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Power-law dependence of the optical conductivity observed in the quantum spin-liquid compound κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

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The Mott-insulator κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ is the prime candidate of a quantum spin-liquid with puzzling magnetic properties. Our THz and infrared investigations reveal that also the charge dynamics does not follow the expectations for a Mott insulator. We observe a large in-gap absorption where the excess conductivity exhibits a power-law behavior $\sigma_1^{\rm exc}(\omega) \propto \omega^n$ that grows stronger as the temperature decreases and extends all the way through the far-infrared. With $n \approx 0.8$ to 1.5 the exponent is significantly smaller than predicted by Ng and Lee [Phys. Rev. Lett. **99**, 156402 (2007)] for spinon contributions to the optical conductivity. We suggest fluctuations become important in the spin-liquid state and couple to the electrodynamic properties differently compared to the antiferromagnetic Mott insulator κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl. We discuss the various possibilities of how charge fluctuations are influenced by the presence or absence of magnetic order.

PACS numbers: 75.10.Kt 71.30.+h, 74.70.Kn, 78.30.Jw

I. INTRODUCTION

Among the two-dimensional organic charge-transfer compounds, the κ-(BEDT-TTF)$_2X$ family [where BEDT-TTF stands for bis-(ethylenedithio)tetrathiafulvalene] is of particular interest, because the constituting cationic dimers are arranged in an anisotropic triangular lattice (Fig. 1) with a delicate interplay between electronic correlations (given by the on-site Coulomb repulsion U), the effects of low dimensionality and spin frustration.[1,2] While κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl is a Mott insulator with antiferromagnetic order at low temperatures ($T_N \approx 25$ K),[3,4] slight pressure of 300 bar is sufficient to reach the superconducting state with $T_c \approx 12.8$ K.[5] For the Mott insulator κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ hydrostatic pressure of 1.5 kbar is required to become superconducting at 2.8 K.[6]

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ triggered particular interest because at ambient pressure no indication of magnetic order could be observed down to lowest temperatures, despite the considerable antiferromagnetic exchange of $J \approx 250$ K within the triangular lattice;[7,8] thus it is considered as the first realization of a quantum spin-liquid state suggested by Anderson 40 years ago.[9] Numerous theoretical and experimental work was performed during the last decade in order to explore mainly the thermodynamic and magnetic properties.[10–15] In the high-temperature range, the ^{1}H-NMR relaxation rate shows anomalies around 200 K,[8] the thermopower at 150 K,[16] microwave experiments exhibit a dielectric anomaly at 113 K,[17] while a peak in $\epsilon'(T)$ occurs below 60 K in the radio-frequency range.[18] In addition, a low-temperature anomaly near 6 K has been observed in thermodynamic,[7,10] transport,[11] dielectric[17] and lattice[19] properties that has not been explained satisfactorily.

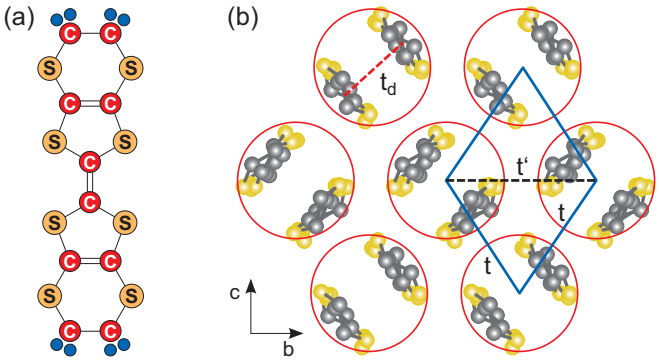

FIG. 1: (Color online) (a) Sketch of the BEDT-TTF molecule. (b) For κ-(BEDT-TTF)$_2X$ the molecules are arranged in dimers, which constitute an anisotropic triangular lattice within the conduction layer. In the case of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ the plane is labeled as bc, indicated by the arrows, while it is the ca-plane in the case of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl. The inter-dimer transfer integrals are labeled by t and t' and can be calculated by tight-binding studies of molecular orbitals or ab-initio calculations.[12,13,21] With the intra-dimer transfer integral $t_d \approx 0.2$ eV[16,22] and the on-site Coulomb repulsion $U \approx 2t_d$,[23] one obtains at ambient conditions $U/t = 5.5$ with the ratio of the two inter-dimer transfer integrals $t'/t \approx 0.44$ in the case of the Mott insulator κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl. For the spin-liquid compound κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, the effective Hubbard U is larger ($U/t = 7.3$) and most important the transfer integrals $t'/t = 0.83$ are very close to equality.

Also in the charge dynamics the spin-liquid compound κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ reveals a qualitatively different behavior compared to the Mott insulator κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, as first pointed out by Kezsmarki *et al.*[20] While the dc conductivity of both compounds behaves activated at low-temperature, κ-(BEDT-TTF)$_2$-

$Cu_2(CN)_3$ never shows a true Mott gap in the optical conductivity. On the contrary, a large excess absorption is found that increases with decreasing temperature. This frequency-dependent conductivity follows a power law over an extremely large spectral range from 20 cm^{-1} up to the mid-infrared. Our findings quantitatively do not follow the predictions of Ng and Lee who suggested that the gapless spinons contribute to the optical conductivity inside the charge gap.[24] Instead, we discuss alternative explanations for this unusual excess conductivity.

II. EXPERIMENTAL DETAILS

Single crystals of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ (abbreviated as κ-CN) and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (κ-Cl hereafter) were grown by electrochemical methods and can reach up to 2×2 mm^2 in size with nicely shining surfaces; the thickness was typically 0.1 mm in the case of κ-CN and 0.4 mm for κ-Cl specimens. Temperature dependent optical reflection experiments $R(\nu,T)$ were performed in a wide frequency range using several Fourier transform infrared spectrometers ($23-12\,000$ cm^{-1}) with an infrared microscope attached to it;[25,26] in addition the high-frequency optical properties (up to 35 000 cm^{-1}) were determined by spectroscopic ellipsometry at room temperature. For $T<100$ K the optical transmission was measured in the THz range ($18-46$ cm^{-1}) using a coherent source spectrometer.[27] In all cases, the light was polarized in the two main directions of the crystal planes, indicated also in Fig. 1(b). In order to perform a Kramers-Kronig analysis,[28] the data were extrapolated at low-frequency according to the dc conductivity measured by the standard four-probe method. Alternative approaches by $R(\nu\rightarrow0)=$ const. and Hagen-Rubens extrapolation (for elevated temperatures) were tested, but yield only minor changes for $\nu<30$ cm^{-1} and basically no modifications above. We made sure that the low- and high-frequency extrapolations and data analysis was consistent for both compounds in order to enable a quantitative comparison.

