Thermal and quantum fluctuations and the disruption of orbital/magnetic order in $KCuF_3$

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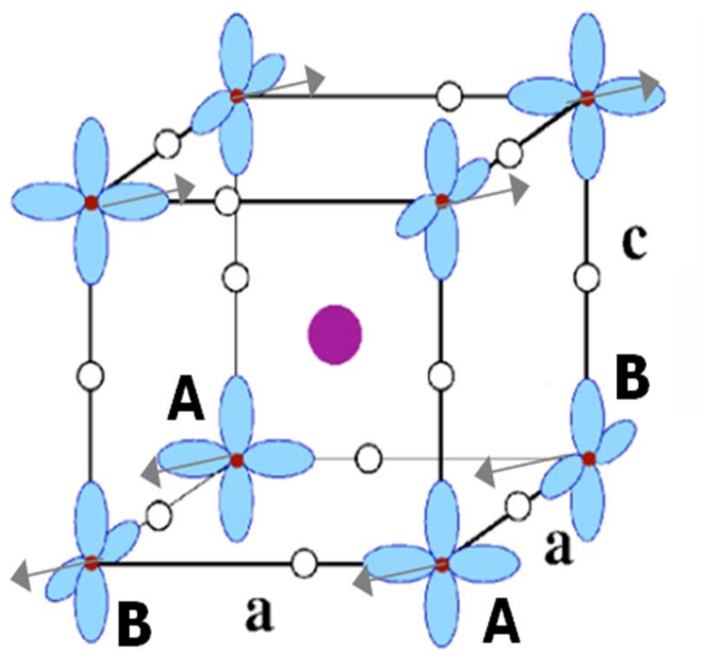


Support: Dept. of Energy, Division of Materials Sciences, Grant DEFG02-07ER46453

Collaborators:

Growth, characterization, and Raman studies of $KCuF_3$

Shi Yuan (UIUC)

X-ray studies of $KCuF_3$

James Lee (UIUC)

Peter Abbamonte (UIUC)

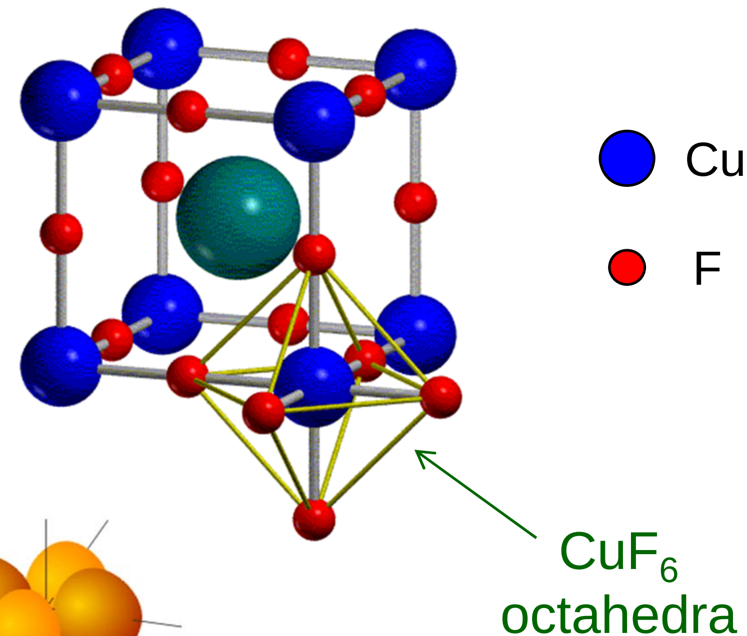
Paul Goldbart (UIUC)

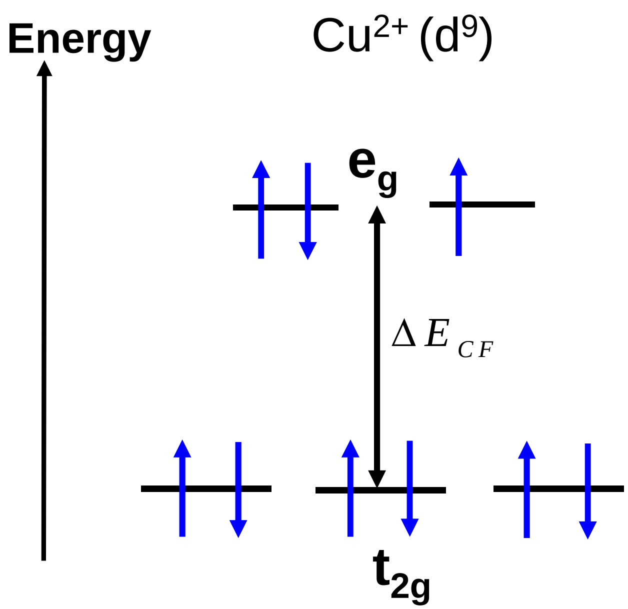
Siddhartha Lal (UIUC)

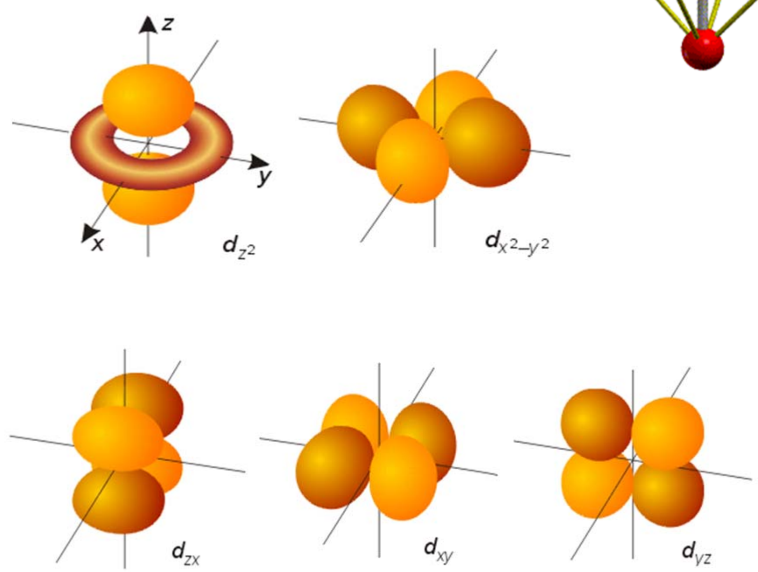
Standard View: $KCuF_3$ is a relatively simple 'model' spin-1/2 orbital-ordering material

- Simple perovskite structure with one hole in the d-band:

$$t_{2g}^{\;6} e_g^{\;3}$$

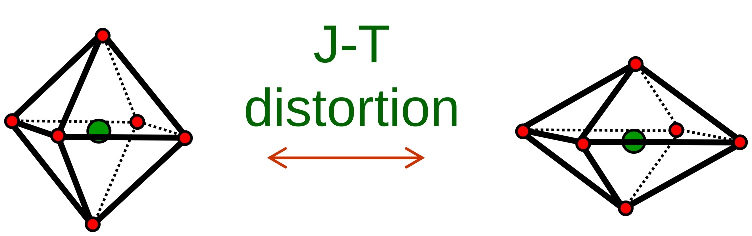


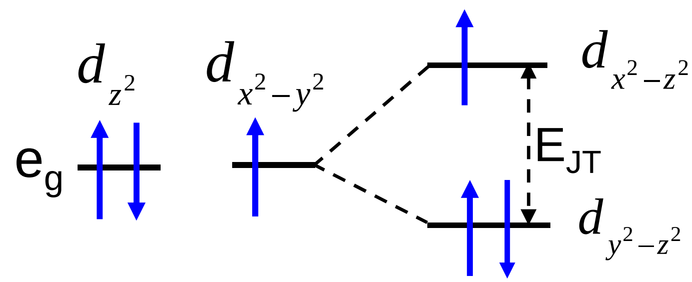




Orbital order in $KCuF_3$:
Kugel-Khomskii (KK) orbital order*

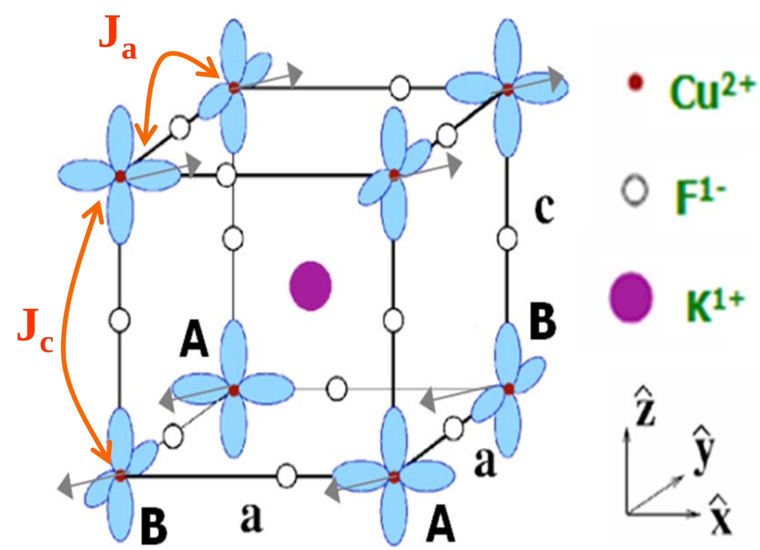
*Kugel, Khomskii, Sov. Phys. Usp. 25 (1982)





Standard KK view of $KCuF_3$:

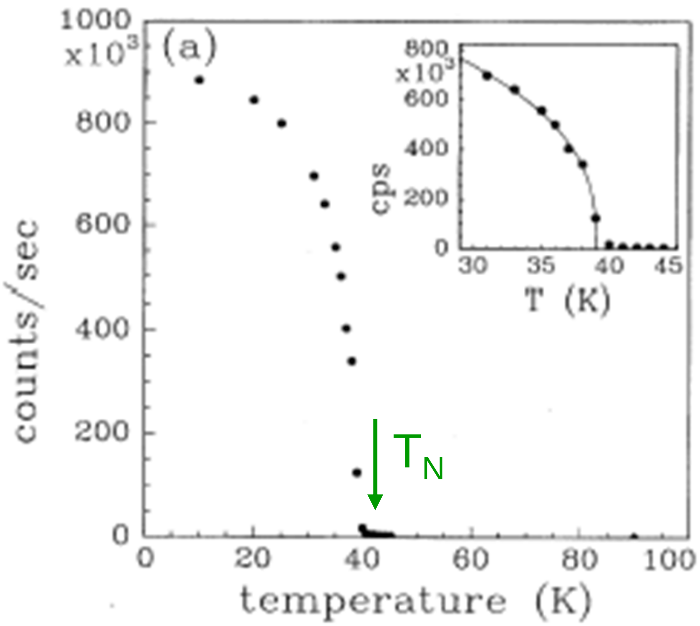
- cubic-to-tetragonal "orbital-ordering" transition at T_{oo} ~ 800 K

