Lattice dynamics coupled to charge and spin degrees of freedom in the molecular dimer-Mott insulator $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl

Masato Matsuura*,1 Takahiko Sasaki,2 Satoshi Iguchi,2 Elena Gati,3 Jens Müller,3 Oliver Stockert,4 Andrea Piovano,5 Martin Böhmer,5 Jitae T. Park,6 Sananda Biswas,7 Stephen M. Winter,7 Roser Valentì,7 Akiko Nakao,1 and Michael Lang3

1Neutron Science and Technology Center, Comprehensive Research Organization for Science and Society (CROSS), Tokai, Ibaraki 319-1106, Japan
2Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
3Institute of Physics, SFB/TR49, Goethe-University Frankfurt, 60438 Frankfurt (M), Germany
4Max-Planck-Institut für Chemische Physik fester Stoffe, D-01185 Dresden, Germany
5Institut Laue-Langevin, 6 rue Jules Horowitz, 38042 Grenoble Cedex 9, France
6Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Lichtenbergstr. 1, 85748 Garching, Germany
7Institute for Theoretical Physics, SFB/TR49, Goethe-University Frankfurt, 60438 Frankfurt (M), Germany

Inelastic neutron scattering measurements on the molecular dimer-Mott insulator $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl reveal a phonon anomaly in a wide temperature range. Starting from $T_{\text{ins}} \sim 50-60$ K where the charge gap opens, the low-lying optical phonon modes become overdamped upon cooling towards the antiferromagnetic ordering temperature $T_N = 27$ K, where also a ferroelectric ordering at $T_{\text{FE}} \approx T_N$ occurs. Conversely, the phonon damping becomes small again when spins and charges are ordered below $T_N$, while no change of the lattice symmetry is observed across $T_N$ in neutron diffraction measurements. We assign the phonon anomalies to structural fluctuations coupled to charge and spin degrees of freedom in the BEDT-TTF molecules.

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Electronic ferroelectricity, where electrons and their interactions play the key role, has been in the focus of recent scientific efforts [1–3]. Whereas conventional ferroelectricity originates from electronic degrees of freedom, such as spin and charge, which offers an alternative route to control the system’s ferroelectric properties. Electronic ferroelectricity, driven by spin degrees of freedom, is often found in frustrated magnetic systems with non-collinear spin structures [2, 3]. In case of the charge-driven variant, the electric dipoles arise from charge order or charge disproportionation in combination with dimerization, which has been found in inorganic oxides [3] and organic charge-transfer salts [4–10].

The $\kappa$-(BEDT-TTF)$_2$X family, where BEDT-TTF is bis-(ethylenedithio)tetrathiafulvalene C$_6$S$_4$[(CH$_2$)$_2$]$_2$, is known to comprise bandwidth-controlled dimer-Mott systems where pairs of strongly interacting BEDT-TTF (in short ET) molecules form the dimers. In the dimer-Mott insulator picture, one π-hole carrier with spin $S = 1/2$ is localized on a molecular dimer unit. The charge degrees of freedom may become active when this localization is no longer symmetric with respect to the center of the dimer but rather adopts an asymmetric state characterized by a charge disproportionation within the dimer [11, 12]. Such a charge disproportionation scenario was suggested as the origin of the relaxor-type dielectric anomaly observed in the quantum-spin-liquid-candidate material $X = \text{Cu}_2(\text{CN})_3$ (κ-CN) [8, 13] – a suggestion which has created enormous attention as it highlights the important role of the intra-dimer charge degrees of freedom. Since relaxor ferroelectrics are known to consist of nanometer-sized domains, the relaxor-like dielectric anomaly in κ-CN suggests the presence of an inhomogeneous charge disproportionation. Recently, Lunkenheimer et al. have reported clear ferroelectric signatures in the related dimer-Mott system $X = \text{Cu}[\text{N(CN)}_2]\text{Cl}$ (κ-Cl) around the antiferromagnetic ordering temperature $T_N = 27$ K [8, 12, 13]. As in this system long-range ferroelectricity of order-disorder type is observed at $T_{\text{FE}} \approx T_N$, κ-Cl represents an ideal system to study the coupling of the charge- to the spin- and lattice degrees of freedom in a dimer-Mott insulator.