Temperature-dependent measurements of the in-plane dc resistivity were performed on crystals from the same batch as used for the optical investigations. The contacts were made by pasting four gold wires directly onto the specimen with a small amount of carbon paint. In order to avoid heating the current was kept below 10 μA.[29]

III. RESULTS AND ANALYSIS

The temperature dependent resistivity of κ-CN and κ-Cl plotted in Fig. 2(a) demonstrates the insulating behavior of both compounds, but also important differences: cooling from room temperature κ-Cl crosses over from a semiconducting phase to a Mott insulator at $T_M\approx40$ K and orders antiferromagnetically around $T_N=25$ K.[29,30] For κ-CN the resistivity continuously

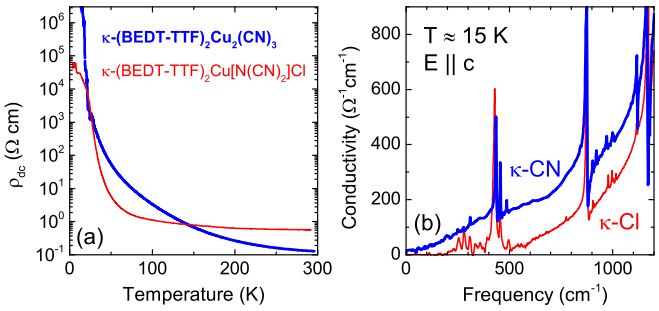

FIG. 2: (Color online) (a) The temperature dependence of the in-plane dc resistivity of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ (bold blue line) and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (light red line) evidences an insulating behavior. (b) The low-temperature optical conductivity (κ-CN: $T=13$ K; κ-Cl: $T=20$ K) does not show a Mott gap, but also reveals important differences between both compounds.

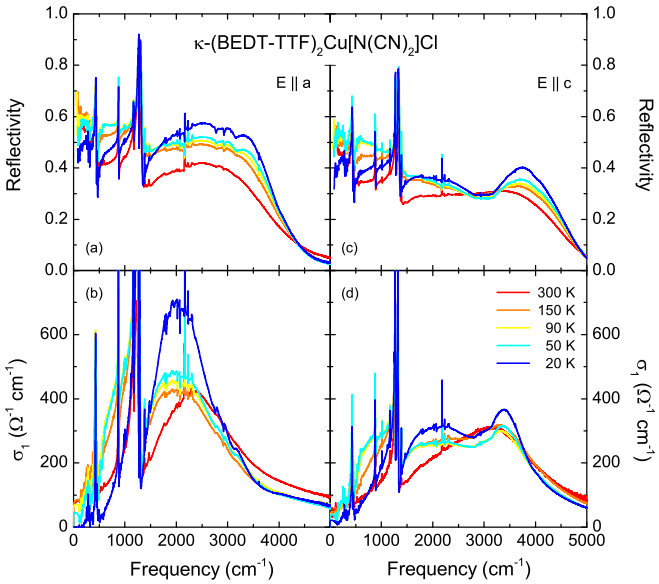

FIG. 3: (Color online) Evolvement of the optical reflectivity and conductivity of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl as the temperatures is varied. For both polarizations of the light, a gap opens upon cooling and the spectral weight shifts to higher energies.

increases upon cooling without any anomaly. Although no single activation energy can be extract,[16,20] below approximately 100 K the slope of the Arrhenius plot $\rho(T)\propto\exp\{\Delta/T\}$ corresponds to $\Delta\approx200$ K, right in the range of the exchange coupling J. The in-plane optical conductivity of both compounds [Fig. 2(b)] vanishes for low frequencies and temperatures, but the in-gap conductivity is significantly larger for κ-CN compared to κ-Cl. When extrapolating $\sigma_1(\omega)$ linearly to zero, we may identify the Mott gap around 500 cm^{-1} for κ-Cl at $T=20$ K; however, it is not as well pronounced and with stronger vibronic contributions than reported from early measurements.[31]

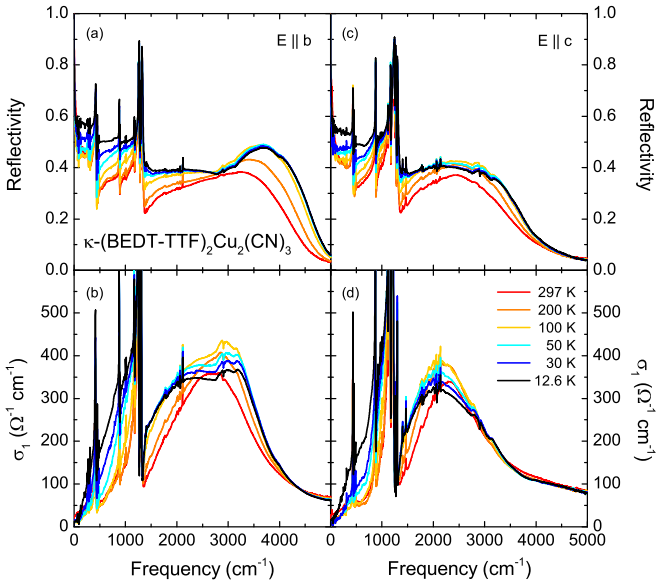

FIG. 4: (Color online) Optical reflectivity and conductivity of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ measured at different temperatures along the two in-plane polarizations as indicated. As the temperature is lowered the low-frequency reflectivity and conductivity rises, very much in contrast to κ-(BEDT-TTF)$_2$-Cu[N(CN)$_2$]Cl displayed in Fig. 2.