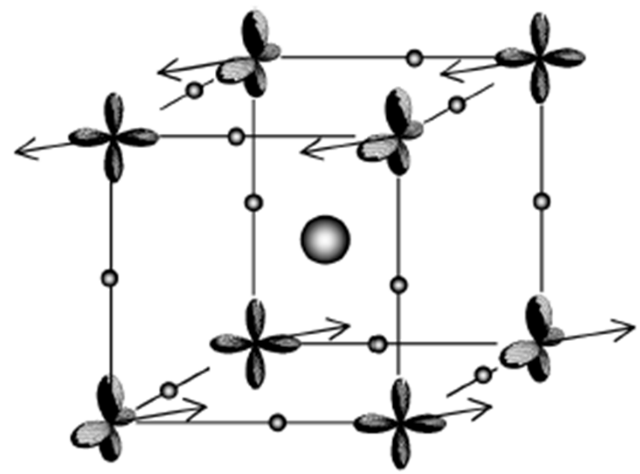


Binggeli, PRB, **70**, 085117 (2004)

Problems with the standard view of $KCuF_3$: Suppressed magnetic ordering temperature

Tennant et al. PRB (1995)





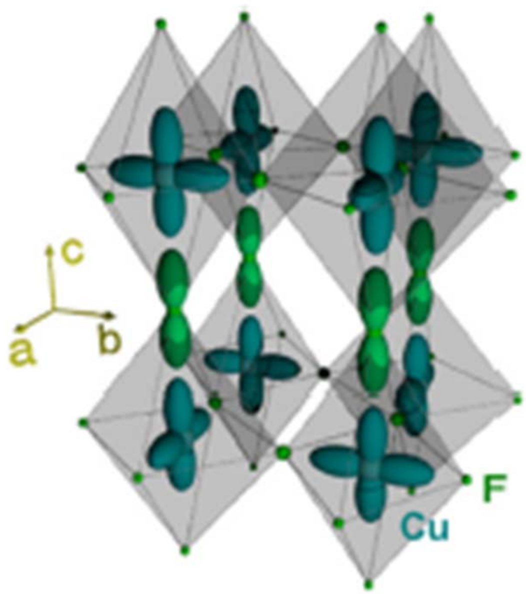
A-type antiferromagnetic order

T_N = 40 K ~ (1/20)T_{oo}

⇒ Suppressed antiferromagnetic ordering temperature suggests magnetic frustration

Problems with the standard view of $KCuF_3$: Unexplained superexchange anisotropy

J_{ab} ~ 2 K



J_c ~ 200 K

- large superexchange anisotropy, $|J_c|/J_a$~100

  ⇒ 1D antiferromagnetic chains

J_c ~ 100 J_{ab} ! (Satija et al. PRB (1980))

Neutron scattering: spin fluctuations in $KCuF_3$ exhibit 1D quantum critical scaling down to T_N!

Quantum criticality and universal scaling of a quantum antiferromagnet

BELLA LAKE[1,2*†], D. ALAN TENNANT[2,3‡], CHRIS D. FROST[3] AND STEPHEN E. NAGLER[1]
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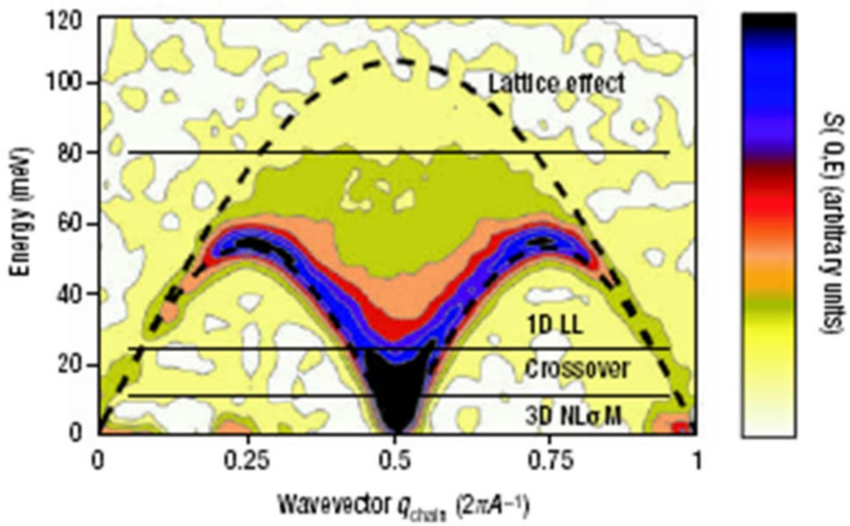
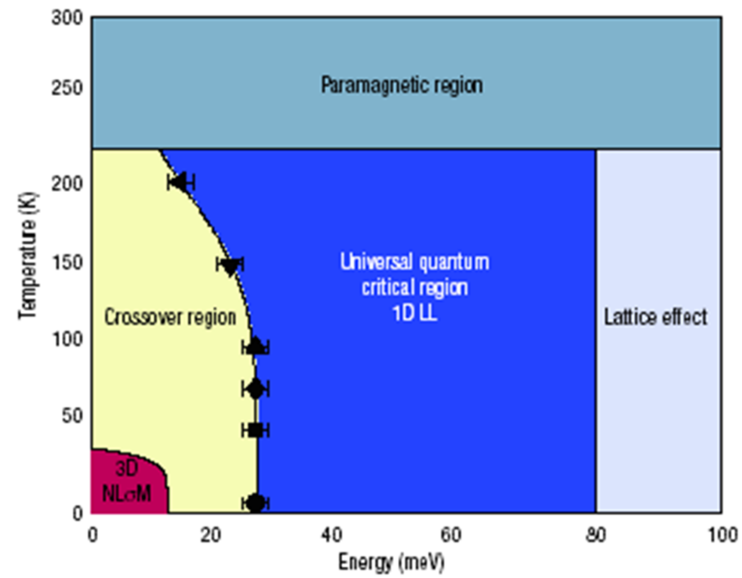
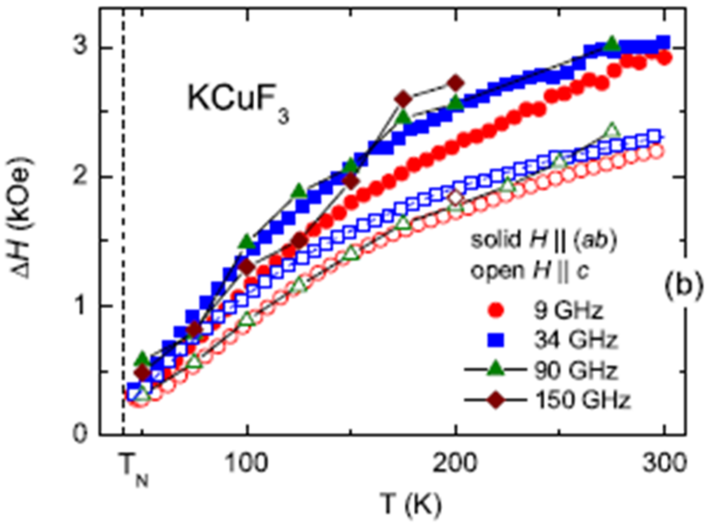
Nature Materials (2005)





Problems with the standard view of $KCuF_3$: Unexplained structural anomalies

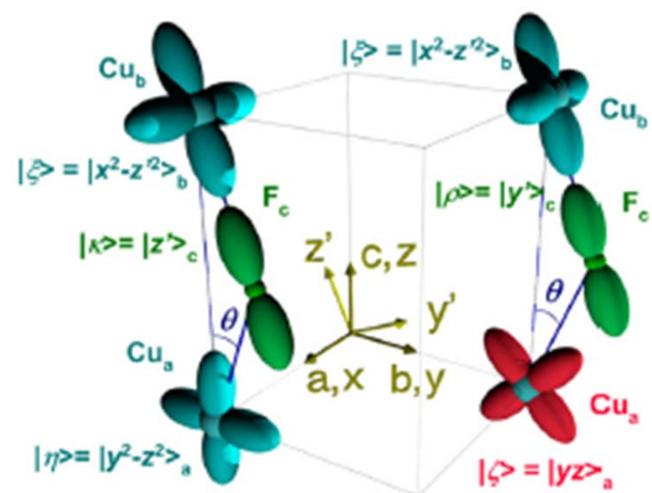
(Eremin et al. PRL (2008))



- Crystallography indicates $KCuF_3$ has a tetragonal structure

  ⇒ But, other measurements (e.g., anomalous electron spin resonance (ESR) linewidth) indicate a static Dzyaloshinsky-Moriya (DM) vector consistent with orthorhombic symmetry

Suggests dynamical fluctuations of orthorhombic domains, but nature of fluctuations is unknown!

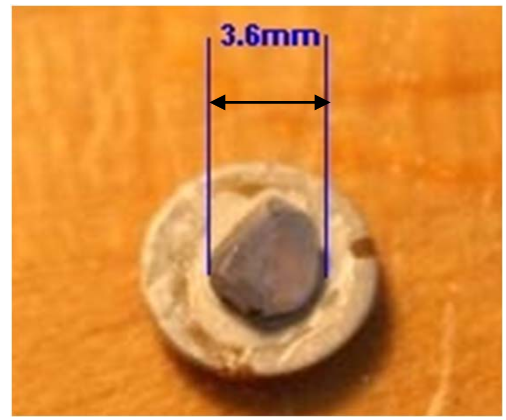


To explore these puzzles, we grew $KCuF_3$ single crystals for Raman and X-ray studies