It is fair to say that the origin of the electric dipoles in these dimer-Mott insulators is still under debate. Whereas for κ-Cl and κ-CN a definite proof of charge disproportionation is still missing [10], clear evidence for charge order within the ET dimers has recently been found for the more weakly dimerized compound $X = \text{H_g(SCN)}_2\text{Cl}$ [12], making this system a prime candidate for electronically-driven ferroelectricity within the $\kappa$-(ET)$_2$X family [10].

Given that there is a finite electron-lattice coupling, fluctuations of the electric dipoles are expected to give rise to anomalies in the lattice dynamics which can be sensitively probed by neutron scattering. In fact, for relaxor ferroelectrics, neutron scattering studies have been able to reveal a phonon anomaly upon the appearance of inhomogeneous and fluctuating polar domains [13]. Unfortunately, systematic inelastic neutron scattering (INS) studies on organic charge-transfer salts have often been hampered due to the lack of sufficiently large

*Electronic address: m.matsuura@cross.or.jp
single crystals with only a few exceptions: for instance, a sizable phonon renormalization effect on entering the superconducting state was reported for the organic superconductor $\kappa$-(ET)$_2$Cu(NCS)$_2$ [13]. Thanks to major recent improvements in focusing the neutron beam, however, the situation has improved considerably. As we demonstrate in this work, the largely enhanced neutron flux at the sample position in state-of-the-art triple-axis spectrometers [20, 21] now enables such INS studies to be performed even on small single crystals of organic charge-transfer salts. Here we report an INS study of the lattice dynamics and its coupling to the charge- and spin degrees of freedom for the dimer-Mott insulator $\kappa$-Cl. By using an array of co-aligned single crystals of deuterated $\kappa$-Cl with total mass of 7 mg and 9 mg, we were able to detect clear phonon signals the amplitude of which shows a striking variation upon changing the temperature. We found that the low-lying optical phonon modes at 2.6 meV become damped below the onset temperature of the dimer-Mott insulating state in which the $\pi$-carriers start to localize on the dimer sites. This phonon damping becomes small again on cooling below $T_N$. In contrast to conventional displacive ferroelectrics, however, there is no divergence of the phonon intensity nor any change in the lattice symmetry at $T_N$ where also the dielectric anomaly was observed. Thus, in $\kappa$-Cl the lattice is clearly coupled to the charge- and spin degrees of freedom but appears not to be the driving force of the antiferromagnetic/ferroelectric phase transition at $T_N/T_{\text{FE}}$.

Deuterated single crystals of $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl were grown by electrochemical crystallization. The Néel temperature was determined to be $T_N = 27$ K from magnetic susceptibility measurements as shown in Fig. 4(d), which is identical to the ordering temperature reported for hydrogenated $\kappa$-Cl [22]. INS experiments were performed on the triple-axis spectrometers IN8 at the Institut Laue-Langevin [22] and PUMA at the Heinz Maier-Leibnitz Zentrum [21]. All data were collected with a fixed final neutron energy of 14.7 meV using a doubly focused Cu analyzer for IN8 and a doubly focused pyrolytic graphite (PG) analyzer for PUMA. The initial neutron energy was selected by a doubly focused PG monochromator for both IN8 and PUMA. A PG filter was placed in front of the analyzer to suppress the scattering of higher-order neutrons. To improve the signal-to-noise ratio, two monochromators were co-aligned for the neutron experiments on IN8 and PUMA, respectively. In all experiments, the samples were slowly cooled with 1 K/min around $T = 75$ K to minimize disorder in the ET molecules’ ethylene endgroup orientations [23, 24]. The single crystals were mounted so as to access the $(h0l)$ and $(hk0)$ scattering plane for INS and neutron diffraction measurements, respectively. Throughout this paper, we label the momentum transfer in units of the reciprocal lattice vectors $a^* = 0.484$ Å$^{-1}$, $b^* = 0.210$ Å$^{-1}$ and $c^* = 0.741$ Å$^{-1}$. The instrumental energy resolution for IN8 linearly increases from 0.45 meV ($E = 0$) to 0.84 meV ($E = 10$ meV). To relate the fit parameters to the scattering function of the sample, convolution of the instrumental resolution at $E = 3$ meV has been included and computed using the RESTRAX simulation package [25]. We assume flat dispersions within $Q$-width of the resolution ellipsoid since optical dispersions close to the $\Gamma$-point are flat.

