Lattice Effects and Entropy Release at the Low-Temperature Phase Transition in the Spin-Liquid Candidate κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

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The spin-liquid candidate κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$ has been studied by measuring the uniaxial expansion coefficients α_i, the specific heat, and magnetic susceptibility. Special emphasis was placed on the mysterious anomaly around 6 K—a potential spin-liquid instability. Distinct and strongly anisotropic lattice effects have been observed at 6 K, clearly identifying this feature as a second-order phase transition. Owing to the large anomalies in α_i, the application of Grüneisen scaling has enabled us to determine the corresponding specific heat contribution and the entropy release. Comparison of the latter with available spin models suggests that spin degrees of freedom alone cannot account for the phase transition. Scenarios involving charge degrees of freedom are discussed.

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Organic charge-transfer salts show a rich variety of quantum phases resulting from the interplay of electronic correlations, low dimensionality, and frustrated magnetic interactions (see Refs. [1,2] for recent reviews). Recently, much excitement has been generated by the proposal of a quantum spin-liquid (QSL) state in the κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$ salt [3]. This system is a half-filled Mott insulator, where $(BEDT\text{-}TTF)_2^+$ dimers form a quasi-two-dimensional triangular lattice characterized by *interdimer* hopping amplitudes $t' \sim t$. The material lacks long-range magnetic order down to 32 mK [3], a small fraction of the estimated nearest-neighbor Heisenberg exchange coupling $J/k_B \simeq 250$ K [3,4]. This observation has stimulated numerous works aiming at an identification of the QSL state and its potential instabilities. A number of important questions have been raised such as the nature of the low-energy excitations [5,6], as well as the actual degree of frustration. According to Refs. [7,8], the system is less frustrated ($t'/t \sim 0.8$) than was previously thought [9], raising the question of how, under these conditions, a QSL state can be stabilized over magnetic order [4,10–15].

A central issue, which may hold the key for understanding the puzzling low-T properties, is posed by the mysterious anomaly around 6 K, about which very little is known. It appears as a hump in the specific heat [5], the NMR relaxation rate [3,16], and the thermal conductivity [6]. Various scenarios have been suggested including a crossover from a thermally to a quantum disordered state [5] or an instability of the QSL. For the latter, a spin-chirality ordering [17], a Z_2 vortex formation [18], a pairing of spinons [19], an exciton condensate [20], or a nematic paired state [21] have been discussed. Unfortunately, neutron scattering—the technique of choice for identifying a potential order parameter—is very difficult to apply due to the organic nature of the material. However, according to Refs. [19,20], the lattice strain could constitute such a sensitive probe as the QSL instabilities discussed there break the lattice symmetry.

In this Letter, we report on a study of lattice effects by means of thermal expansion measurements. Our data reveal a distinct and strongly anisotropic anomaly at 6 K—clear evidence for a second-order phase transition. The application of a thermodynamic analysis enabled us to determine the entropy release at the transition. This quantity provides a crucial test for any model attempting to describe the low-T properties of this material.

The thermal expansion measurements were carried out by using an ultrahigh-resolution capacitive dilatometer (built after [22]) enabling the detection of length changes $\Delta l \geq 10^{-2}$ Å. The calorimetric and magnetic measurements were performed employing a microcalorimeter [23] and a SQUID magnetometer (Quantum Design Magnetic Property Measurement System), respectively. The single crystals used were prepared by following the standard procedure [24]. The crystals, taken from two independently prepared batches, have the shape of flat distorted hexagons with dimensions of about $1 \times 0.8 \times 0.1$ mm^3. The uniaxial pressure exerted on the crystal by the dilatometer ranges from 1 to 6 bar.