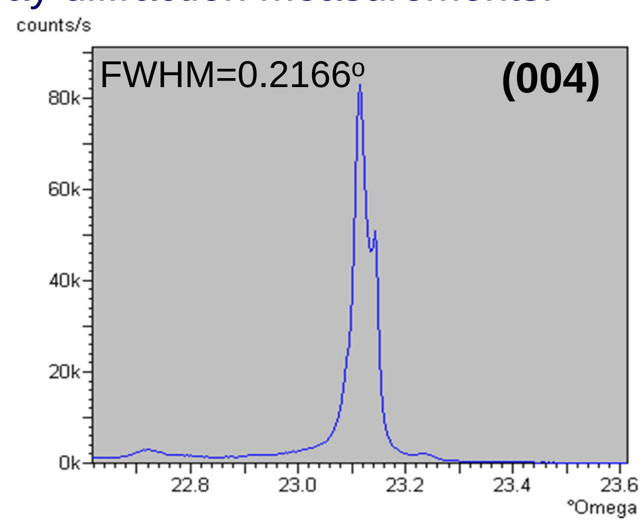
Shi Yuan **(UIUC)**

- aqueous solution precipitation method

- large ($4 \times 4 \times 4$ mm^3) single crystals

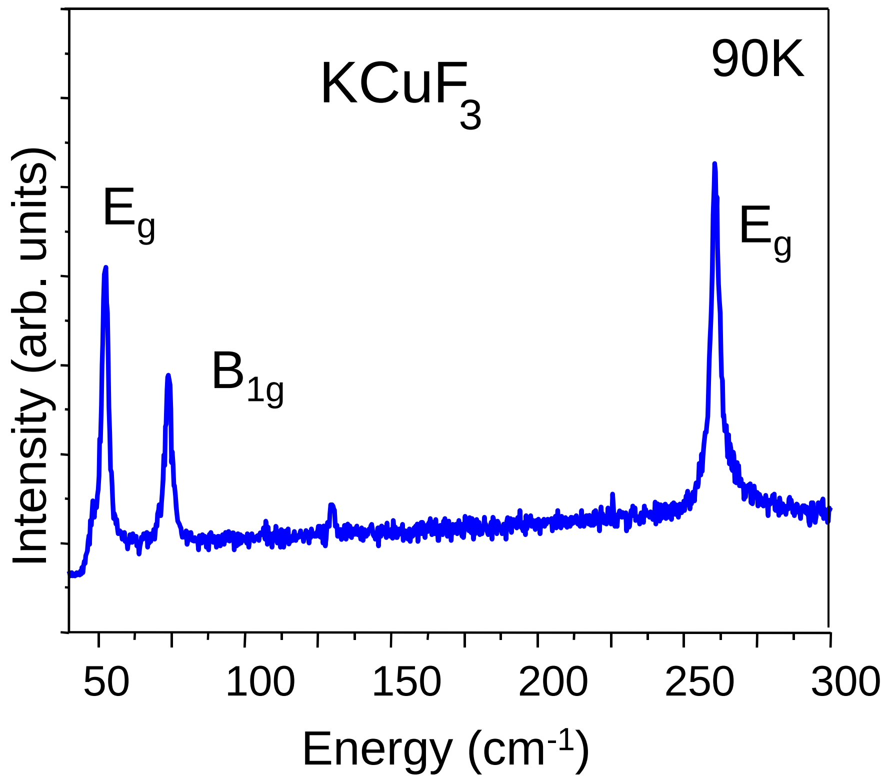


x-ray diffraction measurements:



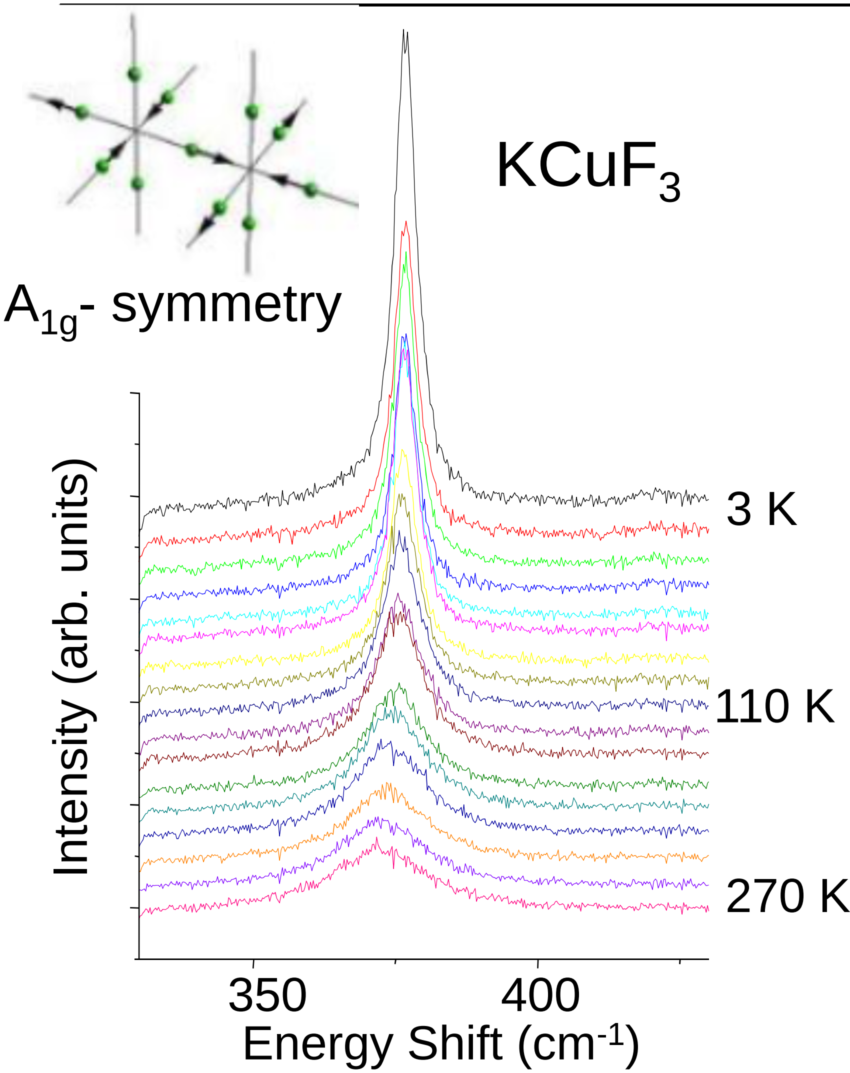
- The value of in-plane lattice parameter, *a*=*b*=8.25Å, is consistent with reference value

Inelastic light (Raman) scattering phonon spectrum of $KCuF_3$

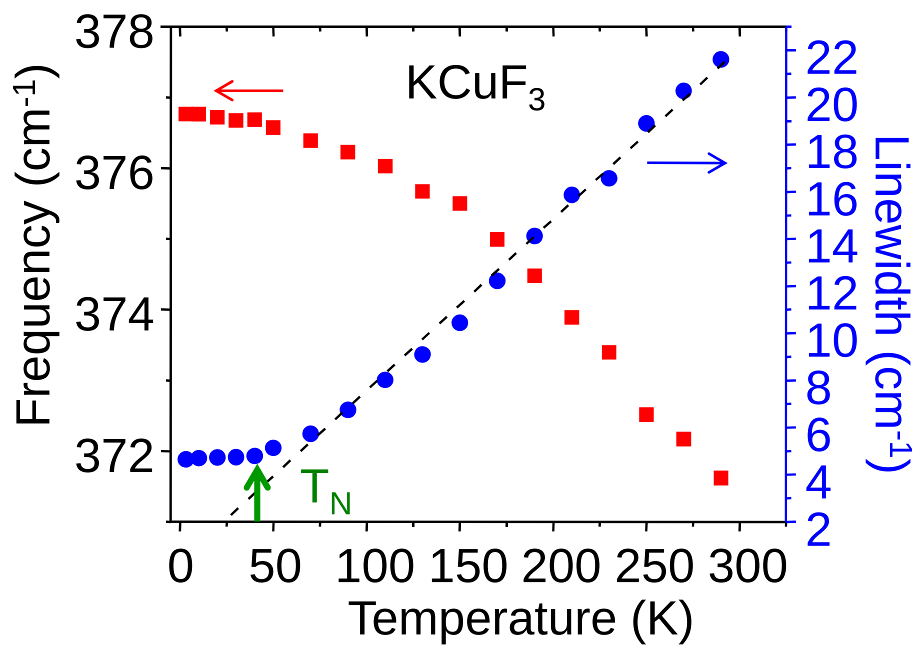


- Raman spectrum of phonons similar to that observed at low temperatures in previous studies

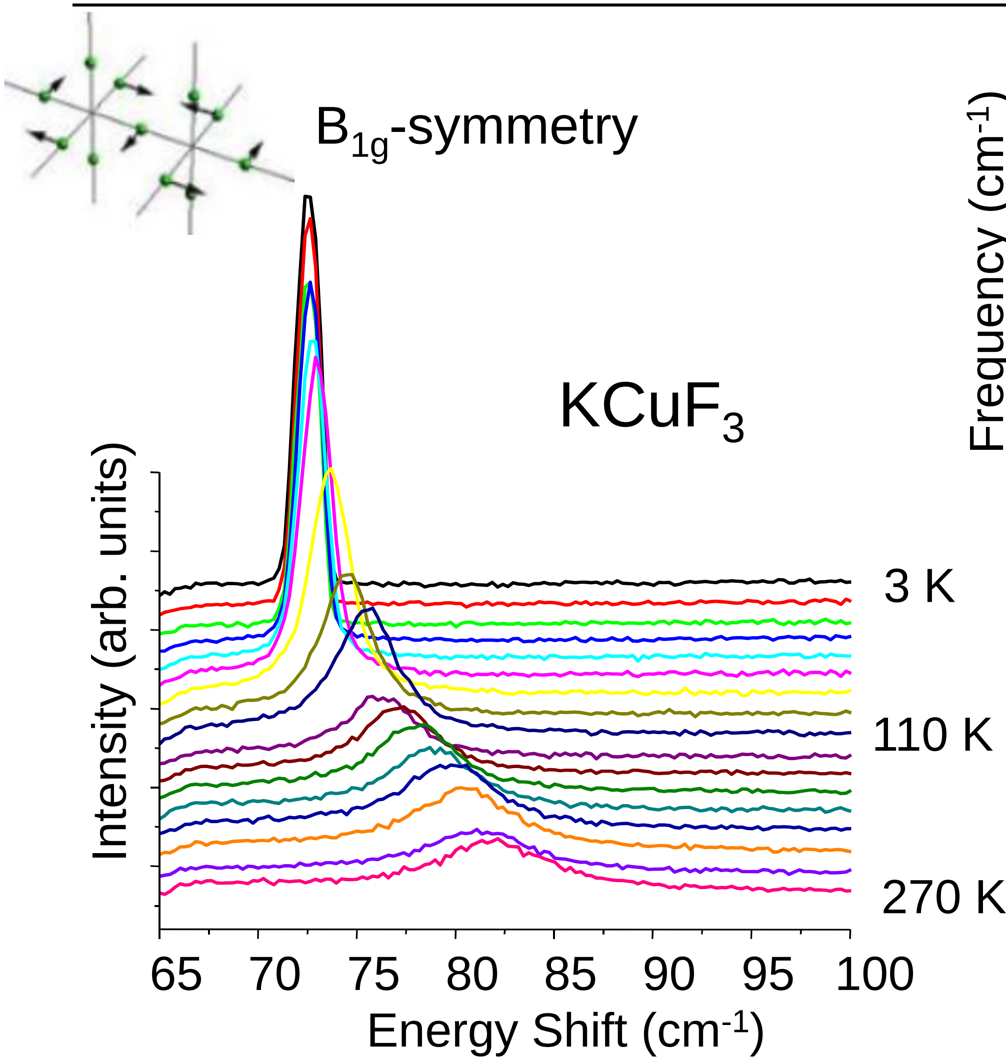
The 370 cm^{-1} A_{1g} phonon in $KCuF_3$ exhibits a conventional temperature dependence