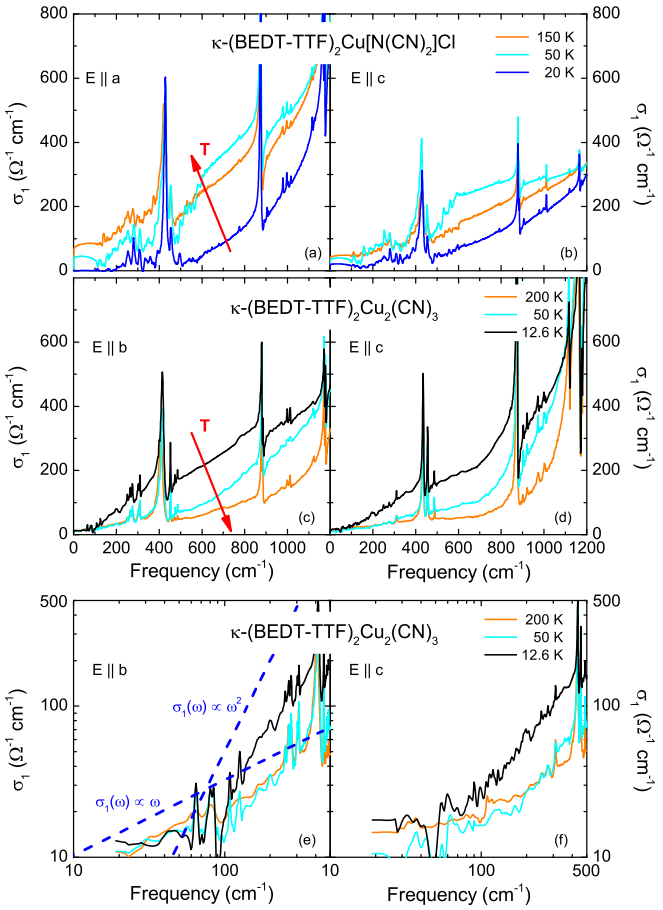

FIG. 5: (Color online) Optical conductivity of (a,b) κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl and (c,d) κ-(BEDT-TTF)$_2$-Cu$_2$(CN)$_3$ for the two in-plane polarizations. The temperature evolution is completely different for the two compounds, as indicated by the red arrows. (e,f) The low-frequency conductivity of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ plotted in a double logarithmic fashion in order to demonstrate the power-law behavior. The blue dashed lines correspond to $\sigma_1(\omega) \propto \omega$ and $\sigma_1(\omega) \propto \omega^2$, respectively.

In Fig. 3 the frequency-dependent reflectivity and conductivity of κ-Cl is plotted for different temperatures and polarizations using data taken by Faltermeier *et al.*[26] Since the optical properties of κ-(BEDT-TTF)$_2$Cu[N-(CN)$_2$]Br$_x$Cl$_{1-x}$ ($0 \leq x < 1$) have been presented and extensively analyzed during the last years, we refer to Refs. 26,32–34 for a detailed discussion.

Here we concentrate on the spin-liquid compound. In Fig. 4 the infrared reflectivity and conductivity of κ-CN are displayed for different temperatures; the data are in accord with previous measurements.[20,35] The optical response is governed by a broad peak in the mid-infrared caused by transitions between the lower and upper Hubbard band and intra-dimer excitations; in addition a large number of vibrational modes extend down to 100 cm^{-1}. The transition between the Hubbard bands peaks around 2100 cm^{-1} while the intra-dimer excitations center around 3000 cm^{-1} (more pronounced for $E \parallel b$); this is marginally lower in energy than for κ-Cl.[26] Calculations by density functional theory and tight binding methods yield an intra-dimer transfer integral $t_d \approx 170$ meV with a slight increase upon cooling,[21] in accord with our observations. The Hubbard band, on the other hand, shifts to lower energies as the temperature is reduced.

A. Mott gap

While at first glance the optical spectra of both Mott-insulators might look the same at room temperature, there are significant differences as far as the temperature dependence is concerned; Fig. 5 makes it particularly clear. In the case of κ-Cl the Mott insulating state gradually develops upon cooling, seen in Fig. 5(a,b) by the drop of the optical conductivity in the far-infrared range. Accordingly the spectral weight shifts to higher frequencies as the temperature is reduced.[33] The Mott gap increases upon cooling and arrives at $\Delta_\rho(k_B/hc) \approx 500$ cm^{-1} for $T = 20$ K and might become slightly larger in the $T \to 0$ limit. Systematic investigations as a function of effective correlations U/t by applying chemical pressure[26,32,33] confirm this assignment.

The optical conductivity of κ-CN, however, exhibits the *opposite temperature dependence* [Fig. 5(c,d)], and it is not possible to identify a clear-cut energy gap from our optical measurements. While in the low-frequency limit ($\nu \to 0$) the conductivity decreases upon cooling

[according to the insulating behavior observed in the dc resistivity, Fig. 2(a)], above approximately 100 cm^{-1} the infrared conductivity actually rises. This is in stark contrast to the opening of an energy gap inferred from $\rho(T)$; instead it indicates that additional excitations develop for low temperatures, which extend down to small frequencies. In other materials, such as cuprates, where a pseudogap develops upon cooling even in the superconducting systems,[36] the in-gap spectral weight is reduced with lowering temperature and shifts to higher energies. In the present case of the quantum spin-liquid compound κ-CN, however, the conductivity behaves completely different with a strong frequency and temperature dependence of $\sigma_1(\omega, T)$. The in-gap absorption increases with lowering temperature.

B. Spinon excitations

In order to explain the strong in-gap excitations, Ng and Lee suggested that due to coupling with the internal gauge field, spinons may contribute to the optical conductivity of a spin liquid.[24] They predict a strongly enhanced conductivity within the Mott gap compared to the two spin wave absorption in a Néel-ordered insulator. It results in a power-law absorption at low frequencies, i.e. for energies smaller than the exchange coupling $J \approx 250$ K. For low frequencies ($\hbar\omega < k_B T$) the optical conductivity $\sigma_1(\omega) \propto \omega^2$, while for $\hbar\omega > k_B T$ the power law should increase to $\sigma_1(\omega) \propto \omega^{3.33}$.

In order to check whether such a behavior can indeed be found in the spin-liquid compound κ-CN, we first tried to fit our conductivity data directly by the expected power law $\sigma_1(\omega) \propto \omega^n$. The double-logarithmic plot in Fig. 5(e,f) allows us to readily determine the exponent n: for high temperatures we obtain $n \approx 1$ at small frequencies with a slight increase to $n \approx 1.5$ above 150 cm^{-1}. For $T = 12.5$ K, $\sigma_1(\omega)$ rises even slower than linear at low frequencies with a crossover to $n = 2$ for $\nu > 70$ cm^{-1}. The power-law exponents are slightly smaller for $E \parallel c$ compared to $E \parallel b$. While we might find a qualitative agreement with theory of optical excitation of gapless spinons, the experimentally obtained power laws are weaker by a factor of two compared to the proposed ones.

