High-magnetic-field-induced insulating phase in an organic conductor

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We report electrical transport, skin depth, and magnetocaloric measurements in the τ-phase series of organic conductors at very high magnetic fields. In the field range above 36 T these materials show a magnetic field induced phase transition from a metallic to an insulating state. The transition, which is a bulk thermodynamic phenomenon, is Pauli, rather than orbital, in origin.

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In low-dimensional metals, high magnetic fields often act to reduce the effective dimensionality, thereby inducing a metal-to-density wave state.[1] This is most evident in quasi-one-dimensional Bechgaard and related organic salts.[2,3] Even in the case of quasi-two-dimensional materials, the magnetic field plays an important role in determining the ground state properties.[4,5] In such cases the interaction of the magnetic field with the electronic structure is generally orbital, and dependent on field direction. In contrast, the insulator-to-metal transition in, for instance, $\lambda-(BETS)_2FeCl_4$,[6] and the metal-to-insulator transition described in this report, are driven primarily by isotropic Pauli mechanisms.

Our main experimental result is the universal behavior of the resistance of all isostructural members of the τ-phase pyrazino class of organic conductors[7–9] in very high ($B>36$ T) magnetic fields. Here we find a metal-to-insulator transition above a temperature-dependent and hysteretic threshold field $B_{\rm th}$. An overview of the field-temperature phase diagram of these materials is shown in Fig. 1. $B_{\rm th}$ is only weakly dependent on magnetic field direction; hence the mechanism that drives the transition at $B_{\rm th}$ may be primarily isotropic, or Pauli-like in origin. The purpose of this paper is to provide complementary electrical transport and bulk thermodynamic information to describe this unconventional magnetic field induced insulating state.

The structure of the τ-phase unit cell is unique amongst the general class of charge transfer salts (CTS).[10] Unlike conventional CTS materials with a charge transfer ratio of 2:1, here it is $2:(1+y)$ (where $y\approx0.75$) and the anions occupy two different sites in the unit cell. A 2:1 ratio does exist in each conducting layer as (AuX_2) (where $X=$Br and I) linear anion lies along the c axis between a square array of P-DMEDT-TTF donors. The $(AuX_2)_y$ anions are arranged in the interlayer ab planes where their orientation alternates by 90° between layers. Since P-DMEDT-TTF is asymmetric (see Fig. 1 inset), the donor stacking involves alternating directions within each successive layer. Hence, due to the very low symmetry of the donor and anion arrangement, four donor layers are necessary to complete the unit cell,[9] and the result is an unusually large inter-planar dimension: ($a,b,c\approx7.4,7.4,68$ Å). τ-[P-(S,S)-DMEDT-TTF]$_2$(AuBr$_2$)$_{1+y}$ and τ-[P-(S,S)-DMEDT-TTF)$_2$(AuI$_2$)$_{1+y}$ (hereafter referred to as τ-AuBr$_2$ and τ-AuI$_2$, respectively) are analogous except for the replacement of bromine for iodine. The prefix P refers to the pyrazino (N-N) configuration of the P-DMEDT-TTF donor molecule. Disorder can be introduced into the τ-phase system with a racemic mixture of two isomers (R,R *and* S,S) of the donor molecules.[11,12] The racemic system studied in the present work is τ-[P-(r)-DMEDT-TTF]$_2$(AuBr$_2$)$_{1+y}$ [hereafter $\tau(r)$-AuBr$_2$]. The compound τ-[P-(R,R)-DMEDT-TTF]$_2$(AuBr$_2$)$_{1+y}$ was also investigated yielding very similar results to τ-AuBr$_2$.

