Magnetic Field-Induced Lattice Effects in a Quasi-2D Organic Conductor Close to the Mott Metal-Insulator Transition

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We present ultra-high-resolution dilatometric studies in magnetic fields on a quasi-two-dimensional organic conductor \( \kappa-(D8-BEDT-TTF)_{2}Cu[N(CN)_{2}]Br \), which is located close to the Mott metal-insulator (MI) transition. The obtained thermal expansion coefficient, \( \alpha(T) \), reveals two remarkable features: (i) the Mott MI transition temperature \( T_{MI} = (13.6 \pm 0.6) \) K is insensitive to fields up to 10 T, the highest applied field; (ii) for fields along the interlayer \( b \)-axis, a magnetic-field-induced (FI) phase transition at \( T_{FI} = (9.5 \pm 0.5) \) K is observed above a threshold field \( H_{c} \sim 1 \) T, indicative of a spin reorientation with strong magneto-elastic coupling.

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I. INTRODUCTION

Currently, strong activities in condensed matter physics have been directed towards a better understanding of correlation effects in low-dimensional systems. The strong interaction between electrons in these systems gives rise to several interesting phenomena. Among them, the Mott metal-to-insulator (MI) transition can be considered as one of the most prominent examples. Organic conductors of the \( \kappa \)-phase (BEDT-TTF)\(_2\)X family (BEDT-TTF, or simply ET, refers to the donor molecule bis(ethylenedithio)tetrathiafulvalene and X to a monovalent anion) have been recognized as appropriate systems for studying phenomena originating from the interplay of electron-electron and electron-lattice interactions in reduced dimensions, for a recent review see, e.g., [2].

These substances are built by layers of interacting dimers, i.e. \( (ET)_{2}^{+} \), sandwiched by sheets of insulating polymeric counter anions \( X^{-} \), giving rise thus to a quasi-two-dimensional electronic lattice. Their ground states can be tuned by chemical substitution and/or applying external pressure, see, e.g., the pressure-temperature (\( P-T \)) phase diagram in Fig.1. While the salt with \( X = Cu[N(CN)_{2}]Cl \) (\( \kappa-Cl \) in short) is an antiferromagnetic Mott insulator (AFI) with \( T_{N} \approx 26 \) K, the salt with \( X = Cu[N(CN)_{2}]Br \) (\( \kappa-HS-Br \) in short) is a superconductor (SC) with \( T_{c} \approx 11 \) K, the highest \( T_{c} \) at ambient pressure among all ET-based organic compounds investigated up to date. Interestingly enough, for \( X = Cu[N(CN)_{2}]Br \), the exchange of the hydrogen atoms of the ethylene end groups of the ET molecules by deuterium results in an antiferromagnetic insulating ground state, corresponding to a shift on the pressure axis towards lower pressure[2]. The insulating state in the \( P-T \) phase diagram is separated from the metallic/superconducting range by an S-shaped first-order phase transition line (thick solid line in Fig.1) which ends in a second-order critical point, indicated by \( (P_{0}, T_{0}) \) in Fig.1 see Ref[2] and references therein for details. Hence, due to their close proximity to the MI boundary, fully deuterated salts of \( \kappa-(ET)_{2}Cu[N(CN)_{2}]Br \), abbreviated to \( \kappa-D8-Br \) hereafter, have been recognized as suitable systems for exploring the Mott MI transition. The magnetic properties of the \( \kappa \)-phase (ET)\(_2\)X family, especially the \( X = Cu[N(CN)_{2}]Cl \) salt, have been investigated by vari-