C. Decompose the spectra

As can be seen in Figs. 2 and 3, the spectra of κ-CN and κ-Cl are rich in vibrational excitations. Most of them are due to internal vibrations of the BEDT-TTF molecules, with many of them excited via electron-molecular vibrational (emv) coupling[25] which results in asymmetric Fano resonances. They are best taken into account by the cluster model (see for example Rice[37] and Delhaes and Yartsev[38]) that describes the optical properties of molecular clusters with arbitrary geometry and equilibrium charge density distribution.[26,39] In addition,

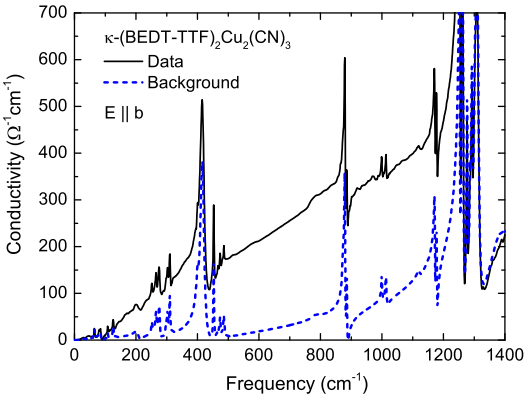

FIG. 6: (Color online) Optical conductivity of κ-(BEDT--TTF)$_2$Cu$_2$(CN)$_3$ ($E \parallel b$, $T = 12.6$ K) and background due to molecular and lattice vibrations and interband transitions, which is subtracted in order to retrieve the possible electronic and spinon contributions.

vibrations of the anions as well as lattice vibrations are present.

Due to strong electronic correlations, in these Mott insulators itinerant carriers are absent at low temperatures, as discussed in detail in Ref. 26. Thus except for elevated temperatures, no Drude-like contribution is found in the spectra. Transitions between the Hubbard bands can be identified in the optical conductivity as maxima slightly above 2000 cm^{-1}. Intradimer transitions cause a band around 3000 cm^{-1} that shows up as a shoulder or separate maximum.[35] Both contributions form the dominant mid-infrared band; we describe these excitations by the Lorentzian model.

The uncoupled vibrational features and electronic excitations were fitted by the Lorentz model[28]

$$\hat{\sigma}^{\mathrm{Lorentz}} = \sigma_1(\omega) + \mathrm{i}\sigma_2(\omega) = \frac{Ne^2}{m} \frac{\omega}{\mathrm{i}(\omega_0^2 - \omega^2) + \gamma\omega} \quad (1)$$

centered around the eigenfrequency ω_0 with a width $\gamma = 1/\tau$. Depending on the interaction of the vibrational excitations with the electronic background, the modes may become asymmetric and have to be modeled by[40]

$$\hat{\sigma}^{\mathrm{Fano}} = \mathrm{i}\sigma_0(q - \mathrm{i})^2(\mathrm{i} + x)^{-1} \quad , \quad (2)$$

where σ_0 is the background, $x = (\omega^2 - {\omega_0}^2)/\gamma\omega$ (γ and ω_0 are the linewidth and the resonant frequency, respectively) and q is the Fano parameter reflecting the degree of asymmetry of the peak. As an example, in Fig. 6 the optical conductivity for κ-CN is displayed as measured at $T = 12.6$ K for $E \parallel b$; we also plot the background contributions due to intra- and inter-molecular vibrational excitations, due to transitions between the Hubbard bands and by intra-dimer excitations.

In order to disentangle the various contributions we simultaneously fitted the measured reflectivity and conductivity spectra in the frequency range below 1100 –

1400 cm^{-1} (depending on temperature and polarization) by

$$\hat{\sigma}(\omega) = \hat{\sigma}^{\text{background}}(\omega) + \hat{\sigma}^{\text{exc}}(\omega) = \sum_i \hat{\sigma}_i^{\text{Lorentz}} + \sum_j \hat{\sigma}_j^{\text{Fano}} + \hat{\sigma}^{\text{exc}}(\omega) \quad , \quad (3)$$

where we used a minimum number of Lorentz terms $\hat{\sigma}_i^{\text{Lorentz}}$ and of Fano terms $\hat{\sigma}_i^{\text{Fano}}$. A similar fitting procedure was previously applied successfully for the analysis of the substitutional series κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]-Br$_x$Cl$_{1-x}$.[34] For the excess conductivity contribution we added two power-law terms with different prefactors A and B and exponents n and m:

$$\sigma_1^{\text{exc}} = A\,\omega^n|_{\omega<\omega_c} + B\,\omega^m|_{\omega>\omega_c} \quad . \quad (4)$$

The crossover frequency between the regions of two power-law exponents was found to be at 600 cm^{-1} at T = 300 K and increasing to 800 cm^{-1} for low temperatures. The automated procedure was based on the root-mean-square deviation of the fit compared to the experimental data. The uncertainty for the exponent was estimated to be ± 0.2 and indicated by error bars in Fig. 8.

D. Power laws

The residual conductivity $\sigma_1^{\text{exc}} = \sigma_1 - \sigma_1^{\text{background}}$ is plotted in Fig. 7 for several temperatures. The same analysis can be done for the polarization $E \parallel c$, yielding very similar results. Above 20 cm^{-1} the conductivity follows a power-law ω^n over a very large range which extends to 600 cm^{-1} at room temperature and up to even 800 cm^{-1} at low temperatures. Above that frequency, a different exponent may be identified in a limited range up to 1200 cm^{-1}. Most important, there is definitely no increase in slope observed when going from low to high frequencies; we cannot identify any crossover to occur at a frequency $\hbar\omega \approx k_B T$, i.e. below 200 cm^{-1}. This cannot be reconciled with the prediction of the spinon theory by Ng and Lee.[24]

In Fig. 8 we summarize the temperature dependence of the exponent n obtained in the high and low-frequency range for the two directions of polarization. It starts with a linear dependence $\sigma_1^{\text{exc}} \propto \omega$ at ambient temperature, but then increases to almost $n \approx 1.5$ when approaching $T \approx 50$ K. A noticeable change is observed when cooled down further: the power-law exponent saturates or even decreases to about 1.25. Taking the uncertainty of determination into account, the low-temperature value is approximately $n = 1.35 \pm 0.1$ for both directions. Interestingly, also the higher-frequency exponent significantly drops for $T < 50$ K, and $\sigma_1^{\text{exc}}(\omega) \approx$ const. below 20 K. At no time the power-law in conductivity approaches a quadratic behavior in frequency or even larger exponents n or m.

