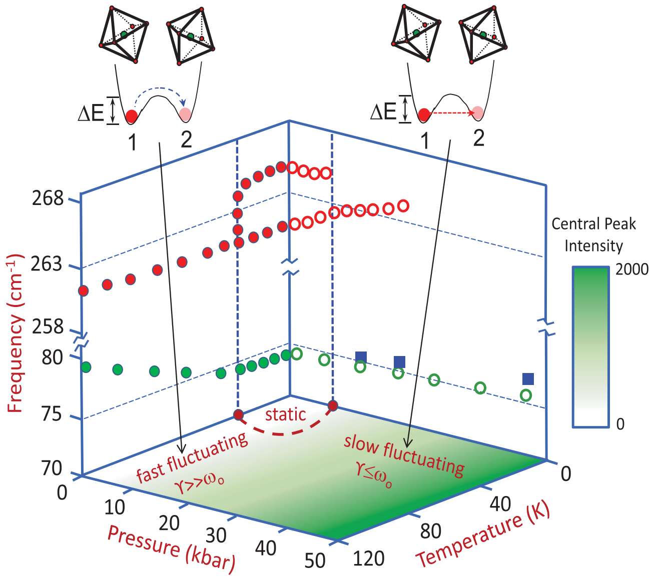

FIG. 3 (color). PT phase diagram for the CuF_6 octahedral fluctuations in $KCuF_3$. Horizontal axes represent the temperature and pressure. The contour plot on the horizontal plane represents the measured fluctuational response integrated intensity, with dark green = 2000 counts and white = 0 counts, 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.

where γ is the pseudospin (CuF_6 octahedral orientation) fluctuation rate, $J' = k_B T - J$ is the renormalized exchange coupling, $\bar{\omega}_0\{= \omega_0[1 - (g^2/J')]^{1/2}\}$ is the renormalized phonon frequency, and $\Gamma_1\{= (\omega^2 - \omega_0^2)/\gamma J'\}$ 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_0), i.e., for $\gamma \gg \omega_0$, this model predicts phonon mode softening as the temperature decreases towards the structural phase transition ($T \longrightarrow T_c$) [17], as illustrated in the inset 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 Ref. [16]) and 72 cm^{-1} B_{1g} [see Figs. 1(a) and 1(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 time scale 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 (γ) of the pseudospin (CuF_6 octahedral orientation) is comparable to or slower than the phonon frequency (ω_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 in 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 frozen arrangement of CuF_6 octahedral tilts.

The pressure results presented here offer evidence for a pressure-tuned quantum melting transition near $T \sim 0$ K in $KCuF_3$ from a static configuration of the CuF_6 octahedra to a phase in which the CuF_6 octahedra are slowly fluctuating on a time scale 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, $\gamma \sim 80\ \mathrm{cm}^{-1}$ (10 meV), is temperature independent [30] 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 to quantum paraelectric phases in $SrTiO_3$ [1,31] and $KTaO_3$ [1] at low temperatures, and in KH_2PO_4 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 or 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 or 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 cannot 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 Letter, so there is a negligible Bose factor contribution in the Raman spectra presented in Figs. 1 and 2.

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