In Fig. 1, we show the results of the uniaxial expansion coefficients $\alpha_i(T) = l_i^{-1} dl_i/dT$ measured along the in-plane $i = b$ and c axes and the cross-plane a axis below 200 K. Besides the distinct anomalies at low temperatures, which will be discussed below, the data reveal strongly anisotropic expansivities. Surprisingly, a particularly strongly pronounced anisotropy is found for the in-plane data α_b and α_c, both of which deviate markedly from an ordinary lattice expansion. Upon cooling, α_c becomes reduced almost linearly down to 70 K, changes sign at 50 K, and passes through a shallow minimum around 30 K. This contrasts with the pronounced maximum in α_b at $T_{\max} \sim 70$ K. The temperature range around $T_{\max}$ is also

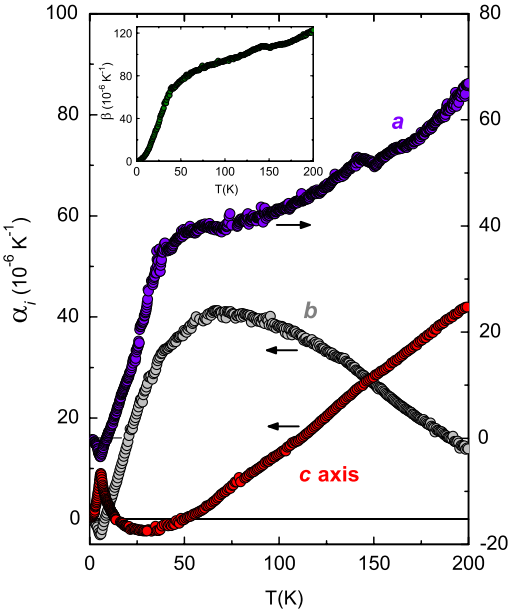

FIG. 1 (color online). Uniaxial expansivities α_i of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ along the in-plane $i = b$ and c axes (left scale) and along the out-of-plane $i = a$ axis (right scale). Inset shows the volume expansion coefficient β.

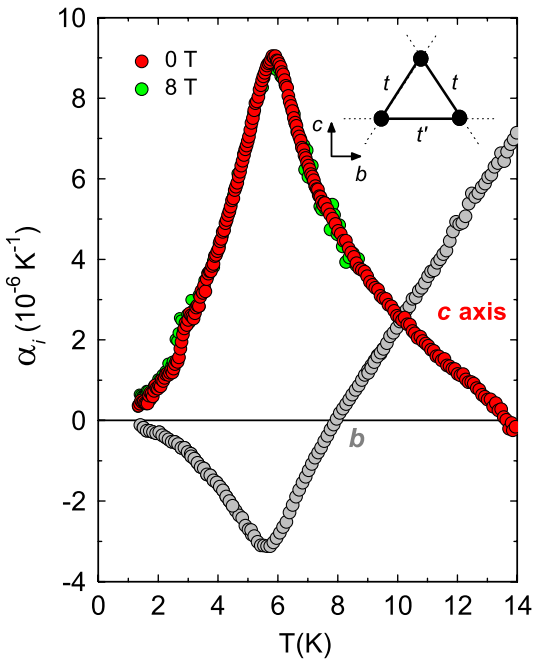

FIG. 2 (color online). In-plane expansivities of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ on expanded scales with α_c taken in $B = 0$ [dark gray (red) circles] and 8 T [light gray (green) circles]. Inset: 2D triangular-lattice dimer model with hopping amplitudes t' and t.

distinct in the out-of-plane data α_a, where a shoulder appears. The anomalous T dependencies in α_i suggest that, besides phonons, other excitations contribute significantly to the thermal expansion. For example, the sign change in α_c for T below about 50 K followed by a minimum indicates a substantial negative contribution which is maximum around 30 K. Such a broad negative anomaly, lacking any signature in the magnetic properties [3], may have different origins such as geometrical frustration and/or quenched disorder (see, e.g., [25]). Likewise, a rounded feature, similar to the one observed in the magnetic susceptibility $\chi(T)$ at $T_\chi \approx 85$ K [3], is expected at $T_\alpha \sim T_\chi$ as a result of short-range antiferromagnetic correlations [26]. Irrespective of the nature of the various anomalies in α_i, the distinct α_b versus α_c anisotropy implies pronounced T-dependent in-plane lattice distortions. The effect is particularly distinct for $T \lesssim 50$ K, where upon cooling the b-axis lattice parameter strongly contracts (large positive α_b) while the c-axis lattice constant expands ($\alpha_c < 0$). Since the hopping amplitudes t' and t depend sensitively on the lattice parameters, we expect that cooling in this temperature range is accompanied by an increase of t'/t (cf. inset of Fig. 2).