Figures 1(a) and (b) show the crystal structure of $\kappa$-Cl consisting of layers of ET molecules separated by thin anion sheets. The ET molecules form dimers, resulting in a dimer-Mott insulating ground state. Since the distance between the ET molecules within the dimer reflects the degree of dimerization, some of the modes are expected to couple more strongly to the electronic degrees of freedom than others. One of such modes is a breathing mode of the ET dimers, shown schematically by thick arrows in Figs. 1(a) and (b). The scattering intensity of phonons in neutron scattering is proportional to $(Q \cdot \xi)^2$, where $Q$ is the momentum transfers between the initial and final state of the neutron, and $\xi$ is the polarization vector of the phonon mode. Thus, the breathing of the ET dimers can best be measured when $Q$ is large and parallel to $\xi$ of the breathing mode as shown in Fig. 1(c). We measured the phonon spectra mainly at (603) to detect changes in the low-lying vibrational modes which are likely coupled to the charge- and spin degrees of freedom; changes will be detected for any vibrational mode which has a component parallel to [003].

Figures 2(a)-(c) show constant-$Q$ scans at (603) measured at various temperatures. At $T = 100$ K, we observe clear phonon peaks at $E = 2.6, 6, 8$, and 11 meV shown by the closed arrows. (See Figs. S1 and S2 in the Supplemental Material for the details of the dispersion [20]). The peak width for the low-lying modes at $E = 2.6$ meV (full-width-at-half-maximum; 2.3 meV) is considerably larger than the energy resolution (0.5 meV) indicating a
finite lifetime due to phonon-phonon or electron-phonon interactions. For an anharmonic phonon, the energy dependence of the scattering function can be expressed by the damped harmonic-oscillator function: \[ \frac{\Gamma_q \hbar \omega}{[\hbar^2 (\omega^2 - \omega_q^2)]^2 + (\Gamma_q \hbar \omega)^2} \] where \( \hbar \omega \) is the energy transfers between the initial and final state of the neutron, and \( \Gamma_q \) denotes the damping factor. The lifetime of the phonons is inversely proportional to \( \Gamma_q \). The enhanced phonon width, when compared to the energy resolution, suggests a strongly anharmonic lattice, consistent with the observation of large expansion coefficients in the \( \kappa-(ET)_2X \) family \[23\]. On cooling, the well-resolved peak from the low-lying optical modes at 2.6 meV changes into a sloped signal at \( T = 75 \) K, whereas the three modes at 6, 8, and 11 meV remain at almost the same energy [Fig. 2(b)]. When the damping factor \( \Gamma_q \) becomes comparable to \( \omega_q \), the phonon spectrum changes into a single peak at \( E = 0 \).

The sloped spectrum can be explained by an increasing \( \Gamma_q \) for the low-lying optical modes, which indicates the short lifetime of these modes. Similar phonon spectra at low energies are observed down to \( T_N = 27 \) K [Fig. 2(c)]. Below \( T_N \), the truly inelastic nature of the low-lying optical modes become again visible.

Figure 3(a) shows the temperature dependence of the damping factor \( \Gamma_q \) for the low-lying optical modes. Note that \( \Gamma_q \) is comparable to \( \omega_q \) in a wide temperature range for \( T_N < T < 75 \) K, indicating the damped nature of the low-lying optical modes. In addition to the phonon anomaly, we find that the energy width of the
Bragg peaks is broadened in the same temperature range (Fig. S3 in the Supplemental Material), suggesting an unstable lattice in this temperature region. Thus, the lattice of $\kappa\text{-Cl}$ shows anomalous behavior in a wide temperature range above $T_N$.