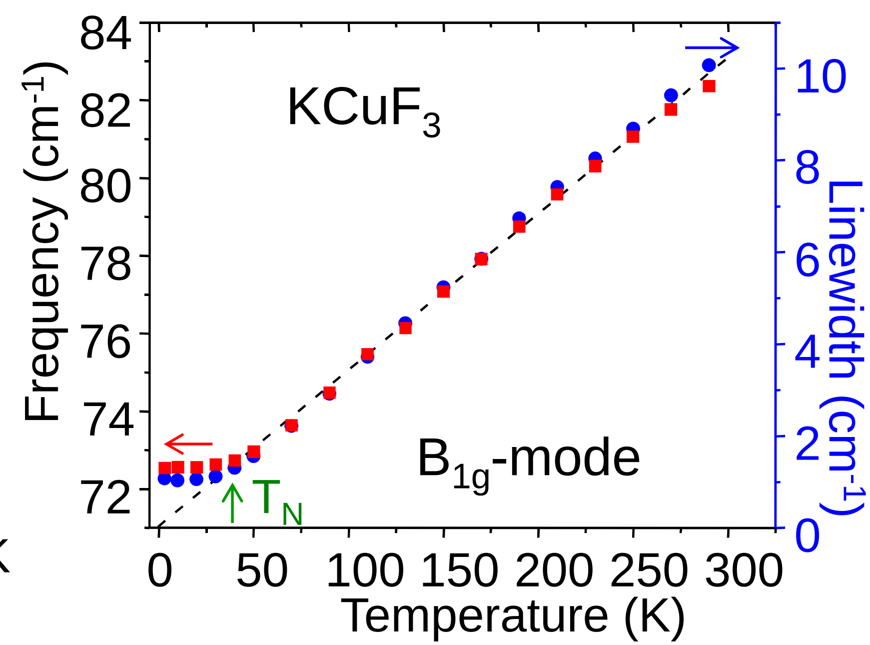


- Temperature-dependence of A_{1g} mode frequency typical of that expected from anharmonic effects



The 72 cm^{-1} B_{1g} phonon in $KCuF_3$ exhibits 'mode softening' with decreasing temperature

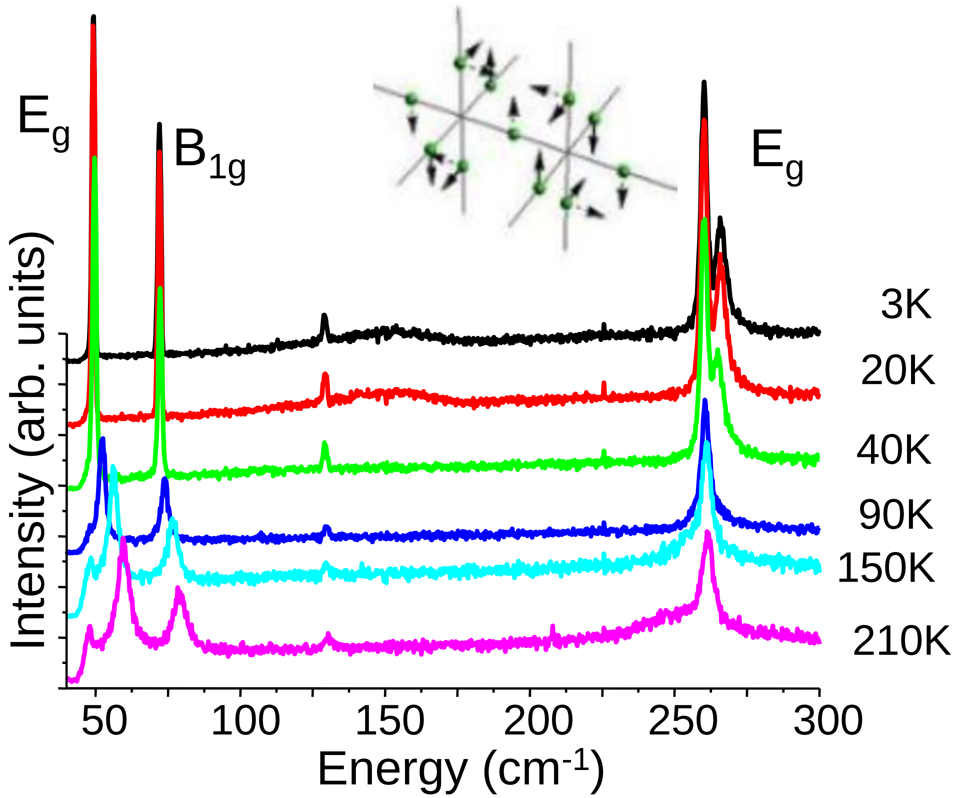


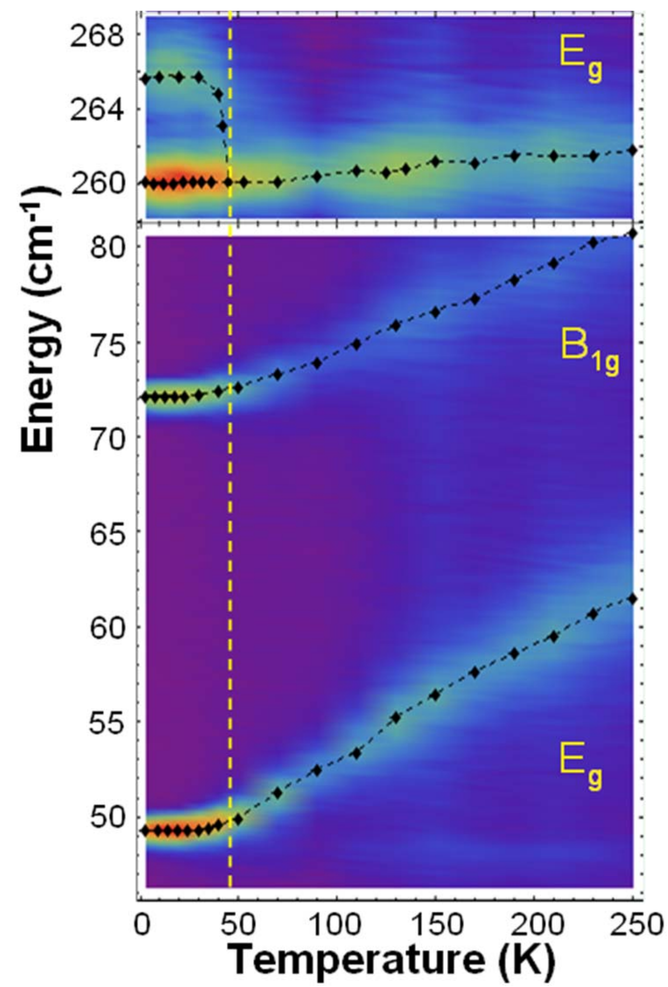


- Temperature-dependent softening of B_{1g} mode frequency indicates **thermally driven structural fluctuations** well below T_{oo}!

Two-step stabilization of orbital order in $KCuF_3$:
Fluctuational regime halted by structural transition just above T_N

- $KCuF_3$ is characterized by structural (and spin) fluctuations down to a tetragonal-to-orthorhombic structural transition at 50 K, which appears to help stabilize orbital/magnetic order

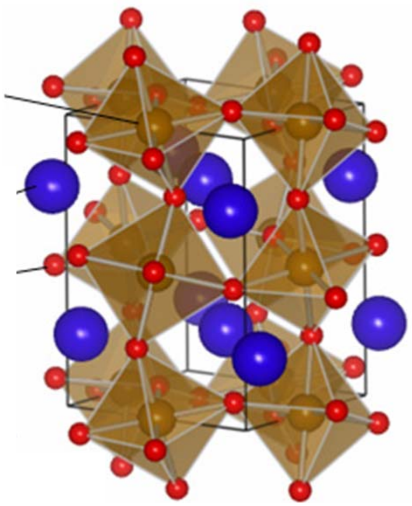




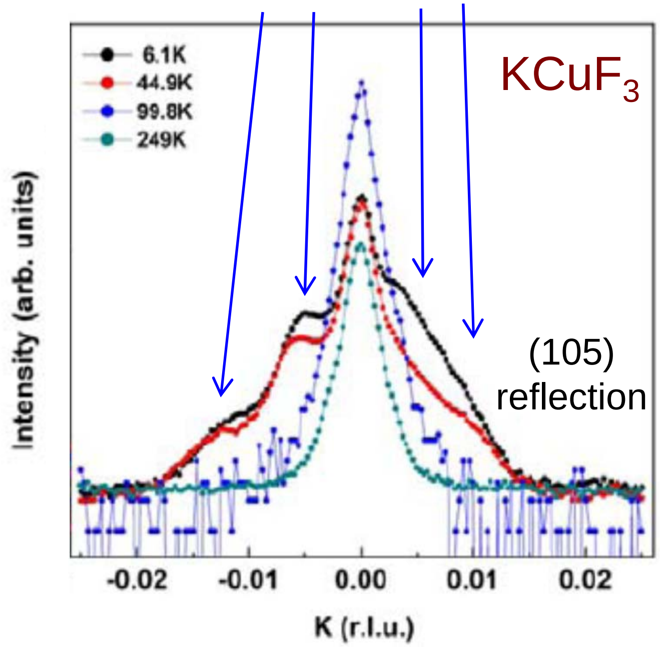
What's responsible for structural fluctuations in $KCuF_3$?

$\Rightarrow$ X-ray evidence for rotations of CuF_6 octahedra

- (105) Bragg reflections not allowed by Kugel-Khomskii orbital ordering, but ARE consistent with $GdFeO_3$-type rotations of CuF_6 octahedra



Sidebands suggest many equivalent configurations of octahedral distortions

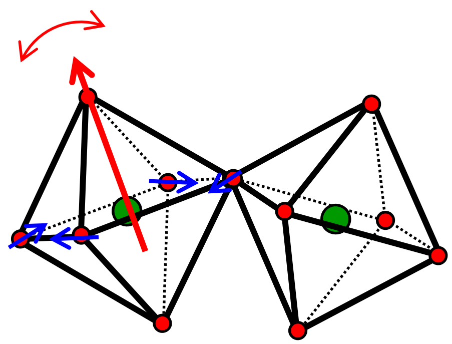


James Lee
(Abbamonte group, UIUC)

Peter Abbamonte
(UIUC)

Raman and x-ray results suggest these $GdFeO_3$ fluctuations persist down to 50 K, then "lock-in" just prior to the Neel transition into a "glassy" configuration

Phonon softening via “molecular fluctuations”:
Critical dynamics of pseudospin-phonon coupling*



*Yamada, Takatera, Huber, J. Phys. Soc. Japan (1974)

Related models discussed for:

- Displacive phase transitions (Halperin and Varma, PRB (1976))
- Dynamics of Jahn-Teller transitions (Pytte, PRB (1971))
- Dynamics of ferroelectrics (Silverman, PRL (1970))

Phonon KE — Phonon PE — Pseudospin-Pseudospin coupling — Pseudospin-Phonon coupling