Turning to the anomaly at 6 K, shown in Fig. 2 on expanded scales, the uniaxial expansivities reveal a distinct peak of positive (α_c) and negative (α_b and α_a; cf. Fig. 1) sign, which is most strongly pronounced in α_c. The shape of this feature and its sharpness are clear indications of a phase transition, albeit of distinctly non-mean-field type [27], signaling the presence of strong critical fluctuations (see, e.g., [28,29]). Measurements taken upon cooling and warming at a very slow rate of ± 1.5 K/h failed to detect any hysteresis, consistent with a second-order transition. Around 3 K the α_c data reveal indications for yet another anomaly of much smaller size, reproducible in detail in consecutive runs. We stress that the features at 6 and 3 K in α_c remain unaffected by a magnetic field of 8 T applied along the c axis (cf. Fig. 2). Remarkably enough, the volume expansion coefficient $\beta = \alpha_a + \alpha_b + \alpha_c$ shows a much less peculiar behavior (cf. inset of Fig. 1). In particular, β varies smoothly around 50 K and lacks any anomaly at 6 K, i.e., $\Delta\beta|_{6\ \mathrm{K}} \approx 0$. According to the Ehrenfest relation, this implies that the 6 K transition is practically insensitive to hydrostatic pressure.

In Fig. 3 we show results of the specific heat on a small single crystal of mass $\lesssim 100$ μg for temperatures $2 \leq T \leq 10$ K. The data reveal a smooth increase with T and a humplike feature around 6 K, consistent with literature results [5]. Evidently, the quantity of interest—the contribution associated with the phase transition $\delta C^{\mathrm{trans}}$—is difficult to separate from the background C^{bg}. Although C^{bg} is likely to be dominated by the lattice specific heat C^{ph} (unfortunately unknown) it may also contain other contributions. Attempts to separate $\delta C^{\mathrm{trans}}$ by subtracting from the measured specific heat C^{ph} of a related salt with a different anion [5] involve considerable uncertainties. In order to overcome this problem, we use an ansatz, which has proved particularly valuable for analyzing phase transitions in organic materials [30]. The approach is based on

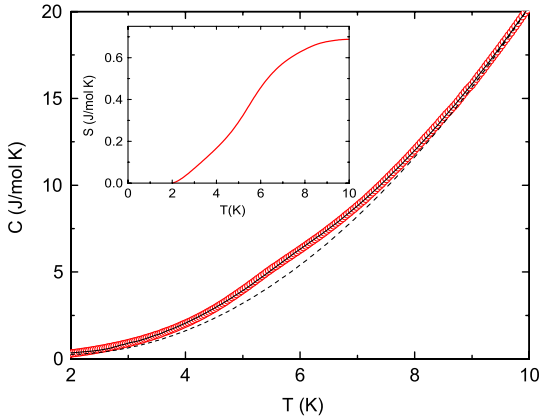

FIG. 3 (color online). Specific heat of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ between 2 and 10 K. Solid line represents the result of a least-squares fit of $C_{\rm fit}(T)$ (see text), yielding a smooth background $C^{\rm bg}$ (broken line). Inset: Entropy $S^{\rm an}$ obtained by integrating $\delta C^{\rm an}/T$ from 2 to 10 K.

the assumption of a proportionality between corresponding contributions to the expansivity and specific heat $\delta\alpha_i \propto \delta C$. This so-called Grüneisen scaling applies provided that there is only one relevant energy scale in the T range of interest (see [26] and references cited therein). In what follows, we focus on the range $2 \leq T \leq 10$ K, where this assumption should be valid. First, the data in Fig. 2 were used to extract the anomalous contribution $\delta\alpha_c^{\rm an}$ associated with the peak anomaly around 6 K. To this end, smooth background curves were subtracted from α_c and α_b such that the remaining contributions show the scaling behavior $\delta\alpha_c^{\rm an} \propto \delta\alpha_b^{\rm an}$ required by thermodynamics (cf. Fig. 4). Note that due to the large size of the anomaly in α_c, uncertainties in the background have only little affect on