Overdamped soft modes are often seen near structural phase transitions in a variety of materials. In the overdamped regime, the scattering function $S(Q, \omega)$ is approximated as 

$$S(Q, \omega) = \frac{(2\pi)^3}{v_0}|F(Q)|^2 \frac{k_B T}{h \omega_q^2} \pi \omega^2 + \gamma_q,$$

where $v_0$ is the unit cell volume, $F(Q)$ is a dynamical structure factor, and $\gamma_q = \frac{\omega_q^2}{2v}$. Thus, the integrated intensity of an overdamped soft mode ($I_{\text{damp}} = \int S(Q, \omega) d\omega$) is proportional to $k_B T/\omega_q^2$. As $\omega_q = 0$ goes to zero at the transition temperature, the intensity of the damped soft mode diverges and $T/I_{\text{damp}}$ goes to zero. Figure 3(b) shows the temperature dependence of $T/I_{\text{damp}}$ for the low-lying optical modes. Clearly, $T/I_{\text{damp}}$ does not vanish at $T_N$, which indicates that the structural change is not the primary order parameter for the phase transition at $T_N$. This is consistent with the observation of only a small anomaly in the thermal expansion at $T_N \approx T_{\text{FE}}$ for $\kappa\text{-Cl}$ [22]. Instead, other degrees of freedom show divergent behavior at $T_N$, namely $(T/T)^{-1}$ of $^1H$ NMR for the spin [22] and the dielectric constant for the charge degrees of freedom [14].

Note that the overdamped phonon appears already at $60-75$ K, which is much higher than $T_N$. Figure 3(c) shows the temperature dependence of the scattering intensity at $Q = (603)$ and $E = 1.5$ meV. The effect of the phonon anomaly is clearly seen as an enhancement of the intensity at low energies ($E = 1.5$ meV) for $T_N < T \lesssim 60$ K. The coupling between a phonon mode and a relaxation mode of different origin (represented by a pseudospin) was discussed by Yamada within a pseudospin-phonon coupling model [31]. In this model, the relaxation mode and the phonon mode become strongly coupled when the characteristic frequency and wave vector of the pseudospin’s relaxation mode roughly match those of the phonon mode, which results in a broadening of the phonon in energy. The structural fluctuations between the two ethylene endgroup orientations of the ET molecules, known to occur in the $\kappa$-phase (ET)$_2X$ salts [24, 32], however cannot be the origin of the observed phonon anomaly since the ethylene endgroup motion freezes out in a glassy fashion below about 75 K.

On the other hand, the onset temperature of the phonon anomaly roughly coincides with the rapid increase in the electrical resistivity below $T_{\text{ins}} \sim 50-60$ K, as shown in Fig. 3(d). Optical conductivity measurements have revealed that the charge gap starts to open below $T_{\text{ins}}$ [33, 34], indicating charge localization at the ET dimer site. Even after the itinerant $\pi$-carriers become localized at the dimer site below $T_{\text{ins}}$, the distribution of charge within the dimer remains as an active degree of freedom. The coincidence of the onset temperature of the phonon anomaly and $T_{\text{ins}}$ suggests a coupling between the lattice and this intra-dimer charge degree of freedom. A similar scenario was observed in the organic superconductor $\kappa$-(ET)$_2\text{Cu(NCS)$_2$}$ for the lowest optical mode [19]. We thus expect that the low-lying optical modes are the key modes where the electron-phonon coupling becomes manifest in these organic salts containing ET molecules.

In an attempt to identify the low-lying optical modes with the theoretically obtained vibrational frequencies, we considered the phonon frequencies of the closely related system $\kappa\text{-CN}$ [35] which has a similar arrangement of anion and ET layers as $\kappa\text{-Cl}$, but exhibits considerably less phonon modes. The calculated lowest optical mode in $\kappa\text{-CN}$ at $q = 0$ has an energy of 3 meV and two of the ET-dimer breathing modes, involving also the movements of the anion layers, lie at energies of 4.1 meV and 4.7 meV. The $\kappa\text{-Cl}$ system differs from $\kappa\text{-CN}$ mainly in two ways: (i) the ET-dimers in $\kappa\text{-Cl}$ are alternately stacked along the $b$ axis, thus doubling the unit cell along that direction and (ii) the anion layers consist of chains arranged in a polymeric zigzag pattern, instead of having a more rigid two-dimensional network in $\kappa\text{-CN}$. It is to be expected that these factors will lead to significantly softer spring-constants in $\kappa\text{-Cl}$ compared to $\kappa\text{-CN}$. Such a rescaling of the phonon modes would affect all the phonons in the low-frequency regime. The lowest mode in $\kappa\text{-CN}$ may shift toward very low energies and merge with the elastic peak, which may allow to identify the observed low-lying optical modes in $\kappa\text{-Cl}$ as an ET-dimer breathing mode.