Single crystals of τ-phase materials (square plates of average size $1\times1\times0.2$ mm^3) were grown electrochemically. Resistance measurements (both ac and dc) were four-terminal, interplane or in-plane measurements with current values between 50 nA and 300 μA. Electrical contact was made to the samples with 25 μm gold wires with carbon or silver paint with contact resistances of order 10 ohms. A tunnel diode oscillator (TDO) (Ref. 13) was used for the

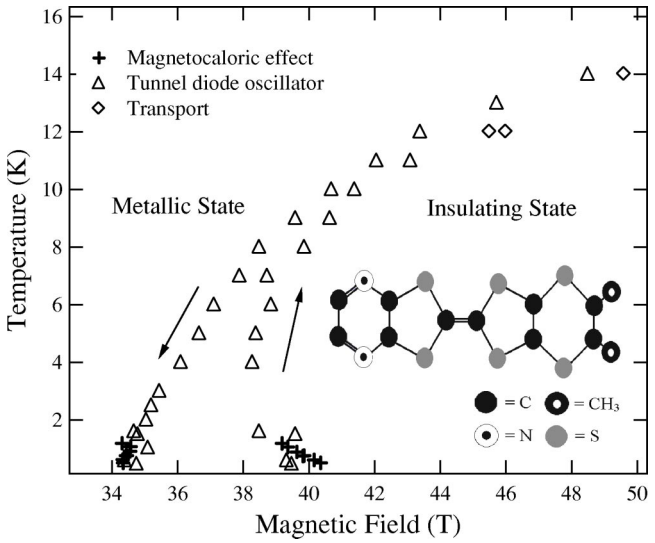

FIG. 1. Schematic high field phase diagram of the τ-phase organic conductors based on the P-DMEDT-TTF donor molecule (inset). The threshold field $B_{\rm th}$ for the high field phase boundaries is based on magnetoresistance and ac skin-depth measurements in pulsed fields, and magnetocaloric measurements in dc fields. Arrows indicate the up-sweep and down-sweep data. (See text and Figs. 3 and 4 for definition of $B_{\rm th}$ in each measurement.)

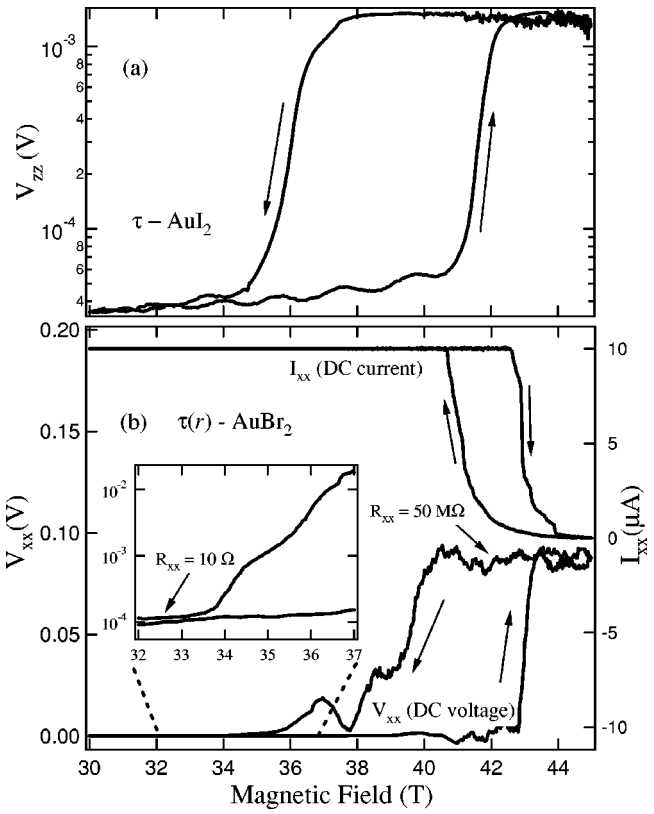

FIG. 2. (a) Interplane (V_{zz}) ac resistance data in dc magnetic fields on τ-AuI_2 at 0.5 K. Shubnikov-de Haas oscillations are observed below the threshold field. (b) In-plane (V_{xx}) dc resistance and current measurements for $\tau(r) - AuBr_2$ in dc magnetic fields at 0.5 K. The current (supplied by a current source with a 1 V compliance and a 10 MΩ series resistance) vanishes above 44 T due to the very high resistance of the sample. Estimated resistance values for both the metallic and insulating states are indicated.