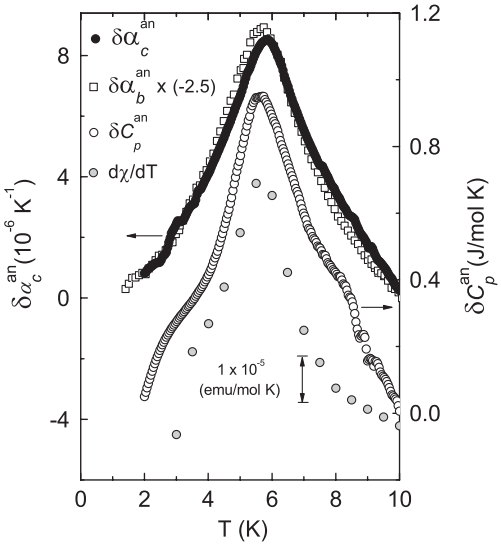

FIG. 4. Phase transition anomalies, derived as described in the text, in α_c and α_b (multiplied by a factor -2.5) (left scale), C (right scale), and $d\chi/dT$ (scale is given by the arrow).

the resulting $\delta\alpha_c^{\rm an}$. With the so-derived $\delta\alpha_c^{\rm an}$ a least-squares fit to the specific heat was performed using the function $C_{\rm fit}(T) = \delta C^{\rm an} + C^{\rm bg} = \frac{1}{\gamma_c}\delta\alpha_c^{\rm an} + C^{\rm bg}$, with a fit parameter γ_c, representing a generalized Grüneisen parameter [26]. A parametrization of the form $C^{\rm bg} = a_0 + a_1 T + a_2 T^2$ was used. The good quality of the fit, yielding $\delta C^{\rm an}$ (cf. Fig. 4) and a smooth background function $C^{\rm bg}$ (broken line in Fig. 3), is reflected by the small residual $[C(T) - C_{\rm fit}(T)]/C(T)$ of less than 1.5% in the range $4 \leq T \leq 10$ K.

The notion of a second-order phase transition at 6 K is also corroborated by reassessing the low-T magnetic susceptibility $\chi(T)$. The results of our experiment, being in good overall agreement with published data [3], are plotted in Fig. 4 as $d\chi/dT$ versus T. The measurements were performed by using a composite sample consisting of a large number of randomly oriented single crystals of total mass of 18.0 mg. As the figure indicates, $d\chi/dT$ shows a distinct peak, the shape and position of which practically coincide with the phase transition anomalies in $\alpha_i(T)$ and $C(T)$. Such a conformity between $d\chi/dT$ and thermodynamic quantities, known from magnetic transitions [31], indicates that spin degrees of freedom are involved to some extent in the transition. However, as will be shown below, their contribution alone appears insufficient to account for the observed entropy release.