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

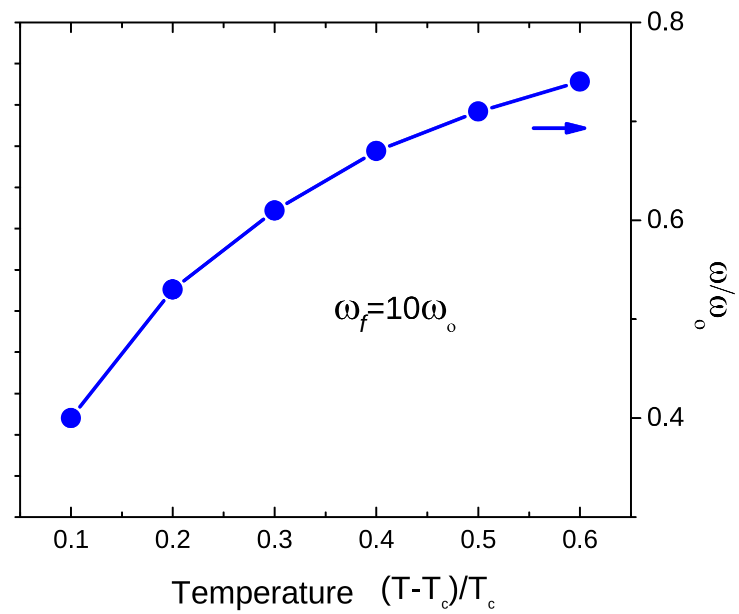
Phonon Response Function:

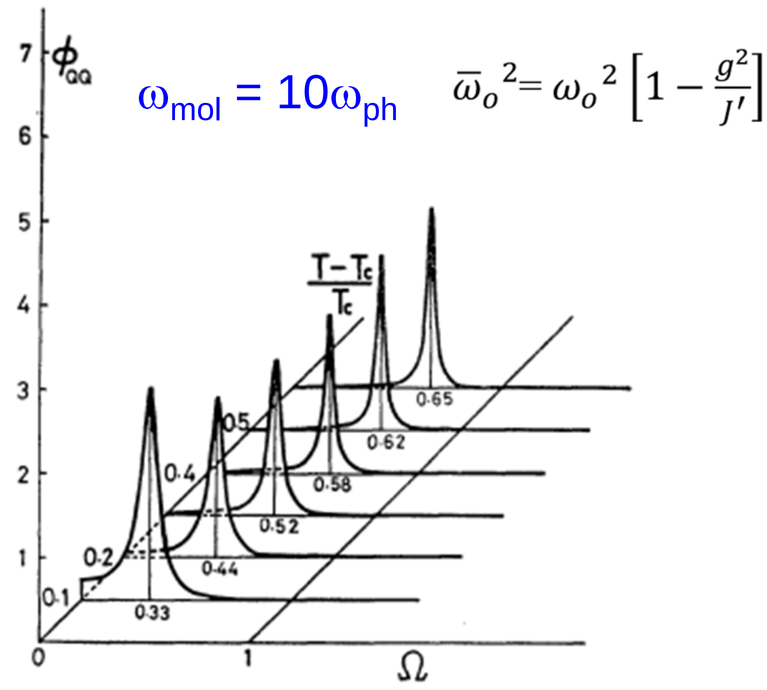
$$\emptyset_{QQ} = \frac{2\gamma k_B T\left\{\frac{g(k)}{\gamma J'}\right\}^2}{\left[\omega^2 - \bar{\omega}_o{}^2\right]^2 + \omega^2\Gamma_1{}^2}$$

Critical dynamics of pseudospin-phonon coupling: **Fast relaxation** of pseudospins (CuF_6 configurations)

Yamada, Takatera, Huber, J. Phys. Soc. Japan (1974)

• Significant phonon mode softening for fast molecular (pseudospin) relaxation
$\Rightarrow \omega_{mol} = 10\omega_{ph}$



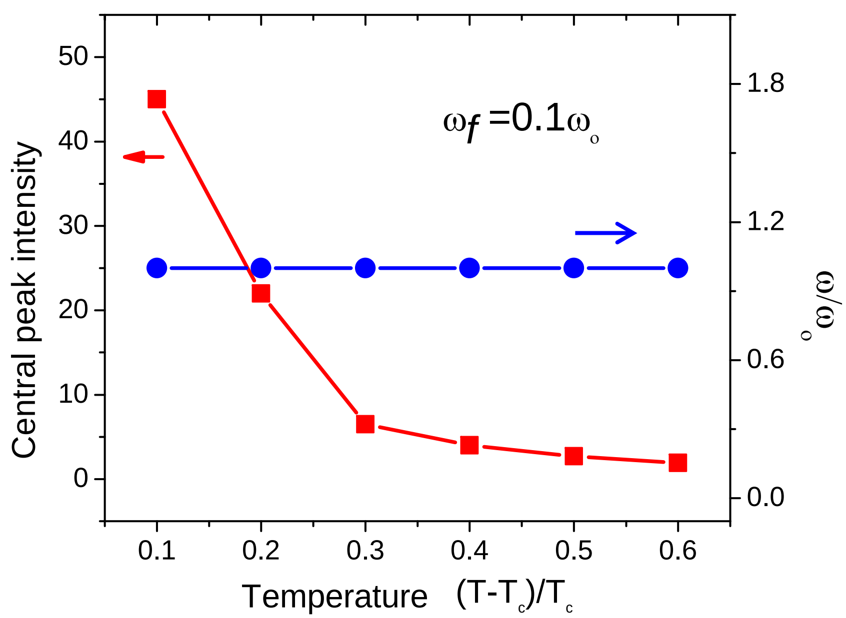


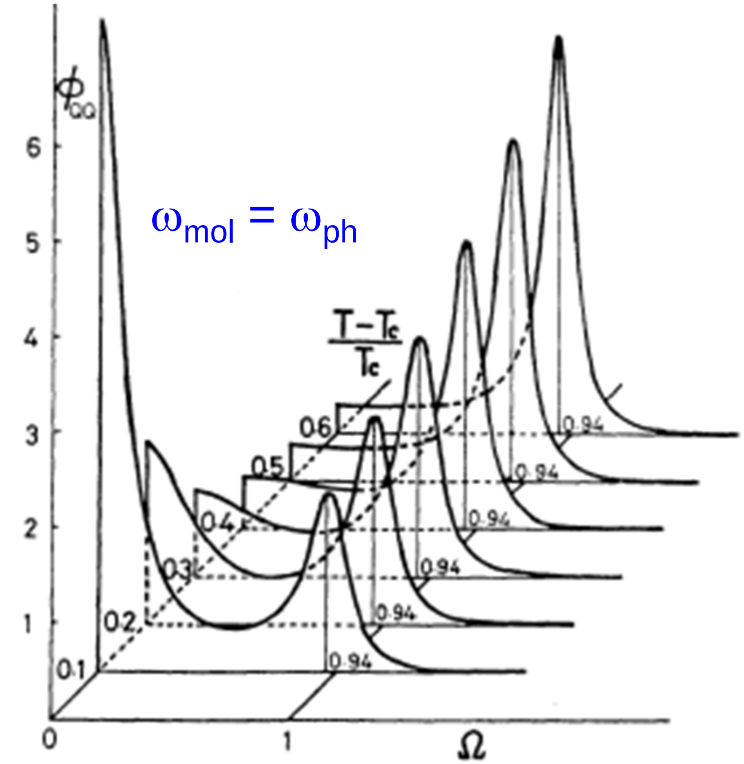
$\Rightarrow$ Phonon ‘sees’ time-averaged octahedral configuration, which changes with decreasing temperature

Critical dynamics of pseudospin-phonon coupling: **Slow relaxation** of pseudospins (CuF_6 configurations)

Yamada, Takatera, Huber, J. Phys. Soc. Japan (1974)*

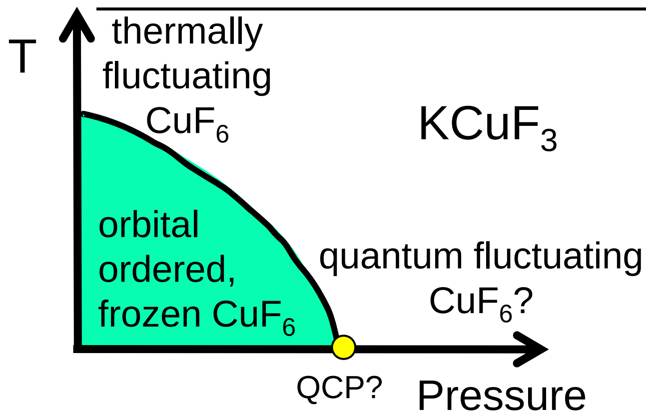
• Slow molecular fluctuations give a broad central peak, no significant phonon mode softening $\Rightarrow \omega_{mol} \leq \omega_{ph}$





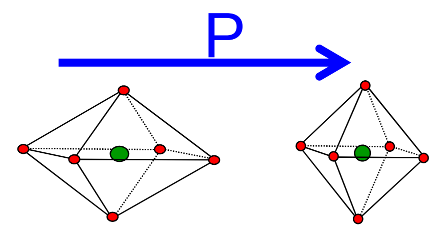
$\Rightarrow$ Central peak reflects Debye relaxation of octahedral (pseudospin) fluctuations

Pressure-tuned "quantum" (T~0) octahedral fluctuations in $KCuF_3$

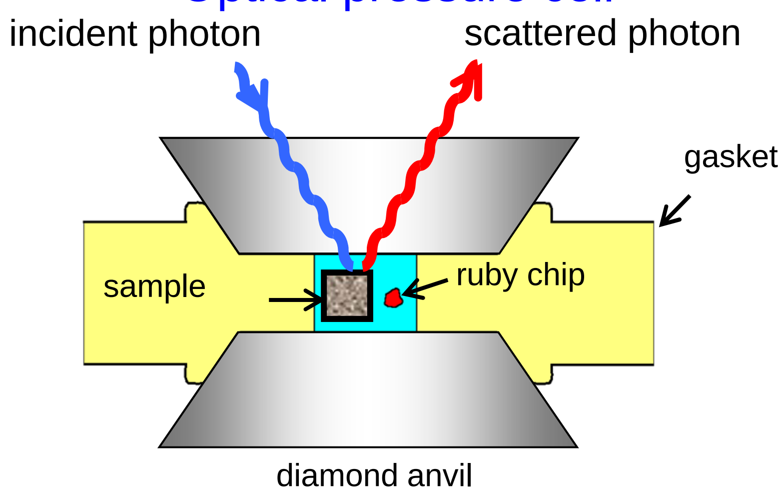


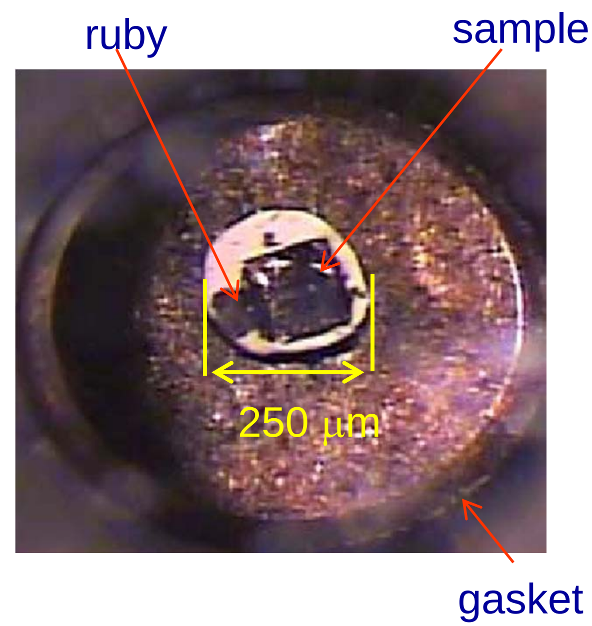
Hydrostatic pressure reduces octahedral tilts and favors lower octahedral volume