The situation is completely different for the Mott-insulator κ-Cl. From Fig. 2(b) it becomes obvious that

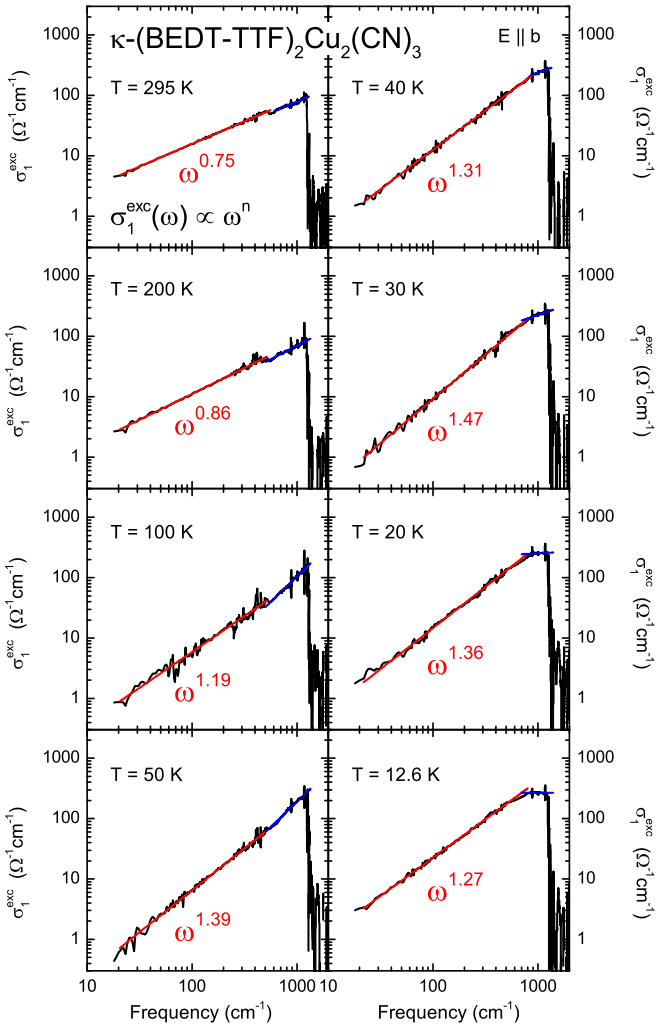

FIG. 7: (Color online) Frequency dependent conductivity of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ after the background due to vibrational and interband excitations has been subtracted. The experiments were performed for the polarization $E \parallel b$ at different temperatures as indicated. A power-law behavior $\sigma_1(\omega) - \sigma_1^{\text{background}}(\omega) = \sigma_1^{\text{exc}}(\omega) \propto \omega^n$ can be extracted over a large frequency range (indicated by red lines). A change in slope may be identified for higher frequencies (blue lines) that becomes in particular obvious at low temperatures. The temperature dependence of the exponents are summarized in Fig. 8 for both polarizations.

the optical conductivity is substantially smaller in the spectral range $\nu < 1000$ cm^{-1}. The Mott gap is well defined for both polarizations and it continuously increases to 500 cm^{-1} as the temperature decreases to 20 K [Fig. 5(a,b)]. The up-shift in spectral weight and the reduced contribution of the conduction electrons below 50 K is rather a consequence of the Mott state than magnetic order.[29,33,41] Tuning the effective correlations U/t by chemical[26,33] and hydrostatic pressure[45] causes spectral weight to shift to lower energies and fill the gap. Although the room-temperature conductivity appears similar for both compounds, the further evolvement is dis-

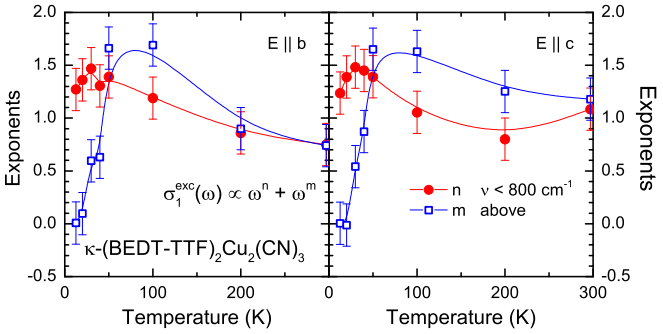

FIG. 8: (Color online) Exponents n (red dots) and m (blue squares) extracted from the power law $\sigma_1^{\rm exc} = A\,\omega^n|_{\omega<\omega_c} + B\,\omega^m|_{\omega>\omega_c}$ measured at different temperatures for the polarizations $E \parallel b$ and $E \parallel c$. The lines correspond to spline interpolations.

tinct: for κ-Cl it is not possible to extract a power-law behavior $\sigma_1^{\rm exc}(\omega) \propto \omega^n$ over a sufficiently large frequency range for any temperature $T < 300$ K.

IV. DISCUSSION

The most important finding of our experiments is the absence of a Mott gap in the optical spectra of quantum spin-liquid compound κ-CN in stark contrast to the magnetically ordered Mott insulator κ-Cl. As the temperature is reduced, κ-CN develops a large excess conductivity.

The low-frequency behavior of the pristine conductivity data highlighted in Fig. 5(e,f) could in fact be caused by optical excitations of gapless spinons, as suggest by Ng and Lee,[24] although the conductivity should increase much faster and exhibit a stronger frequency dependence than it actually does: the low-temperature exponents extracted for the power law are significantly lower than predicted. At $T = 12.6$ K there is a crossover around 70 cm^{-1} where the linear rise increases to a quadratic behavior in frequency. When taking out the vibrational features and interband transitions in our advanced analysis (Sec. III C), this behavior continues all the way up to the mid-infrared spectral range (Fig. 7): this casts some doubt to the present explanation. Even more surprising is the fact, that we do observe the power-law behavior up to room temperature where light-induced spinon excitations should not be observable. A final decision of the applicability of the model can only be based on advanced experiments at lower frequencies and lower temperatures.

