Experimental report

21/09/2023

Proposal: **7-01-513**

Council: 10/2019

Title: Study of lattice contribution to the quantum spin liquid properties in molecular dimer-Mott insulator k-(BEDT-TTF)2Cu2(CN)3

Research area: Physics

This proposal is a new proposal

Main proposer: **Masato MATSUURA**

Experimental team: Andrea PIOVANO
Masato MATSUURA

Local contacts: Andrea PIOVANO

Samples: k-(BEDT-TTF)2Cu2(CN)3

Instrument	Requested days	Allocated days	From	To
IN8	6	5	26/02/2021	04/03/2021
IN3	1	1	18/02/2021	19/02/2021

Abstract:

Molecular dimer-Mott insulators have been in the focus of recent scientific attention due to the wealth of intriguing phenomena including spin liquid behavior, bandwidth-controlled Mott-transition, unconventional superconductivity, and electronic ferroelectricity. In 2014, we initiated first inelastic neutron scattering (INS) experiments on k-(BEDT-TTF)2Cu[N(CN)2]Cl (k-Cl) which exhibits electronic ferroelectricity below TFE ~TN ~25 K, using the triple axis spectrometer IN8. We succeeded to obtain clear phonon signals and found phonon damping in a wide temperature range, which we assign to structural fluctuations coupled to the charge and spin degrees of freedom in the BEDT-TTF molecules. The dielectric response in k-Cl has a striking analogy to that observed in another molecular dimer-Mott insulator namely k-(BEDT-TTF)2Cu2(CN)3 (k-CN), which has become prominent because of its putative spin liquid properties. In this proposal, we aim at comparing the lattice dynamics between k-CN and k-Cl allow for a deep understanding of the coupling of the lattice to the spin degrees of freedom.

Molecular dimer-Mott insulators have been in the focus of recent scientific attention due to the wealth of intriguing phenomena including quantum spin liquid (QSL) behavior, bandwidth-controlled Mott-transition, unconventional superconductivity, and electronic ferroelectricity [1-3]. In 2014, we initiated first inelastic neutron scattering (INS) experiments on κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (κ-Cl), which exhibits the simultaneous occurrence of electronic ferroelectricity and antiferromagnetic spin order below T_{FE} ~T_N ~25 K [3] , using the triple axis spectrometer IN8. Although our sample was relatively small (total mass of two single crystals of ~ 7 mg) for an INS measurement, we succeeded to obtain clear phonon signals and found phonon damping in a wide temperature range T_N<T<60K as shown in Fig.1, which we assign to structural fluctuations coupled to the charge and spin degrees of freedom in the BEDT-TTF molecules [4].

The dielectric response in κ-Cl (inset of Fig.1(b) has a striking analogy to that observed in another molecular dimer-Mott insulator namely κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

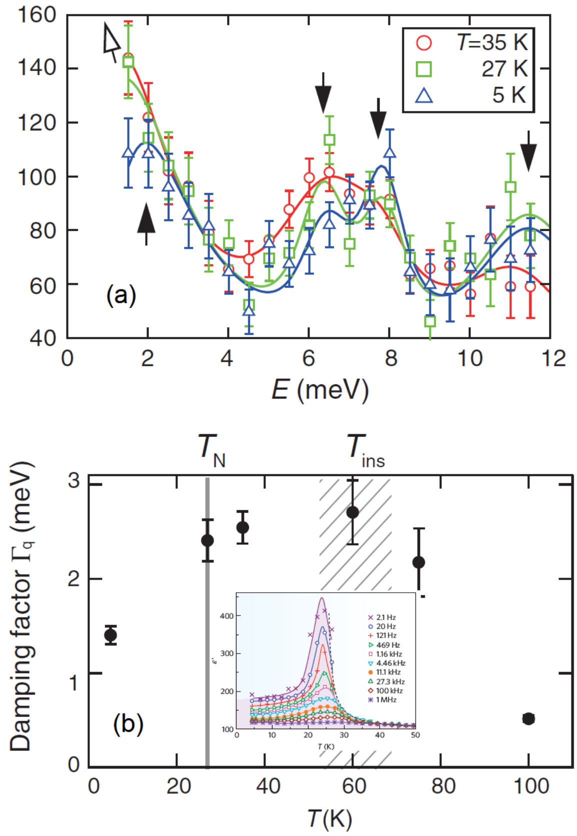

Fig.1 (a) Constant-Q scans at (603) and (b) the temperature dependence of the damping factor for the lowest optical mode for κ-Cl[4]. Inset in (b) shows temperature dependence of dielectric susceptibility [2].