Below $T_N$, the damping of the low-lying optical modes become small as shown in Fig. 3(c) and Fig. 3(a). According to the pseudospin-coupling model [31], the reduction in the damping factor $\Gamma_q$ is due to the decoupling between the lattice and the pseudospins as a consequence of a critical slowing down of the pseudospin fluctuations. Since both dielectric and antiferromagnetic fluctuations freeze out below $T_N$ [14], the recovery of a truly inelastic phonon peak suggests a close correlation between lattice-, spin- and charge degrees of freedom at the phase transition at $T_N \approx T_{\text{FE}}$.

In order to check for the possibility of a change in the crystallographic symmetry at $T_N$, we performed detailed neutron diffraction measurements on a deuterated single crystal of $\kappa\text{-Cl}$ at $T = 35$ K ($> T_N$) and 4 K ($< T_N$) (Fig. S4 in the Supplemental Material). As explained in detail in the supplemental material, we did not find any indications for a crystallographic symmetry lowering at $T_N \approx T_{\text{FE}}$. This supports the picture of electronic ferroelectricity, where instead of the lattice, the spin- or charge degrees of freedom are the driving force of the phase transition in $\kappa\text{-Cl}$.

In discussing our results, we recall that recent vibrational spectroscopy studies failed to detect clear signatures of a charge disproportionation in $\kappa\text{-Cl}$ and $\kappa\text{-CN}$ [10]. On the other hand, our finding of overdamped modes for $T_N < T \lesssim T_{\text{ins}}$ strongly suggests a close cou-
pling between the lattice and the intra-dimer charge degrees of freedom. According to the pseudospin-coupling model [31], the characteristic energy of the charge fluctuations is expected to be in the same range as the low-lying optical modes, $1\sim 2$ meV, for $T_N < T \lesssim T_{\text{ins}}$. This energy scale is two orders of magnitude smaller than that of the charge-sensitive mode studied in the above-mentioned vibrational spectroscopy experiments. Furthermore, a finite DC conductivity is observed even in the "Mott-insulating" state below $\sim T_{\text{ins}}$ reflecting some degree of remaining itinerancy of the fluctuating $\pi$-electrons. The complex and seemingly contradictory picture of the low energy charge dynamics reported so far is likely due to the different time-scales of the investigated characteristic modes.

To summarize, by studying the spectra of selected phonons of the dimer-Mott insulator $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl as a function of temperature, we found clear renormalization effects which can be associated with charge fluctuations. We argue that

the overdamped optical phonon modes, observed in a wide temperature range from $T_{\text{ins}} \sim 50\sim 60$ K down to $T_N \approx T_{FE}$, result from a coupling of the lattice to the intra-dimer charge degrees of freedom. We consider these inelastic neutron scattering results as an important step which may trigger further systematic studies on the lattice dynamics and its coupling to the electronic degrees of freedom in the family of organic charge-transfer salts.

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I. SUPPLEMENTARY MATERIAL

Figure S1 shows contour map of phonon scattering intensity of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl at $T = 5$ K. Phonon spectra below 12 meV consist of several optical branches: a low energy mode at $2 \sim 3$ meV, dispersive modes at $4 \sim 8$ meV and zone-boundary modes at $> 9$ meV. Phonon signals are fitted to damped harmonic oscillator functions convoluted with instrumental resolution for constant-Q cuts, as shown in Figs. S2(a)-(e). Obtained phonon dispersions are summarized in Fig. S2(f). At Γ-point, we observed four optical modes below 12 meV as shown in Fig. S2(a). The three modes at $E = 6$, 8, and 11 meV at Γ-point show similar dispersions: gradual decrease with increasing $q$. On the other hand, the low-lying optical modes at 2 meV at the Γ-point exhibit opposite $q$-dependence to the other modes and merge with the second lowest mode at $q = 0.375$ (rlu). Low-lying acoustic mode, presumably below 1.5 meV, was not observable due to a large tail from incoherent elastic signal.