By integrating $\delta C^{\rm an}/T$ from 2 K up to 10 K, we obtain an entropy $S^{\rm an}$ of (0.69 ± 0.05) J mol^{-1} K^{-1} (cf. inset of Fig. 3), with one mole substance containing $2N_A$ dimers (spins) and N_A denoting Avogadro's constant. This represents a lower bound of the true entropy $S^{\rm trans}$ associated with the phase transition; see below. The so-derived $S^{\rm an}$ corresponds to about $(6 \pm 0.4)\%$ of the system's full spin entropy (this would be $R\ln 2$ for a hypothetical system containing N_A spins with $S = 1/2$, with R the universal gas constant). It can be compared with calculations of the magnetic entropy for 2D triangular-lattice $S = 1/2$ systems, unfortunately available only for the isotropic ($t' = t$) case. For the pure Heisenberg antiferromagnet [32], which may serve as a rough estimate, we find a residual entropy for temperatures $k_B T \leq 0.04J$, corresponding to $T \leq 10$ K for $J/k_B = 250$ K, of only $(2.3 \pm 0.1)\%$ of $R\ln 2$. By including ring-exchange processes, likely to be significant near the Mott transition and which may account for the absence of Néel ordering [10], a somewhat larger value is expected. According to a variational study [12], these ring-exchange processes give rise to a low-T QSL state characterized by gapless fermionic excitations. This implies a spinon contribution to the specific heat of $C_{\rm spinon} = \gamma_{\rm spinon} T$, with $\gamma_{\rm spinon} = (\pi^2/3)k_B^2 N_A n(E_F)$ and a spinon density of states at the "Fermi surface" $n(E_F) = 0.28/t_{\rm spinon}$ [12]. For $t_{\rm spinon} = J$ [12], we find $\gamma_{\rm spinon} = 30$ mJ mol^{-1} K^{-2} and a remaining spinon entropy of 5.2% of $R\ln 2$ for $T \leq 10$ K. In Ref. [21] it has been argued that this QSL state is instable against the formation of

spinon pairs—a nematic QSL state—by which S^{spinon} is released to a full extent or partly (in the presence of impurity scattering).

This residual spinon entropy S^{spinon} appears to be quite close to the experimentally determined entropy release S^{an}, seemingly consistent with the scenario discussed in Ref. [21]. However, by estimating possible errors, the discrepancy between S^{spinon} and S^{an} becomes significant. First, we note that the above-mentioned underestimation of S^{trans} by S^{an} is considerably large for the present case. The reason for this is mainly due to the peculiar non-mean-field shape of the transition, which required a truncation of the high- and low-T flanks in δC^{an} (cf. Fig. 4). Simulations for quantifying the associated error indicate that $S^{\mathrm{trans}}/S^{\mathrm{an}}$ is probably in the range 1.2–1.4. Moreover, we expect that the available low-T spin entropy will be further reduced for an anisotropic triangular lattice ($t' < t$)—very likely the case for the present material [7,8]. Thus, an estimated entropy release S^{trans} of about 7%–8% of $R\ln 2$ has to be contrasted with an available spin entropy of less than 5.2% of $R\ln 2$. We consider this mismatch of about 30%–50%, by which the experimental value exceeds S^{spinon}, to be a strong indication that spin degrees of freedom alone are insufficient to account for the phase transition. An obvious candidate to rationalize the mismatch would be charge degrees of freedom. In fact, according to optical conductivity measurements [33], the charge gap in this material is strongly suppressed indicating the material's close proximity to the insulator-metal transition.

As a possible scenario we mention the proposed formation of an exciton condensate [20]. This is accompanied by a charge modulation breaking lattice symmetry. Objections to this scenario may be due to the lack of clear signatures for a charge modulation below 6 K in ^{13}C-NMR studies [16]. The poverty of evidence, however, might be due to the anomalous inhomogeneous broadening of the NMR spectra [16], possibly obscuring a potential line splitting.

Alternatively, one might consider charge fluctuations at elevated temperatures, causing fluctuating electrical dipoles. Some evidence in support of this has been recently observed in dielectric measurements [34]. Within such a scenario, the 6 K transition might indicate an ordering of those preformed dipoles. We stress that a distinct type of charge ordering, driven by an increase in the degree of frustration t'/t, has recently been predicted for the present material [35]. Because of the ionic nature of the material, ordering phenomena in the charge sector are expected to give rise to distinct lattice effects (see, e.g., [29,30]). Since the charge distribution also affects the magnetic exchange constants via $J \propto t^2/U$ with U the on-site Coulomb repulsion, a response in the magnetic susceptibility is also expected.

In summary, measurements of the uniaxial expansivities on the spin-liquid candidate κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ yield distinct and strongly anisotropic lattice effects at 6 K, clearly identifying this phenomenon as a second-order phase transition. By means of a Grüneisen-scaling ansatz, the corresponding anomaly in the specific heat could be separated. Comparison of the associated entropy release with spin models suggests that charge degrees of freedom are involved in the transition.

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