![Fig. 1: Pressure-temperature, \( P - T \) phase diagram of \( \kappa-(ET)_{2}Cu[N(CN)_{2}]Z \) at zero magnetic field. Broken line labeled \( T_{N} \) indicates the paramagnetic to antiferromagnetic transition, the broken-dotted line labeled \( T_{c} \) corresponds to the transition into bulk superconductivity and the thick solid line labeled \( T_{MI} \) marks the first-order metal-to-insulator transition. D8-Br and H8-Br (position estimated according to [6]) refer to the position of the deuterated and protonated single crystals of \( \kappa-(ET)_{2}Cu[N(CN)_{2}]Br \), respectively. Vertical dotted line indicates the performed \( T \)-sweeps for "D8-Br" crystals, illustrating a crossing of the \( S \)-shaped line. Open symbols refer to literature data for the critical end point \( (P_{0}, T_{0}) \): o[5] ( ), □[7] ( ), □[6] ( ). Position of full circle, corresponding to \( T_{MI} \) for the present crystal, implies that at this point in the phase diagram \( T_{MI} \) coincides with \( T_{N} \), cf[2].](https://example.com/image1.png)
ous experimental techniques, see, e.g. refs.10–12 From the analysis of the NMR line shape, relaxation rate and magnetization data, K. Miyagawa et al.12 were able to describe the spin structure of this state. Below \( T_N = 26 - 27 \) K, they found a commensurate antiferromagnetic ordering with a magnetic moment of \((0.4 - 1.0)\mu_B/dimer\). The observation of an abrupt jump in the magnetization curves for magnetic fields applied perpendicular to the conducting layers, i.e. along the \( b \)-axis, was attributed to a spin-flop (SF) transition. Furthermore, a detailed discussion about the spin-reorientation, taking into account the Dzialoshinskii-Moriya interaction, was presented by D.F. Smith et al.14,15. By resistance measurements under control of temperature, pressure and magnetic field, a magnetic field-induced Mott MI transition was observed by F. Kagawa et al.16 Interestingly enough, similar to this finding for the pressurized \( \kappa \)-Cl salt, a magnetic field-induced MI transition was also observed in partially deuterated \( \kappa-(ET)_2\)Cu[N(CN)]Br.17 Furthermore, from \( ^{13}C \)-NMR studies evidence for phase separation into metallic/superconducting and magnetic phases in \( \kappa \)-D8-Br was reported in the literature.18 From temperature-dependent measurements of the coefficient of thermal expansion, the role of the lattice degrees of freedom for the Mott transition and the Mott criticality were studied. The latter results were found to be at odds with the Mott criticality derived from conductivity19 and NMR20 studies on pressurized \( \kappa \)-Cl. In order to gain more insight into the nature of the state on the insulating side of the Mott transition for the present \( \kappa \)-D8-Br material, we have performed thermal expansion measurements in magnetic fields. In this communication, we present expansivity data on single crystalline \( \kappa \)-D8-Br in magnetic fields up to 10 T and explore the field effects on the various phases in the vicinity of the MI line.

II. EXPERIMENTAL

High-quality single crystals of fully deuterated \( \kappa-(D8-ET)_2\)Cu[N(CN)]Br were prepared according to an alternative procedure as described in Ref.21,22. The single crystal studied here, labelled as \#3 (batch A2907), is identical to the one studied in Ref.9. The linear thermal expansion coefficient, \( \alpha(T) = \Gamma^{-1} (\partial l / \partial T) \) (\( l \) is the sample length), was measured by employing an ultra-high-resolution capacitance dilatometer with a maximum resolution of \( \Delta l / l = 10^{-10} \), built after22. Samples of the organic charge-transfer salts studied here are very sensitive to the quasi-uniaxial pressure exerted by the dilatometer.23 In fact, the uniaxial pressure acting on the crystal, typically a few bars, can be adjusted by setting the starting capacitance. In order to reduce the strain exerted by the dilatometer on the sample to a minimum, a very small starting capacitance was chosen. The experimental data presented were corrected only for the thermal expansion of the dilatometer cell with no further data processing. The alignment of the crystal was guaranteed with an error margin of \( \pm 3^\circ \). In all measurements, the magnetic field is parallel to the measuring direction. Resistance measurements were carried out by employing the standard four-terminal ac technique. In order to reduce cooling-rate-dependent effects associated with disorder of the ethylene end groups of the ET molecules, a cooling rate of \( \sim -3 \) K/h (thermal expansion) and \( \sim -6 \) K/h (resistance) through the glasslike transition around \( 77 \) K was applied. After the initial controlled cool-down, the sample was kept at temperatures below 40 K. Measurements of \( \alpha(T, B = \text{const.}) \) were performed at temperatures ranging from 4.5 K up to about 14 K except for \( B = 0.5 \) T where the measurements were limited to \( T \leq 11 \) K.