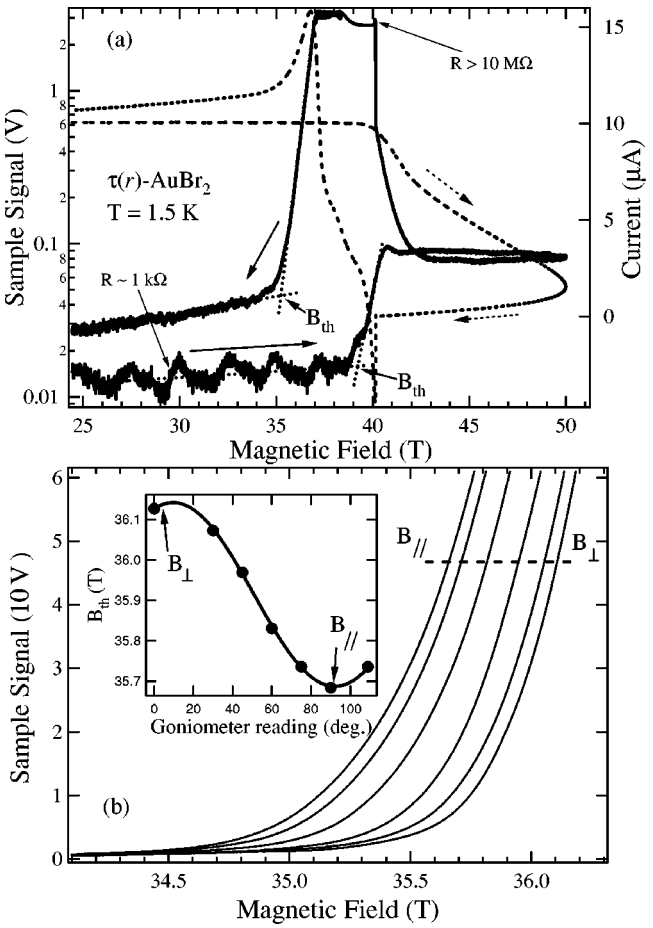

FIG. 3. Interplane (R_{zz}) dc magnetoresistance studies of the high field transition in pulsed fields. (a) Simultaneous measurement of sample voltage (solid line) and current (dashed line) in $\tau(r) - AuBr_2$ at 1.5 K. Estimated resistance values for both the metallic and insulating states, obtained from the ratio V_{zz}/I_{zz}, are indicated. Transients in the current are due to rapid metal-insulator switching effects (Ref. 14). (b) Field orientation dependence of the threshold field for the insulator-to-metal (down sweep) transition. Inset: values for B_{th} vs angle determined at a constant signal level (dashed line).

skin-depth study and a calorimeter platform in an evacuated capsule was employed for the magnetocaloric study. Experiments were carried out at the National High Magnetic Field Laboratory (NHMFL) dc field facilities in Tallahassee and at NHMFL–Los Alamos with pulsed magnets.

The field-induced metal-to-insulator transition in the pyrazino τ-phase materials was measured in a dc hybrid magnet up to 45 T [Fig. 2 and Fig. 4(b)], and in pulsed fields (6 ms rise time) up to 60 T [Fig. 3 and Fig. 4(a)]. The values of B_{th} in Fig. 1 were obtained from temperature dependent resistance measurements on $\tau(r) - AuBr_2$ [as in Fig. 3(a)], skin depth studies on $\tau - AuBr_2$ [as in Fig. 4(a)], and magnetocaloric measurements on $\tau(r) - AuBr_2$ [as in Fig. 4(b)]. (Definitions of B_{th} used in Fig. 1 are given in the respective figures.) In Fig. 2(a) the interplane ac magnetoresistance for $\tau - AuI_2$, is shown for low temperature ac transport data. For fields above B_{th}, the interplane resistance R_{zz} increases by orders of magnitude, and in some cases becomes unmeasurable by conventional transport methods. B_{th} is temperature dependent, moving to higher fields with increasing temperature. The Shubnikov–de Haas (SdH) effect, which has been studied previously[15] in $\tau - AuBr_2$, is observed below B_{th} in this case. (The slightly hysteretic nature of the oscillation phase is not at present understood.) Figure 2(b) shows the in-plane dc voltage signal, V_{xx} of $\tau(r) - AuBr_2$. This measurement was performed to further check the isotropic nature of the metal-insulator transition. (We note that for in-plane dc measurements, the current path for high resistance conditions can become irregular, even reversing sign. This is the cause of the additional structure in the dc signal above B_{th}.) The sample current, monitored through a series resistor, vanishes in the high field insulating phase.