(e.g., Hucker, Tranquada, et al., PRL (2010) for $(La,Ba)CuO_4$ and Steffens et al., PRB (2008) for Ca_2RuO_4)

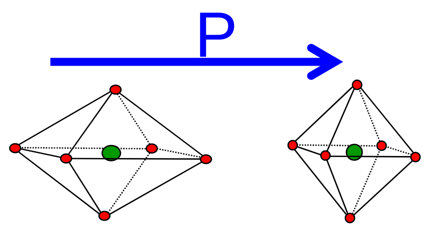


Optical pressure cell

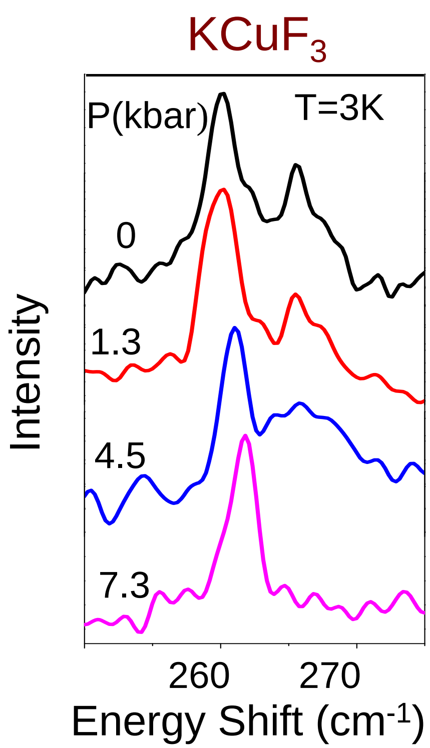


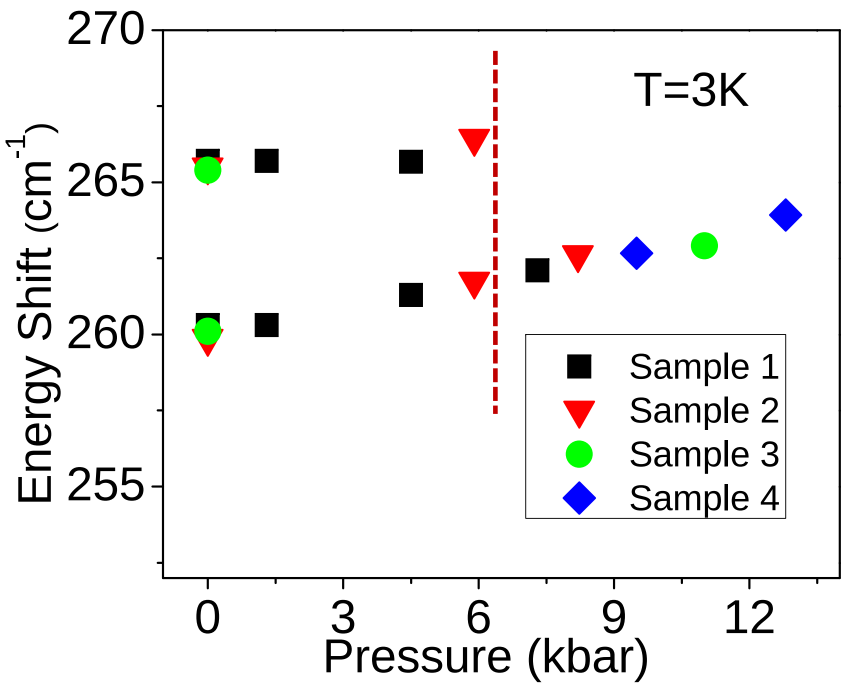


Reversing the low temperature structural phase transition with pressure in $KCuF_3$

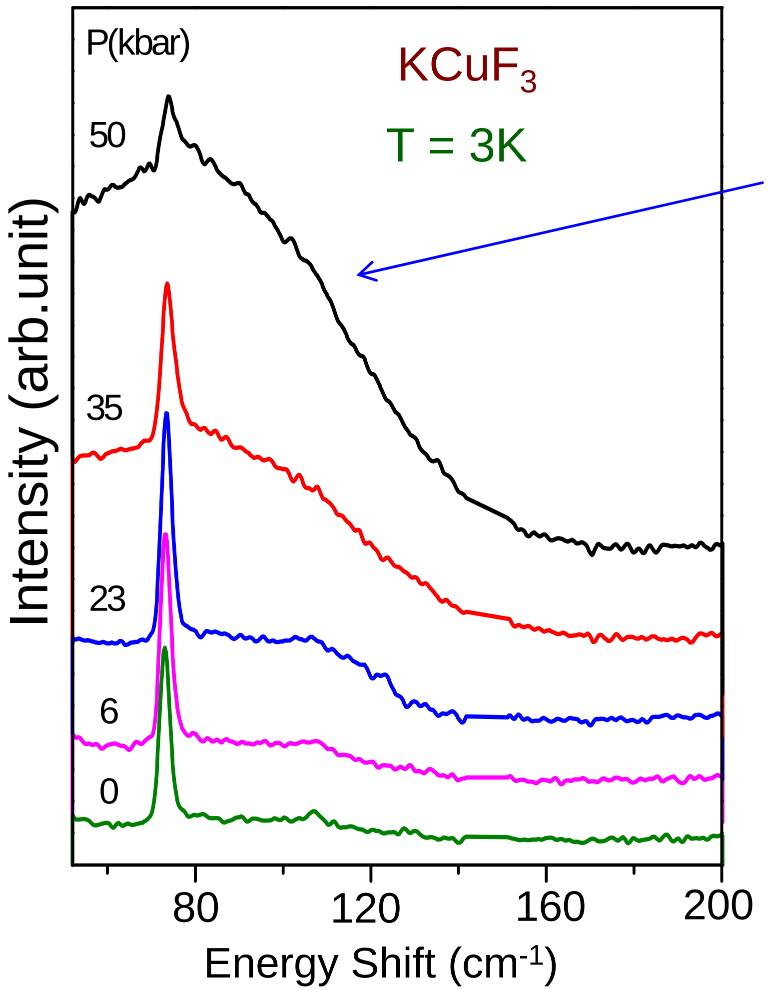


⇒ Pressure-tuned orthorhombic-to-tetragonal structural transition in $KCuF_3$ at T = 3 K



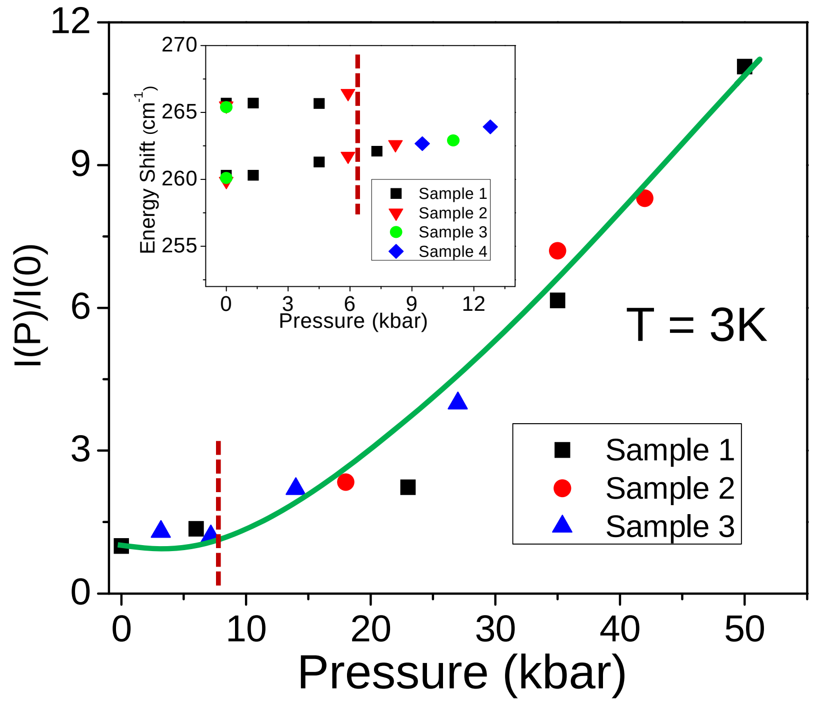


Pressure-induced central peak in $KCuF_3$: Slow quantum fluctuations of CuF_6 octahedra



$$\chi''(\omega) \sim \frac{\omega\Gamma}{\omega^2 + \Gamma^2}$$

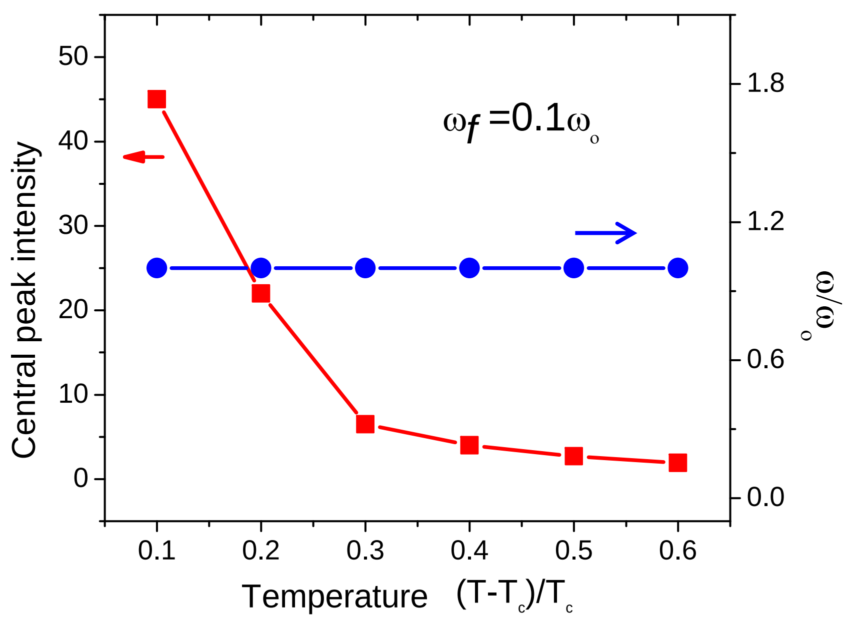
⇒ Pressure-induced 'simple relaxational' response in $KCuF_3$ at T = 3 K; **Γ ~ 10 meV**