III. RESULTS AND DISCUSSION

The thermal expansion coefficient along the interplane \( b \)-axis in zero magnetic field is displayed in Fig.2. Upon cooling, an anomaly at \( T_g \approx 77 \) K is observed. This anomaly has been attributed to a glasslike transition, which has been discussed in the literature in connection with the freezing out of the ethylene end groups24 and anion-ordering.25,26 Upon further cooling, a second anomaly around \( T_F = 30 \) K is observed. This feature has been assigned to critical fluctuations associated with the second-order critical-end point of the first-order line27,28, indicated by the full up triangle in Fig.1. Further decreasing of the temperature reveals a pronounced anomaly around \( T_{MI} = 13.6 \) K. As discussed in Ref.10, this pronounced negative expansivity peak reflects the \( b \)-axis lattice effect upon crossing the first-order MI transition line; cf. the inset of Fig.2 showing the anomaly in \( \alpha_b(T) \) at \( T = T_{MI} \) which coincides with the metal-insulator transition revealed by resistivity. The peak of the anomaly in \( \alpha_b(T) \) was taken as the thermodynamic transition temperature. The first-order character of the transition was confirmed by the observation of hysteresis in both \( R(T) \) and relative length changes (\( \Delta l / l \)) around \( T_{MI} \) for another crystal2. The drop of the resistance at \( T_c = 11.6 \) K, accompanied by a tiny kink (indicated by the arrow), is caused by the freezing out of the ethylene end groups24,26. Upon further cooling under a weak field of 1 T, however, a second negative peak, centered around \( T_{F1} = 9.5 \) K, can be observed. This second peak becomes more pronounced at 2 T and saturates in size at a field of about 4 T. A closer inspection of the data in Fig.2 reveals the existence of a double-
a transition from SC to a low-resistive state was found for fields exceeding about 1 T\textsuperscript{29}. This state was found to transform into a high-resistive state via jump-like increases in the resistance upon further increasing the field to 10 T\textsuperscript{29}. This behavior was interpreted by the authors as a field-induced first-order SC-to-Insulator transition and related to the theoretical scheme based on the SO(5) symmetry for superconductivity and antiferromagnetism, first proposed by Zhang\textsuperscript{30} for the high-\textit{T\textsubscript{c}} cuprates. Likewise, a drastic \textit{B}-induced increase in the resistance was observed also for the \textit{\kappa}-(ET)\textsubscript{2}Cu[N(CN)\textsubscript{2}]Br salt when tuned close to the MI transition by hydrostatic pressure\textsuperscript{8}. Here it was argued that the marginally metallic/superconducting phases near the Mott transition undergo a field-induced localization transition in accordance with theoretical predictions, see, e.g., Ref.\textsuperscript{11} and references cited therein. Hence, based on these observations we expect that close to the Mott-MI transition in the present fully deuterated \textit{\kappa}-(ET)\textsubscript{2}Cu[N(CN)\textsubscript{2}]Br salt the electronic states may undergo drastic changes upon increasing the field. This may explain the growth of the anomaly in \(\alpha_b(T)\) with increasing fields \(H > H_c\). In fact, the initial rapid growth and the tendency to saturation above about 4 T is very similar to the evolution of the resistance, i.e. the increase of \(R(B, T = \text{const.})\) with field revealed in the above-mentioned transport studies\textsuperscript{29}. The observation of a field-induced transition at \(T_{FI} < T_{MI}\) raises the question on the nature of the intermediate phase that forms in the temperature window between \(T_{MI}\) and \(T_{FI}\) for fields \(H > H_c\). In the present stage of the investigations, i.e. by lacking a detailed magnetic characterization of this state, we speculate that this phase represents a paramagnetic insulator (PI), consistent with the notion of the SF transition, cf. the preliminary phase diagram shown in Fig.\textsuperscript{3}. We stress that no such field-induced effects were observed for fields along the \(a\)- and \(c\)-axis (not shown), also corroborating our claim of a SF transition. In fact, in Ref.