Conventionally, the κ-phase BEDT-TTF compounds are treated theoretically as half-filled systems with one electron per dimer.[2,46,47] Recently two approaches were brought forward both based on a quarter-filled extended Hubbard model that includes the interaction V between molecules on the same but also different dimers. In general, within Hubbard-type models there is no contribution from spins to optics; however, besides single electron conductivity, singlets might form which move around leading to an additional contribution to the optical conductivity.

On this ground, Hotta derives an effective dipolar-spin model.[48] She suggests that despite the strong intra-dimer coupling t_d quantum electric dipoles are formed on the dimers which interact with each other and thus modify the exchange coupling J between the spins on the dimers, crucial for the formation of the spin-liquid state. The quantum electric dipoles fluctuate by t_d. For large t_d a dimer Mott insulator is stable, forming a dipolar liquid, but if V is large compared to t_d, charge order emerges (dipolar solid). Mazumdar and collaborators[49] proposed a paired-electron crystal for which singlet-paired states coexist with charge ordering.

Although optical investigations rule out any significant charge disproportionation,[50,51] charge and spin fluctuations might be present in κ-CN. A proposed paired-electron liquid or dipolar liquid could explain the linear temperature dependence of the heat capacity that evidences gapless fermionic excitations.[10] Here the finite entropy comes from the singlets forming the ground state. At the same time, spin excitations remain gapped, as inferred from measurements of the thermal conductivity.[11] These mobile singlets of the fluctuating paired-electron liquid contribute to the optical conductivity differently than single electrons probed by dc transport. It is highly desirable to further investigate this scenario theoretically and extract possible power-laws in the optical conductivity. As far as experiments are concerned, we plan optical investigations in the presence of an external magnetic field in order to influence the ground state. Pratt *et al.* discovered that a small magnetic field produces a phase transition between a spin-liquid phase and an antiferromagnetic phase.[15]

At the present point, we are not definite whether the power-law behavior is just fading out we above ω_c, or whether we actually enter another regime. In favor of the later scenario is the surprising fact that we observe the same development with temperature for both orientations. At low temperatures the conductivity becomes frequency independent for $\omega > \omega_c$. This is consistent with fluctuations to diminish. It is interesting to note that the power-law exponent n of the excess conductivity decreases with temperature and can be extrapolated to zero around a temperature which is comparable in energy with $\hbar\omega_c$.

As another approach to gain information about the in-gap excitations, we have performed an extended Drude analysis of the optical conductivity of κ-CN.[28] From that we obtain the frequency dependence of the scattering rate $1/\tau(\omega)$ and the effective mass $m^*(\omega)$ at different temperatures. Unfortunately, the results do not allow us to draw any conclusion that go beyond the present speculations.

The dependence $\sigma_1^{\rm exc}(\omega, T) = A(T)\,\omega^n$ observed for the conductivity of quantum spin-liquid compound κ-CN could in fact be caused by fluctuations. The contribution $A(T)$ significantly increases with lowering temperature

which infers quantum fluctuations. In the vicinity of a quantum critical point,[52,53] power-law behavior is often observed and quantum fluctuations become more pronounced when T is reduced. We have to keep in mind, however, that this behavior is observed up to rather high frequencies and at elevated temperatures, far beyond the regime quantum fluctuations should be dominant.

It is also not clear why this behavior saturates around 50 K, since no magnetic, charge, or structural order is revealed at any temperature. It coincides with anomalies in the dielectric properties.[17,18] Hotta proposed a dipolar-spin liquid[48] assuming quantum electric dipoles on the dimers that interact with each other through the dipolar spin coupling. However, there are no indications of charge order in these κ-phase compounds,[50,51] and soft modes and collective charge excitations commonly show up at much lower frequencies.[54,55] We suggest that charge fluctuations are strongly enhanced in the vicinity of a quantum critical point and correspond to a much larger energy scale than commonly observed in the case of quantum fluctuations in the spin degree of freedom.

Most important, a very similar dielectric anomaly was observed in the in-plane and out-of-plane properties of κ-Cl[50,56,57] where the Mott gap is clearly developed at low temperatures and no in-gap contribution are present in the optical conductivity. Tomić and collaborators suggested that grain boundaries, linked to magnetically ordered domains in κ-Cl, might move, thus causing a strong dielectric contribution.[50] This argument, however, does not hold for κ-CN where no magnetic order is present down to lowest temperatures. Pressure dependent investigations on κ-Cl showed that the bandwidth-controlled Mott criticality involves critical fluctuations in charge,[58] spin,[59] and lattice.[60,61] Nothing like that is known for the spin-liquid compound κ-CN for the intermediate temperature range. While this issue can be clarified by further experimental studies, considerable theoretical work is required in order to describe the power-law behavior the dimer Mott insulator with a quantum spin-liquid state, in the low-frequency limit as well as in the far-infrared range.

There remains the question whether the behavior changes at the 6 K anomaly. There seems to be some effect on the transport and dielectric properties,[11,17] which could also influence the optical properties. At the present time, we are not able to perform optical reflection experiments at temperatures well below 5 K in order to reliably detect modifications in the power-law exponent or even a breakdown of this behavior. Experiments at ^{3}He temperatures are in preparation.

V. CONCLUSION

From our optical investigations of two Mott-insulators with very similar triangular structure but different magnetic ground states, we can conclude that only the magnetically ordered organic salt κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl exhibits a well defined Mott gap at low temperatures. The quantum spin-liquid compound κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ reveals a power-law behavior in the frequency-dependent conductivity that becomes stronger as the temperature decreases. We suggest spin and charge fluctuations get important in the spin-liquid state and couple to the electrodynamic properties differently compared to an antiferromagnetic Mott insulator. The paired-electron liquid proposed by Clay and Mazumdar[49] or the dipolar spin liquid suggested by Hotta[48] might be possible scenarios. The power-law $\sigma_1^{\rm exc}(\omega)$ observed in an extended range of frequency and temperature remains a puzzle that calls for further investigations of how charge fluctuations are influenced by the presence or absence of magnetic order.

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[1] K. Kanoda and R. Kato, Annu. Rev. Condens. Matter Phys. **2**, 167 (2011).