Figure S3 shows the temperature dependence of the energy width (Full-Width-at-Half-Maximum; FWHM) of the $(603)$ peak. The energy width at $T = 80$ K is almost resolution-limited $0.36 \pm 0.015$ meV. At near $T_N$, the $(603)$ peak is broadened in energy: the energy width increases to $0.44 \pm 0.03$ meV at $T = 35$ K then goes back to $0.38 \pm 0.02$ meV at $T = 5$ K. The broader peak than the instrumental energy resolution, suggesting an unstable lattice for $T_N < T < 75$ K.

In order to check for the possibility of a change in the crystallographic symmetry at $T_N$, we performed detailed neutron diffraction measurements on a deuterated single crystal of κ-Cl at $T = 35$ K ($> T_N$) and 4 K ($< T_N$) by using the Extreme Environment Single Crystal Neutron Diffractometer SENJU installed at the Japan Proton Accelerator Research Complex Materials and Life Science Experimental Facility. Figure S4 shows the intensity contour maps in the $(hk0)$ scattering plane measured at (a) $T = 35$ K and (b) 4 K. The Bragg peaks at $T = 35$ K appear at $(hk0)$ with $h = 2n$ and $(0k0)$ with $k = 2n$, where the indexes are enclosed within circles, consistent with the space group Pnma reported in the literature. Among the four acentric subgroups of Pnma: P2$_1$2$_1$2$_1$, Pna2$_1$, Pnm2$_1$, and Pma2$_1$, only Pna2$_1$ has the same reflection condition as Pnma. The other acentric space groups give additional reflections $(hk0)$ with $h = 2n + 1$ and $(0k0)$ with $k = 2n + 1$, as indicated by arrows in...
FIG. S2: (a)-(e) Constant-Q cuts of $\kappa$-Cl at $(6+q,0,3)$ measured at $T = 5$ K. The solid lines are fits to damped harmonic oscillator functions. We convoluted the instrumental resolution to the model cross sections assuming flat dispersions by using the RESTRAX simulation package [3]. Arrows indicate energies of the phonon modes. Data were obtained by using IN8 spectrometer. (f) Observed phonon dispersions of $\kappa$-Cl at $T = 5$ K. Thick lines in (f) are guide to the eyes.

Fig. S4(b). At $T = 4$ K, no additional superlattice peaks at these expected reflections were detected within an upper limit of $10^{-2}$ of the intensity of the main Bragg peaks. Moreover, the reflection conditions do not change from those at $T = 35$ K. Whereas a structural analysis assuming Pma2$_1$ for the 4 K data yields strongly anomalous thermal factors, the Pna2$_1$ model for the 4 K data converges with reasonable thermal factors. Although we
cannot rule out the existence of very weak superlattice peaks for $T < T_N$, possible structural changes due to inequivalent ET molecules within the dimer should be quite small. The lack of any indications for a crystallographic symmetry lowering at $T_N = T_{FE}$ supports the picture of electronic ferroelectricity, where instead of the lattice, the spin- or charge degrees of freedom are the driving force of the phase transition in $\kappa$-Cl.

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FIG. S4: Contour map of neutron diffraction intensity within the reciprocal space defined by the orthogonal [1 0 0] and [0 1 0] axes of deuterated $\kappa$-Cl measured at (a) $T = 35$ K and (b) 4 K. The indexes with circle in (a) denote the reflection conditions: $(h00)$ with $h = 2n$ ($n$ is integer) and $(0k0)$ with $k = 2n$ for the space group of Pnma. The arrows in (b) indicate indexes of expected additional reflections $(hk0)$ with $h = 2n+1$ and $(0k0)$ with $k = 2n+1$ for the acentric subgroups of Pnma.