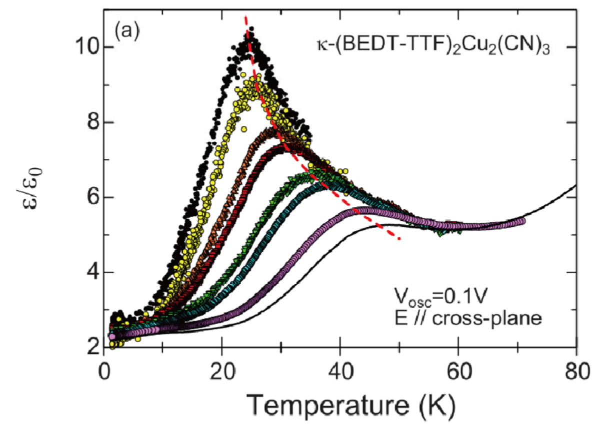

Fig.2 The temperature dependence of the dielectric constant for κ-CN measured at various frequencies [1].

(κ-CN) (Fig.2), which has become prominent because of its putative spin liquid properties [1]. In κ-CN, despite the absence of a magnetic phase transition, anomalous behavior at low temperatures around T^* ~ 6 K has been observed in various quantities. Provided that an intra-dimer charge disproportionation mechanism is responsible for the dielectric response in κ-CN as proposed for κ-Cl [2], we expect to find clear phonon anomalies for intra-dimer breathing modes in κ-CN as for κ-Cl. To probe lattice effects and their coupling to charge- and spin fluctuations associated with the 6 K anomaly, we performed INS study on κ-CN by using the triple axis spectrometer IN8.

Forty-seven deuterated single crystals with a total mass of ~26 mg were used for the experiments. The crystals were mounted so as to access (*0kl*) scattering plane. The final neutron energy was fixed to 14.7meV. To obtain large neutron flux and good energy resolution, doubly focused Cu monochromator and analyzer were used.

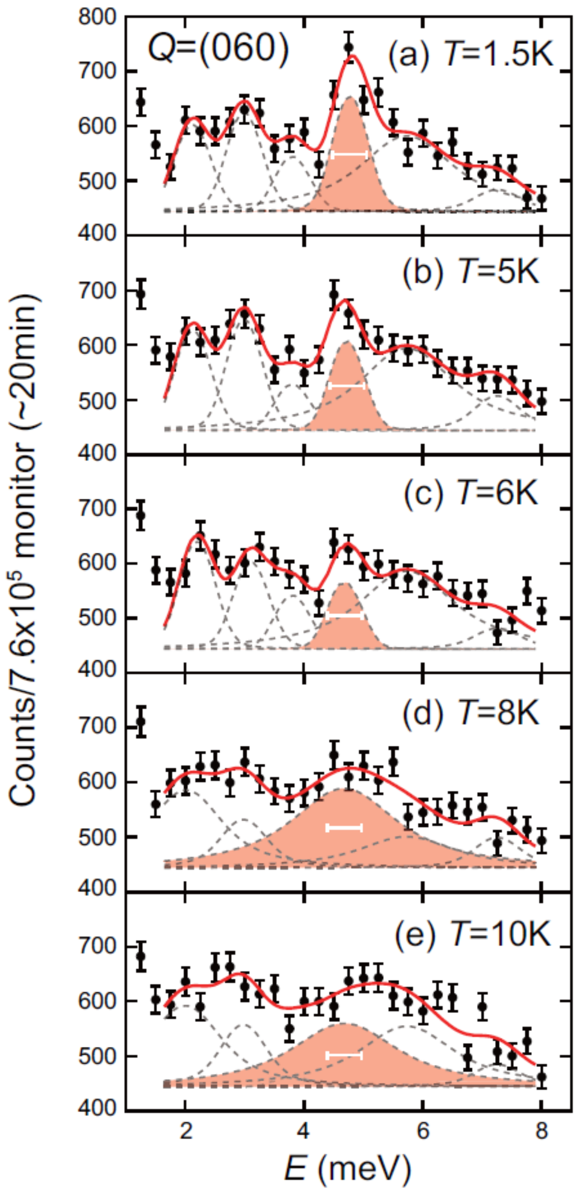

Fig. 3 Temperature dependence of constant-Q scans at (060). The red curves are the sum of the fits to damped harmonic oscillator functions convolved with the experimental resolution. The horizontal bars represent the instrumental energy resolution at E = 4.7 meV.

Figure 3 shows phonon spectrum of κ-CN measured at *Q*=(060). We observed clear optical phonon modes at *E*=2.0, 2.9, 3.7, 4.7, 5.7, and 7.2 meV [5], consistent with results of optical conductivity measurements on κ-CN [6]. According to density-functional-theory calculations [6], the peak at 4.7 meV can be assigned to an intradimer breathing mode. As the temperature rises, the intensity of this mode reduces, and all peaks become broad above 6 K. Since the linewidth of the peak is inversely proportional to the phonon lifetime, the broadening of these peaks indicates that the phonon lifetime becomes substantially reduced above 6 K. Similar to κ-Cl, the bulk of experimental findings on κ-CN indicate fluctuations and ordering phenomena in both the charge- and spin sectors. The abrupt change in the phonon damping and the recovery of long-lived (underdamped) breathing modes of ET-dimers below 6 K can be attributed to a cooperative phenomenon involving the lattice and its coupling to the charge and spin degrees of freedom around 6 K. Our data are consistent with the formation of a valence bond solid state below 6 K.

References

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