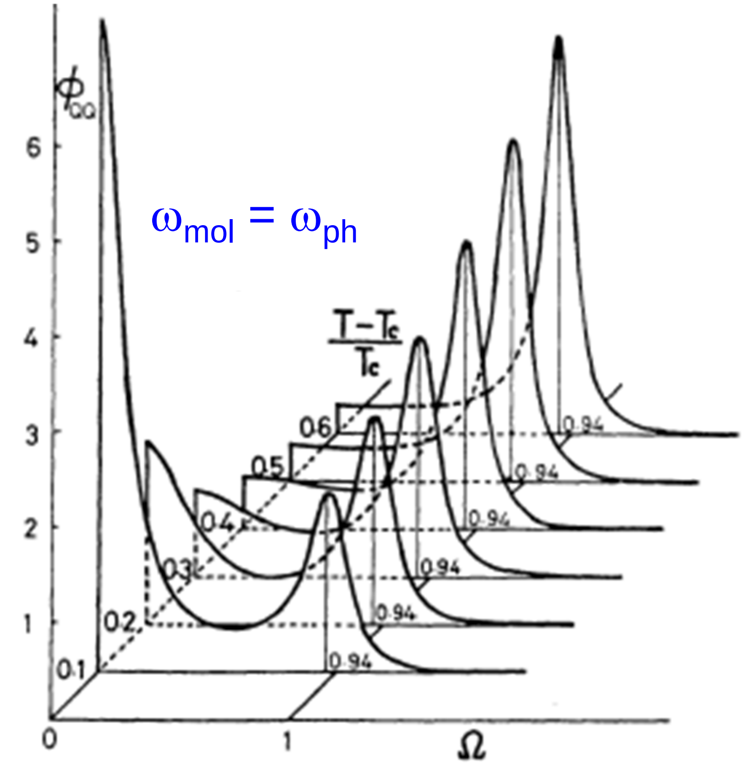


Critical dynamics of pseudospin-phonon coupling:
Slow relaxation of pseudospins (CuF_6 configurations)

Yamada, Takatera, Huber, J. Phys. Soc. Japan (1974)*

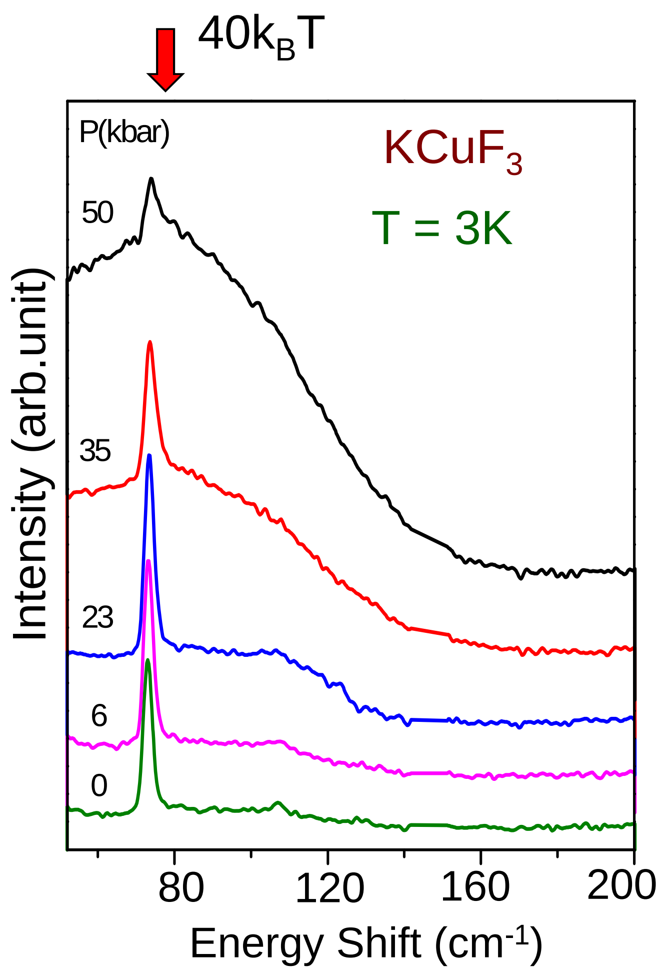
• Slow molecular fluctuations give a broad central peak, no significant phonon mode softening $\Rightarrow \omega_{mol} \leq \omega_{ph}$

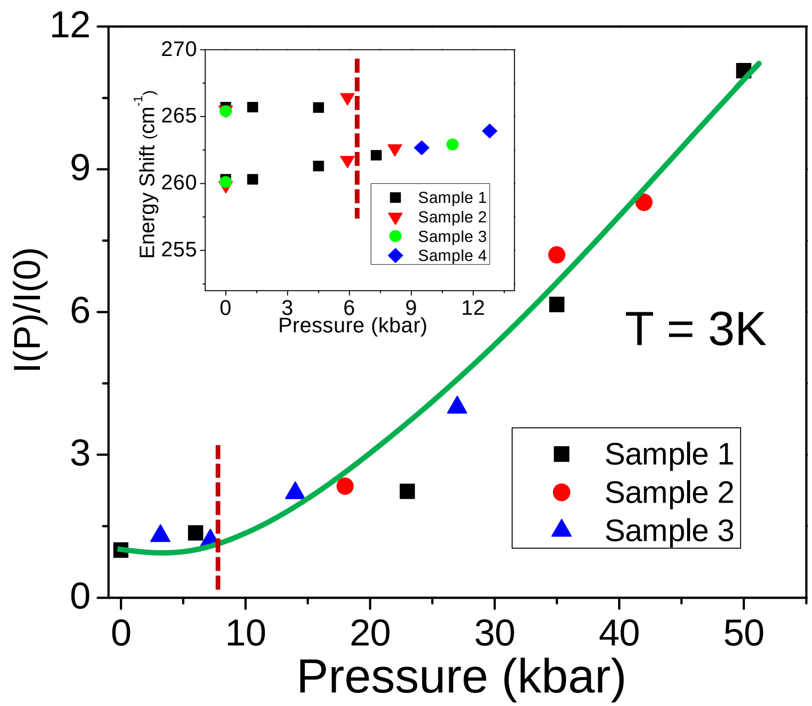




$\Rightarrow$ Central peak reflects Debye relaxation of octahedral (pseudospin) fluctuations

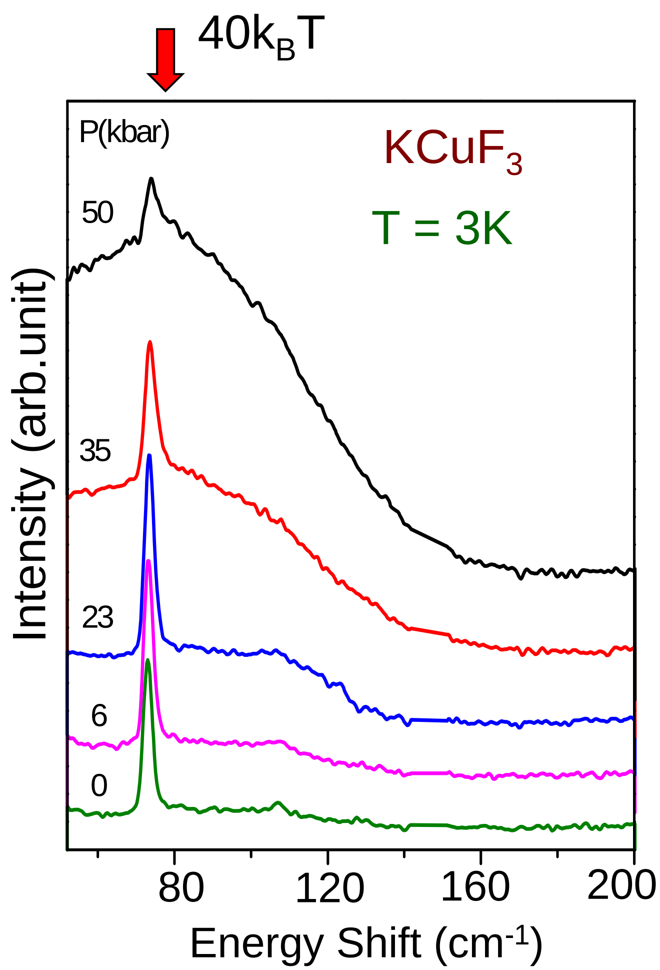
Pressure-tuned central peak development in $KCuF_3$: Slow quantum fluctuations of CuF_6 octahedra

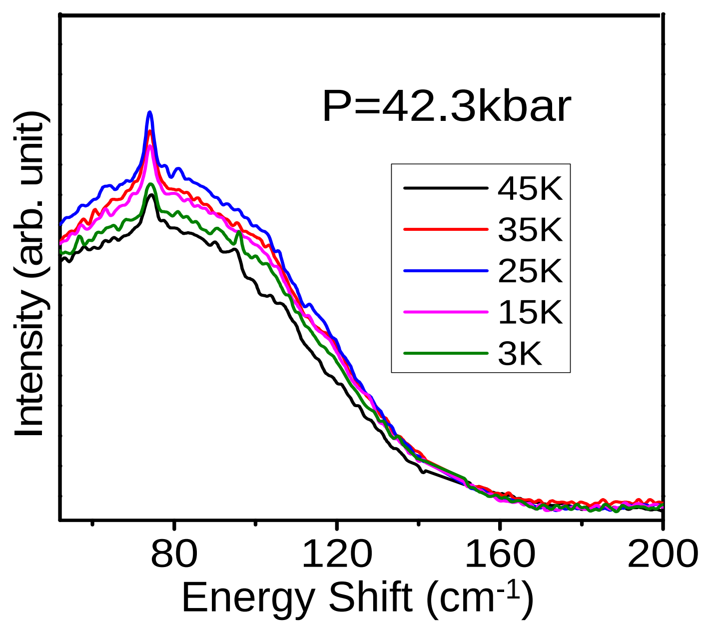




Central peak results from slow fluctuations (Γ~10 meV = 40k_BT) of CuF_6 octahedra
⇒ characteristic fluctuation rate >> k_BT, suggesting zero-point fluctuations

Pressure-tuned central peak development in $KCuF_3$: Slow quantum fluctuations of CuF_6 octahedra