\textsuperscript{13} the authors pointed out that the nature of the interlayer magnetic ordering depends on the direction of the applied magnetic field. In particular, based on a detailed analysis of NMR and magnetization data, taking into account the Dzialoshinskii-Moriya interaction, they found that antiferromagnetic ordering between planes can be observed only for magnetic fields above \(H_c\) applied along the \(b\)-axis. At this point, it is worth mentioning that the term "interplane afm ordering" is used here as defined in Figs. 4 and 5 of Ref.\textsuperscript{13}. Hence, given the absence of lattice effects at \(T_{FI}\) for magnetic fields applied along the \(a\)- and \(c\)-axis, our findings indicate a close relation between interplane antiferromagnetic ordering and the lattice effects observed at \(T_{FI}\). Following the notation used by the authors in Ref.\textsuperscript{13} the magnetization of the \(+(-)\) sublattice at the layer \(l\) is \(M_{+(-)l}\). The staggered and ferromagnetic moments are given by \(M^\text{f}_{l} = (M_{++l} - M_{--l})/2\) and \(M^\text{f}_{l} = (M_{++l} + M_{--l})/2\), respectively. For fields above \(H_c\) applied along the \(b\)-axis, \(M^\text{f}_{l}\) is along \(b\) and \(M^\text{f}_{l}\) is
in the $a$-$c$ plane. $M^A_\parallel$ and $M^B_\parallel$ are antiparallel giving rise to an interplane antiferromagnetic ordering. Our observation of a negative peak anomaly in $\alpha_b(T)$ at $T = T_{FI}$ thus suggests that in order to achieve this particular spin configuration, the gain in exchange energy forces the layers formed by the (ET)$_2^+$ dimers to move apart from each other. Similar dilatometric experiments were carried out on two other $\kappa$-D8-Br single crystals. For both crystals, in contrast to the sharp anomaly at $T_{FI} \approx 9.5$ K under magnetic fields shown in Fig. $3$, the effects of magnetic fields result in a smooth change of $\alpha_b(T)$ around the same temperature. Two factors should be considered as a possible explanation for this: i) the crystal alignment upon mounting the sample in the dilatometer. As reported in the literature, see e.g. $^{32}$ SF transitions are strongly dependent on the direction of the applied magnetic field. A minute misalignment of the material’s easy-axis with respect to the applied magnetic field can cause a suppression of the transition; ii) sample inhomogeneities and/or the effect of the pressure exerted by the dilatometer on the sample. For one of these single crystals, we studied the effect of quasi-uniaxial pressure exerted by the dilatometer on the sample and observed that a quasi-uniaxial pressure of some tenth of bars is enough to change the shape of the thermal expansion curves considerably: upon the application of uniaxial pressure of about 65 bar the transition was smeared out over a very wide temperature range $^{23}$. Our thermal expansion results at magnetic fields along the $b$-axis are summarized in the schematic $H$ versus $T$ diagram depicted in Fig. $4$. The dashed line around $\sim 0.5$ T separates the AFI from the SF phase, while the thick line marks the suppression of percolative SC together with the appearance of the spin-reoriented phase.

**IV. SUMMARY**

In conclusion, our thermal expansion studies on fully deuterated $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br under magnetic field reveal the insensitivity of the Mott metal-to-insulator transition temperature under fields up to 10 T, which is in accordance with the proposal of a Mott insulating state with a π-hole localized in a dimer. A field-induced phase transition at $T_{FI} = (9.5 \pm 0.5)$ K is observed, indicative of a spin reorientation with strong magneto-elastic coupling. Further experiments, including magnetostriction measurements both below and above $T_{FI}$ as well as magnetic measurements with $B$ thoroughly aligned along the $b$-axis, will help to better understand the behavior of almost localized strongly correlated electrons in this interesting region of the phase diagram of the $\kappa$-phase (BEDT-TTF)$_2$X charge-transfer salts. A theoretical study on the stability of the Mott
insulating state and the adjacent superconducting phase, taking into account field-induced lattice effects, is highly desired.

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