Interplane measurements of $\tau(r) - AuBr_2$ in pulsed magnetic fields are shown in Fig. 3. In Fig. 3(a) we show the simultaneous current and voltage signals. B_{th} values used in Fig. 1 are determined from the intercepts of the slopes as shown as dashed lines. The oscillations in the up-sweep below B_{th} are due to noise from the pulsed magnet (note log scale) and are not associated with quantum oscillations. Transients in the current (which vanishes above B_{th}) are due

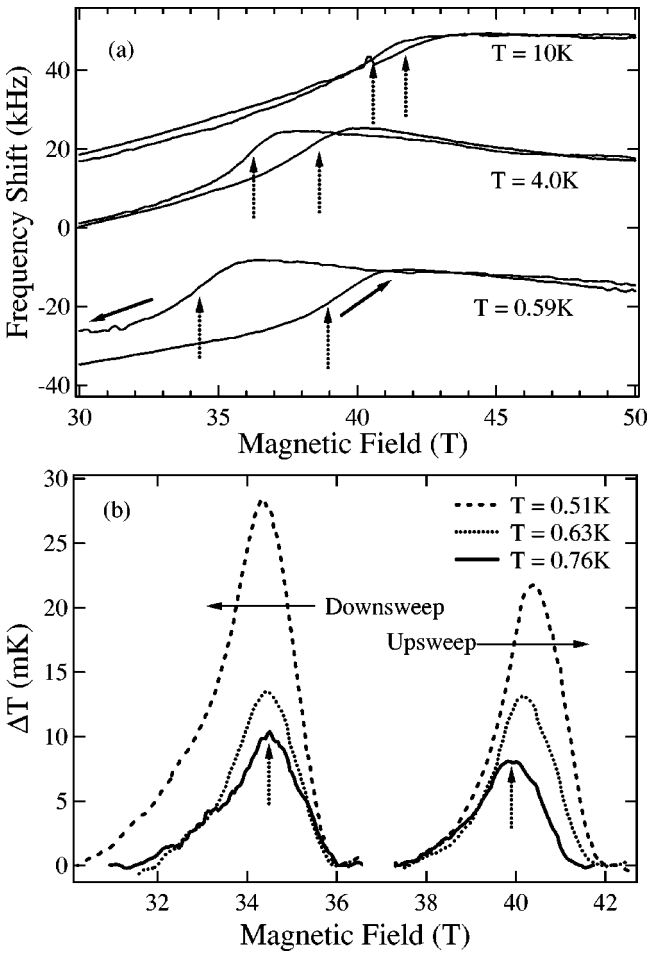

FIG. 4. Bulk properties of the high field transition. (a) Response of a tunnel diode oscillator (TDO) (with background signal removed) at 43 MHz to a $\tau(r)$-$AuBr_2$ sample in the inductor coil in pulsed fields at different temperatures (offset for clarity). The sample orientation is $c//H_{dc}//h_{ac}$. (b) Magnetocaloric effect (with background signal removed) in dc magnetic fields. A temperature rise is observed for both increasing and decreasing field at the hysteretic metal-insulating transition. In both (a) and (b), B_{th} values used in Fig. 1 are determined from the mid-points of the transition signals (shown by arrows).

to the metal-insulator switching that occurs on a 50 μs time scale.[14]

The dependence of the induced metal-insulator transition on the field direction is shown in Fig. 3(b) for pulsed-field measurements of the insulator-to-metal (down sweep) resistance for a systematic variation of field directions from $B//c$ to $B//a$-b. We find that B_{th} decreases only slightly as the field is tilted into the a-b plane.