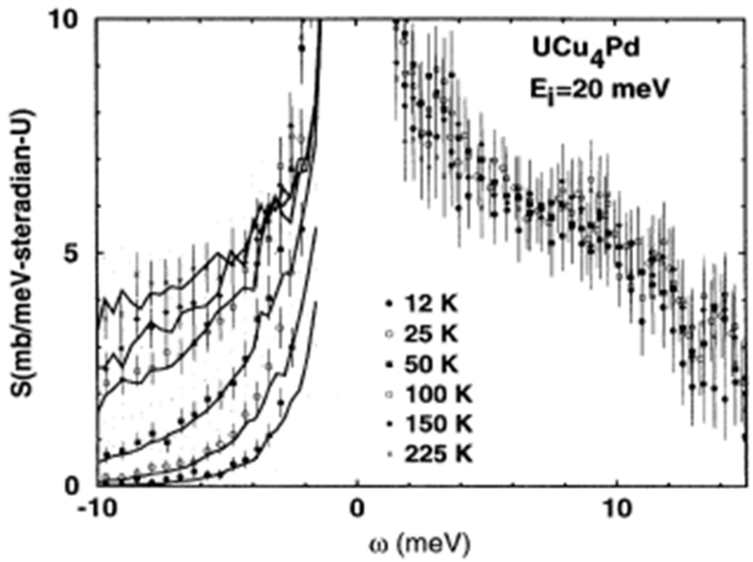




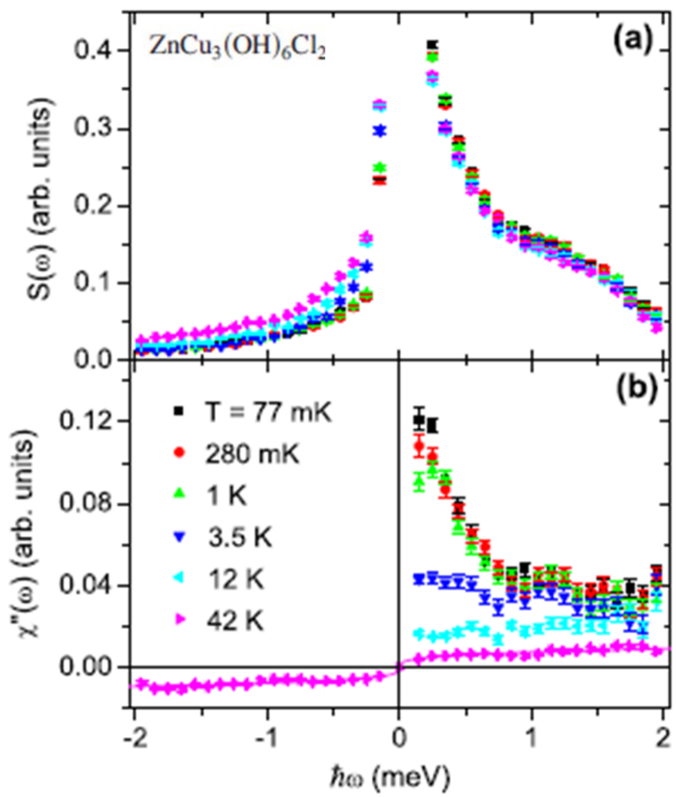
Temperature-independence of central peak also supports quantum fluctuation interpretation (ω>T regime)

Similarity to quantum spin fluctuations observed in various magnetic materials using neutron scattering

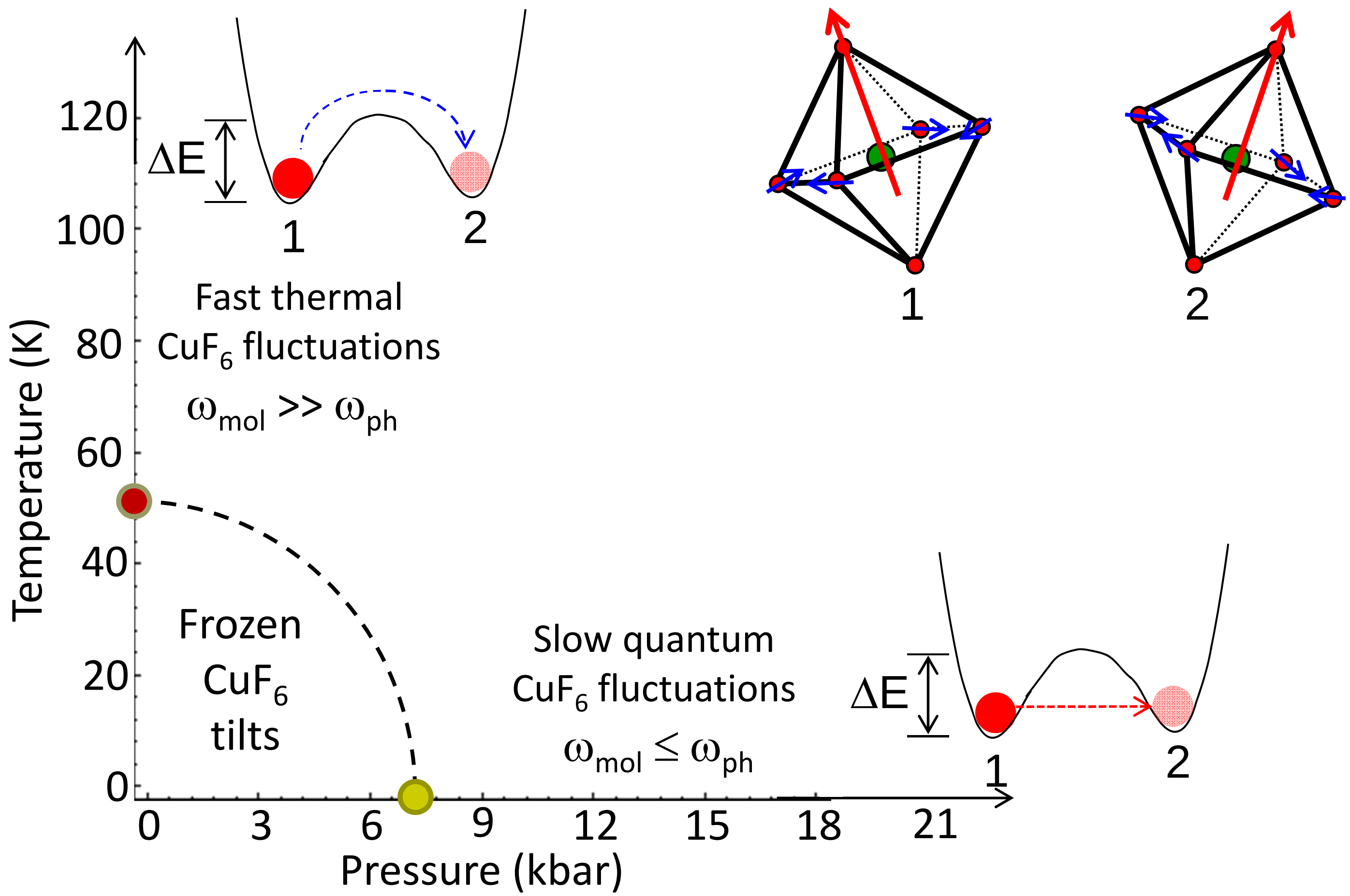
Aronson et al., Phys. Rev. Lett. (1995)



Helton et al., Phys. Rev. Lett. (2010)



Summary of fluctuational behavior observed in $KCuF_3$



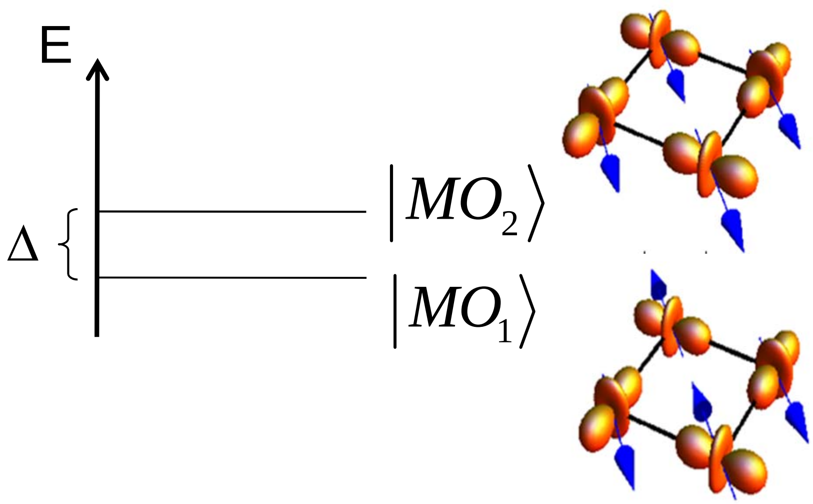
How do octahedral fluctuations frustrate magnetic/orbital order in $KCuF_3$?

Model by Lal and Goldbart supplements the KK model with a direct, orbital exchange term.*

Adding this term creates a near degeneracy of orbital/spin states that dynamically frustrates the spin subsystem

Siddhartha Lal

Paul Goldbart

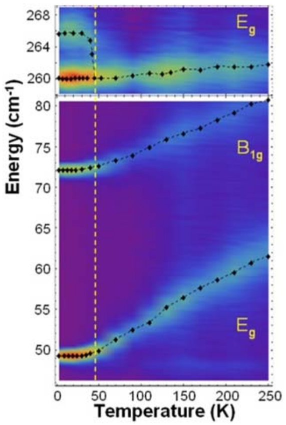


$\Delta \sim 3\text{ K} << k_B T$

$\Rightarrow$ thermal/quantum fluctuations disrupt in-plane magnetic order

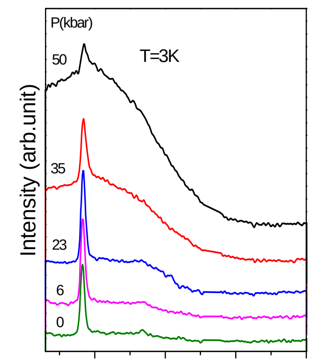
*J.C.T. Lee, S. Lal, S. Yuan, et al., submitted to Nature Physics (2011)

Summary: Thermal and quantum fluctuations of CuF_6 octahedra in $KCuF_3$

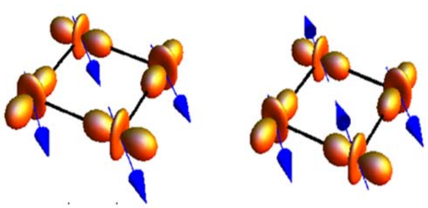


- $KCuF_3$ exhibits phonon mode softening due to thermal fluctuations of the CuF_6 octahedra down to a structural transition near 50 K, just above T_N

- Pressure-dependent measurements show evidence for a pressure-tuned quantum phase transition to a regime characterized by quantum fluctuations of CuF_6 octahedra



- A model of pseudospin-phonon coupling in both fast and slow octahedral fluctuation regimes explains both the temperature- and pressure-dependent spectra



- Adding a direct orbital exchange term to the KK model generates nearly degenerate orbital/spin states that should be susceptible to thermal fluctuations, frustrating magnetic/orbital order down to low temperatures