[2] B. J. Powell and R. H McKenzie, Rep. Prog. Phys. **74**, 056501 (2011).

[3] U. Welp, S. Fleshler, W. K. Kwok, G. W. Crabtree, K. D. Carlson, H. H. Wang, U. Geiser, J. M. Williams, and V. M. Hitsman, Phys. Rev. Lett. **69**, 840 (1992).

[4] K. Miyagawa, A. Kawamoto, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. **75**, 1174 (1995).

[5] J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, K. M. Wathins, J. M. Kommers, S. J. Boryschuk, A. V. S. Crouch, W. K. Kwok, J. E. Schirber, D. L. Overmyer, D. Jung, and M.-H. Whangbo, Inorg. Chem. **29**, 3272 (1990).

[6] U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, H. A. Charlier, J. E. Heindl, G. A. Yaconi, B. J. Love, M.W. Lathrop, J. E. Schirber, D. L. Overmyer, J. Q. Ren, and M.-H. Whangbo, Inorg. Chem. **30**, 2586 (1991).

[7] Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, G. Saito, Phys. Rev. Lett. **91**, 107001 (2003)

[8] Y. Kurosaki, Y. Shimizu, K. Miyagawa, K. Kanoda, G. Saito, Phys. Rev. Lett. **95**, 177001 (2005).

[9] P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973).

[10] S. Yamashita, Y. Nakazawa, M. Oguni, Y. Oshima, H. Jojiri, K. Miyagawa, and K. Kanoda, Nat. Phys. **4**, 459 (2008).

[11] M. Yamashita, N. Nakata, Y. Kasahara, T. Sasaki, N. Yoneyama, N. Kobayashi, S. Fujimoto, T. Shibauchi, and Y. Matsuda, Nat. Phys. **5**, 44 (2008).

[12] K. Nakamura, Y. Yoshimoto, T. Kosugi, R. Arita, and M. Imada, J. Phys. Soc. Jpn. **78**, 083710 (2009).

[13] H. C. Kandpal, I. Opahle, Y.-Z. Zhang, H. O. Jeschke, and R. Valentí, Phys. Rev. Lett. **103**, 067004 (2009).

[14] L. Balents, Nature **464**, 199 (2010).

[15] F. L. Pratt, P. J. Baker, S. J. Blundell, T. Lancaster, S. Ohira- Kawamura, C. Baines, Y. Shimizu, K. Kanoda, I. Watanabe, and G. Saito, Nature (London) **471**, 612 (2011).

[16] T. Komatsu, N. Matsukawa, T. Inoue, and G. Saito, J. Phys. Soc. Jpn. **65**, 1340 (1996).

[17] M. Poirier, S. Parent, A. Côté, K. Miyagawa, K. Kanoda, and Y. Shimizu, Phys. Rev. B **85**, 134444 (2012).

[18] M. Abdel-Jawad, I. Terasaki, T. Sasaki, N. Yoneyama, N. Kobayashi, Y. Uesu, and C. Hotta, Phys. Rev. B **82**, 125119 (2010).

[19] R. S. Manna, M. de Souza, A. Bruhl, J. A. Schlueter, and M. Lang, Phys. Rev. Lett. **104**, 016403 (2010).

[20] I. Kezsmarki, Y. Shimizu, G. Mihaly, Y. Tokura, K. Kanoda, and G. Saito, Phys. Rev. B **74**, 201101 (2006) crossover

[21] H. O. Jeschke, M. de Souza, R. Valentí, R. S. Manna, M. Lang, and J. A. Schlueter, Phys. Rev. B. **85**, 035125 (2012).

[22] K. Oshima, T. Mori, H. Inokuchi, H. Urayama, H. Yamochi, and G. Saito, Phys. Rev. B **38**, 938 (1988).

[23] R.H. McKenzie, Comments Cond. Mat. **18**, 309 (1998).

[24] T.-K. Ng and P. A. Lee, Phys. Rev. Lett. **99**, 156402 (2007).

[25] M. Dressel and N. Drichko, Chem. Rev. **104**, 5689 (2004).

[26] D. Faltermeier, J. Barz, M. Dumm, M. Dressel, N. Drichko, B. Petrov, V. Semkin, R. Vlasova, C. Méziere, and P. Batail, Phys. Rev. B **76**, 165113 (2007).

[27] B. Gorshunov, A. Volkov, I. Spektor, A. Prokhorov, A. Mukhin, M. Dressel, S. Uchida, and A. Loidl, Int. J. of Infrared and Millimeter Waves **26**, 1217 (2005).

[28] M. Dressel and G. Grüner, *Electrodynamics of Solids* (Cambridge University Press, Cambridge, 2002).

[29] S. Yasin, M. Dumm, B. Salameh, P. Batail, C. Mziére, and M. Dressel, Eur. Phys. J. B **79**, 383 (2011).

[30] At elevated temperatures κ-Cl can be described by a semiconductor with a very small gap and temperature independent susceptibility. As the temperature is reduced below $T_M \approx 40$ K it shifts to a much more insulating behavior with field-dependent magnetic properties indicating that effects of electronic correlations become significant. Cf. A. Kawamoto, K. Miyagawa, Y. Nakazawa, and K. Kanoda, Phys. Rev. B **52**, 15522 (1995).

[31] K. Kornelsen, J. E. Eldridge, H. H. Wang, H. A. Charlier, and J. M. Williams, Solid State Commun. **81**, 343 (1992).

[32] J. Merino, M. Dumm, N. Drichko, M. Dressel, and R.H. McKenzie, Phys. Rev. Lett. **100**, 086404 (2008).

[33] M. Dumm, D. Faltermeier, N. Drichko, M. Dressel, C. Méziere, and P. Batail, Phys. Rev. B **79**, 195106 (2009).

[34] M. Dressel D. Faltermeier, M. Dumm, N. Drichko, B. Petrov, V. Semkin, R. Vlasova, C. Mézière, and P. Batail, Physica B **404**, 541 (2009).