To address the bulklike nature of the transition, a $\tau(r)-AuBr_2$ sample was investigated in a tunnel diode configuration where the axis of the inductor coil and the c axis of the sample were colinear with the applied field. Hence the ac field of the 43 MHz coil was perpendicular to the conducting layers of the sample. In this configuration, a finite skin depth of the ac field (typically about 1000 μm for in-plane conductivity in an organic conductor for this frequency range) will reduce the resonant frequency of the TDO oscillator.[13] Measurements were carried out above the transition (18 K) to obtain a background signal, and at lower temperatures to follow the transition. The results are shown in Fig. 4(a) for the change in frequency of the TDO circuit versus magnetic field. Here the lower frequency observed in the metallic state increases, essentially to an ''empty coil'' value, above B_{th}. From this we deduce that the skin depth becomes larger than the coil, i.e., the sample is a bulk insulator.

We have further explored the bulk thermodynamic nature of the transition in terms of the magnetocaloric effect, which has been carried out in both pulsed fields and in the hybrid magnet. In the former case, the sample-bolometer arrangement was in direct contact with ^{3}He, whereas for the dc fields, it was in an evacuated chamber. The dc field data is shown in Fig. 4(b) for the hybrid magnet, where we observe an increase in the sample temperature as B_{th} is crossed for both directions, which is also observed in the pulsed field studies. At 0.5 K, the maximum temperature change $\Delta T = 0.2$ K for the pulsed field measurement ($dB/dt = 8000$ T/s), and $\Delta T = 0.05$ K for the hybrid measurement ($dB/dt = 0.05$ T/s). Eddy current heating effects may play a role as the sample resistance changes rapidly at B_{th}, but this seems unlikely in light of the significant signal seen in the very slow sweep hybrid data. Rather, the thermodynamics is governed by a hysteresis-loop type of behavior [quite possibly similar in functional form to the magnetoresistance data shown in Fig. 2(a)] where the magnetic field does work on the system, regardless of sweep direction through the hysteretic transition.

Clearly, magnetism is a possible source of the high-field hysteretic behavior. Evidence for weak ferromagnetism has been reported in the EDO class of τ-phase materials[16–18] where oxygen replaces the two nitrogen sites [see Fig. 1(b)] in the P-DMEDT-TTF donor. Since there is no magnetic ion present, magnetism must arise either from the bands or from disorder (localized moments). Band magnetism has recently been treated by Arita *et al.*,[19] based on consideration of the very flat, narrow ($E_F \approx 8$ meV) bands that appear at the Fermi level from the tight binding calculations. Although magnetization studies have shown a small ($0.001\mu_B$/formula unit) moment, no hysteresis has been observed in low-field magnetization data.[17] Recent far infrared measurements indicate that the methyl groups show disorder, and it has been suggested that this may lead to electronic localization and magnetism at low temperatures.[20]

Based on the results given above, we conclude that the high field metal-to-insulator transition in the τ-phase materials has the following characteristics. It is specific to the N-N form of the donor molecule, but not to anion-type. By monitoring the current in dc resistance measurements, we have determined that the current vanishes above B_{th} for both interplane and in-plane transport. From skin-depth type investigations, we conclude that above B_{th} the sample is a bulk insulator, and from magnetocaloric measurements, the transition is thermodynamic in nature. Transport measurements in tilted magnetic fields indicate only a weak dependence of B_{th} on orbital effects, and therefore the main mechanism is Pauli-like.

What remains elusive is the origin of the dependent variable (i.e., the analog of χH in the case of ferromagnetism) in the hysteretic loop in the vicinity of B_{th}. As discussed above, magnetism in these materials is very weak. One possibility however would be a metamagnetic-type transition where an antiferromagnetic spin system is coupled to the lattice. This would provide the necessary hysteretic behavior, exhibited by the magnetocaloric data, for a magnetic transition. The origin seems also related to molecular bond and/or conformation effects, given that the *N*-*N* form of the donor facilitates the field induced insulating phase. An investigation of the molecular structure above 36 T, for instance by x-ray diffraction, could test for conformational and/or lattice changes.

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