[35] The mid-infrared properties of both compounds are remarkably similar in their anisotropy and shape, when looking in the same crystallographic directions: $E \parallel a$ and $E \parallel c$ for κ-Cl correspond to $E \parallel c$ and $E \parallel b$ for κ-CN. In the second direction, the Hubbard excitations can be better distinguished from the intra-dimer excitations. Here the transition between the lower and upper Hubbard band shift down as the temperature is reduced, while inter-dimer excitations move up and become more prominent for the horizontal orientation in Fig. 1(b): $E \parallel c$ and $E \parallel b$, respectively. Our assignment (Ref. 26,33,34) was confirmed by calculations that combine density functional theory combined with with dynamical mean field theory. J. Ferber, K. Foyevtsova, H. O. Jeschke, and R. Valentí, arXiv:1209.4466.

[36] T. Timusk and B. Statt, Rep. Prog. Phys. **62**, 61 (1999).

[37] M.J. Rice, Phys. Rev. Lett. **37**, 36 (1976).

[38] Delhaes P., Yartsev V.M., Advances in Spectroscopy, **22**, R.J.H. Clark, R.E. Hester Eds. *John Wiley and Sons, 1993*, p. 199; V. M. Yartsev, O. Fichet, J.-P. Borgion and P. Delhaes. J. Phys. II France **3**, 647 (1993); V.M Yartsev , O.O. Drozdova, V.N. Semkin and R.M. Vlasova, J. Phys. I (France) **6**, 1673 (1996); V.M. Yartsev, in: *Materials and Measurements in Molecular Electronics*, ed. by K. Kajimura and S. Kanoda (Springer-Verlag, Berlin 1996), p. 189; V. M. Yartsev and A. Graja, Int. Journ. of Mod. Phys. B, **12**, 1643 (1998).

[39] R. M Vlasova, N. V. Drichko, B. V. Petrov, V. N. Semkin, D. Faltermeier, J. Barz, M. Dumm, M. Dressel, C. Mézière, and P. Batail, Physics of the Solid State **51**, 1041 (2009); R. M. Vlasova, B. V. Petrov, and V. N. Semkin, Physics of the Solid State **53**, 1781 (2011).

[40] U. Fano, Phys. Rev. **124**, 1866 (1961).

[41] The reports on the magnetic ordering do not agree in all details. Welp *et al.* (Ref. 3) see antiferromagnetic order up to $T_N = 45$ K and a weak ferromagnetic behavior below $T_C = 22$ K. NMR experiments, however, only show antiferromagnetic ordering at approximately 27 K (Ref. 4). Ishiguro and coworkers report antiferromagnetic resonances and find fluctuations well above 35 K (Refs. 42,43). The temperature dependence of the susceptibility $\chi(T)$ starts to decrease below 50 K, getting steeper as the temperature is drops further but vanishes only below 25 K, when the antiferromagnetic grounds state is completely established (Ref. 29). At higher fields, antiferromagnetic resonance have recently been observed in this range (Ref. 44).

[42] H. Ito, M. Kubota, Yu. V. Sushko, N.Kojima, G.Saito and T.Ishiguro, Synth. Met. **70**, 925 (1995).

[43] M. Kubota, G. Saito, H. Ito, T. Ishiguro, and N. Kojima, Mol. Cryst. Liq. Cryst. **284**, 367 (1996).

[44] Á. Antal, T. Fehér, A. Jánossy, E. Tátrai-Szekeres, and F. Fülöp, Phys. Rev. Lett. **102**, 086404 (2009).

[45] N. Drichko, M. Dressel, C. A. Kuntscher, A. Pashkin, A. Greco, J. Merino, and J. Schlueter, Phys. Rev. B **74**, 235121 (2006).

[46] H. Seo, C. Hotta, and H. Fukuyama, Chem. Rev. **104** 5005 (2004); H. Seo, J. Merino, H. Yoshioka, and M. Ogata, J. Phys. Soc. Jpn. **75** 051009 (2006).

[47] J. Merino and R. H. McKenzie, Phys. Rev. B **61**, 7996 (2000); B.J. Powell and R.H. McKenzie, J. Phys.: Cond. Matter. **18**, R827 (2006); J. Merino, M. Dumm, N. Drichko, M. Dressel, and R. H. McKenzie, Phys. Rev. Lett. **100**, 086404 (2008).

[48] C. Hotta, J. Phys. Soc. Jpn. **72**, 840 (2003); Phys. Rev. B **82**, 241104 (2010); Crystals **2**, 1155 (2012).

[49] H. Li, R. T. Clay, and S. Mazumdar, J. Phys.: Condens. Matter **22**, 272201 (2010); S. Dayal, R. T. Clay, H. Li, and S. Mazumdar, Phys. Rev. B **83** 245106 (2011); R. T. Clay, S. Dayal, H. Li, and S. Mazumdar, phys. stat. sol. (b) **249**, 991 (2012).

[50] S. Tomić, M. Pinteric, T. Ivek, K. Sedlmeier, S. Elsässer, R. Beyer, D. Schweitzer, J. A. Schlueter, and M. Dressel, to be published.

[51] K. Sedlmeier, S. Elsässer, R. Beyer, T. Ivek, D. Wu, J. A. Schlueter, and M. Dressel, arXiv:1208.2652.

[52] D. Belitz, T.R. Kirkpatrick, and T. Vojta, Rev. Mod. Phys. **77**, 579 (2005).

[53] H. v. Löhneysen, A. Rosch, M. Vojta, and P. Wölfle, Rev. Mod. Phys. **79**, 1015 (2007).

[54] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press, Oxford, 1977).

[55] M. Dressel, N. Drichko, and S. Kaiser, Physica C **470**, S589 (2010).

[56] M. Pinterić, M. Miljak, N. Biškup, O. Milat, I. Aviani, S. Tomić, D. Schweitzer, W. Strunz, and I. Heinen, Eur. Phys. J. B **11**, 217 (1999).

[57] P. Lunkenheimer, J. Müller, S. Krohns, F. Schrettle, A. Loidl, B. Hartmann, R. Rommel, M. de Souza, C. Hotta, J.A. Schlueter, and M. Lang, Nature Materials **11**, 755 (2012).

[58] F. Kagawa, K. Miyagawa, and K. Kanoda, Nature **436**, 534 (2005).

[59] F. Kagawa, K. Miyagawa, and K. Kanoda, Nature Physics **5**, 880 (2009).

[60] D. Fournier, M. Poirier, M. Castonguay, and K. Truong, Phys. Rev. Lett. **90**, 127002 (2003).

[61] M. de Souza, A. Brühl, C. Strack, B. Wolf, D. Schweitzer, and M. Lang, Phys. Rev. Lett. **99**, 037003 (2007).