

Evidence for coherent interchain electron transport in quasi-one-dimensional molecular conductors

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(Received 20 June 2003; published 23 October 2003)

The angular magnetoresistance of the organic superconductor (TMTSF)₂ReO₄ was measured up to 13.5 T. Exceptionally well-resolved angular magnetoresistance oscillations were observed, and analysis of these oscillations revealed several important features concerning interlayer transport. Lebed resonance dips up to the twenty-first order and subresonance dips corresponding to $p/q = \text{nonintegers}$ were observed. The key finding of this work was that, unlike other organic conductors of the form (TMTSF)₂X, (TMTSF)₂ReO₄ exhibits the Lebed resonance effect only when both p and q are odd integers. A simple explanation for this phenomenon, based on the unique anion ordering with wave vector $(0, 1/2, 1/2)$, is presented. This simple model can be applied to all Bechgaard salts. The analysis shows that interchain electron transport is coherent even though chains are as far apart as 200 Å or more.

DOI: 10.1103/PhysRevB.68.132508

PACS number(s): 74.70.Kn, 72.15.Gd, 72.80.Le

Organic conductors of the form (TMTSF)₂X (where TMTSF is tetramethyltetraselenafulvalene and X represents a monovalent anion such as ClO₄⁻, PF₆⁻, ReO₄⁻, BF₄⁻, or NO₃⁻) are highly anisotropic with a conductivity ratio of $\sigma_a : \sigma_b : \sigma_c = 10^5 : 10^3 : 1$ along the three crystallographic axes.¹ The Fermi surface for the nearly one-dimensional band structure consists of a pair of sheets around $k_a = \pm k_F$ with weak modulations along the k_b and k_c directions. When subjected to changes in temperature, magnetic field, or pressure, these materials exhibit many interesting physical phenomena, including spin-density waves, charge density waves, a superconducting transition, field-induced spin-density waves (FISDW), and the bulk quantum Hall effect. The physical properties of each state are additionally influenced by the type of anion.

In the metallic phase of (TMTSF)₂X, magnetoresistance shows an anomalous dependence on the field direction. Lebed was the first to conjecture the existence of resistance peaks at certain “magic” angles when the field is rotated in the $b'c^*$ plane (the plane perpendicular to the a axis, which has the greatest conductivity).² Experimentally, angular magnetoresistance shows local minima when the applied field is parallel to one of the real lattice vectors in the $b'c^*$ plane.³⁻⁵ The magic angles corresponding to resonances for a triclinic crystal are given by

$$\tan \theta = \frac{p}{q} \frac{b \sin \gamma}{c \sin \beta \sin \alpha^*} - \cot \alpha^*, \quad (1)$$

where θ denotes the field direction measured from the c^* axis, p and q are small integers, $\alpha^* = \cos^{-1}\{(\cos \beta \cos \gamma - \cos \alpha)/\sin \beta \sin \gamma\}$, and α , β , γ , b , and c are lattice constants.³ The first experimental evidence for the Lebed magic angle effect was observed in slowly cooled (TMTSF)₂ClO₄, in which ClO₄ anions are fully ordered with a superstructure wave vector $(0, 1/2, 0)$ below 24 K.^{3,4} This superstructure formation can be taken into consideration in Eq. (1) by simply doubling the lattice parameter b to $2b$.

Subsequent experiments on pressurized (TMTSF)₂PF₆ showed the Lebed resonance in the angle dependent Hall effect as well as in the angular magnetoresistance.⁵

Diverse theories have been put forward to account for the Lebed resonance. Some authors have argued that the commensurability of electron motions along the k_b and k_c axes makes a series of dips at specific angles.^{3,4,6,7} In contrast, Chaikin proposed the existence of hot spots where the scattering rate is high and where the electrons avoid by moving along the direction of the magic angles.⁸ Magic angles have also been derived by calculation of the semiclassical Boltzmann equation including a term modeling the Fermi surface topological effects⁹ or electron-electron interactions.¹⁰

Strong *et al.* accounted for the resonance in terms of the dimensional crossover from two-dimensional (2D) to 3D.¹¹ The motions of electrons along the c axis become coherent and the three-dimensional nature of the material survives, provided that the field points along a lattice vector. This model was supported by measurements of the temperature dependence of the longitudinal resistance R_{xx} in (TMTSF)₂PF₆ at various angles in the $b'c^*$ plane,¹² which showed that the temperature dependence of the resistance is metallic ($dR/dT > 0$) at magic angles but insulating ($dR/dT < 0$) elsewhere.

However, none of the theories put forward to date explains the observation that (TMTSF)₂ReO₄, but not other samples, shows local minima in angular magnetoresistance only at angles corresponding to $p, q = \text{odd integers}$. The displacement of TMTSF molecules as well as the weak periodic potential developed by the ordering of anions is usually considered very small, and is therefore not properly accounted for except when it induces a gap in the Fermi surface. Most theoretical pictures of (TMTSF)₂X systems proposed to date assume that the displacement of TMTSF molecules is very small and the periodic potential developed by the ordering of anions is weak. As a result, these effects are not properly accounted for. However, the angular magnetoresistance measurements of (TMTSF)₂ReO₄ reported here reveal that these effects play a more fundamental role in electron transport than previously thought.

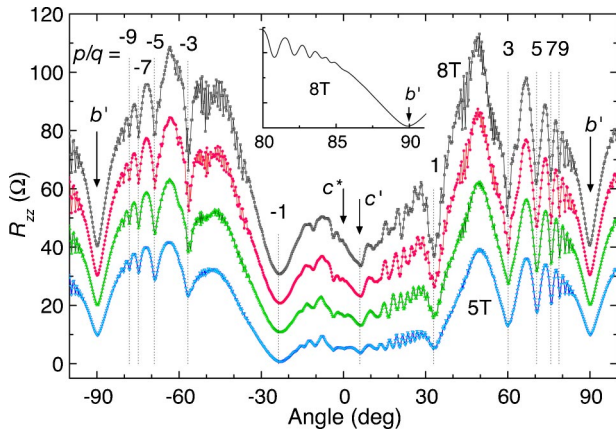


FIG. 1. (Color online) Angle dependence of R_{zz} of $(\text{TMTSF})_2\text{ReO}_4$ under rotation of the field in the $b'c^*$ plane. The field was increased from 5 T to 8 T in increments of 1 T. Successive curves are shifted by 10 Ω for clarity. Applied pressure was 12.2 kbar and temperature was 1.5 K. Both rapid oscillations and resonance effects are clearly visible until far from the c^* axis, as shown in the inset. The resonances occur exclusively where $p/q = \text{odd integers}$, as indicated in the figure.

In the present study, angular magnetoresistance measurements were performed in a 8 T split superconducting magnet at the Korea Basic Science Institute, Daejeon, Korea and in a 14 T superconducting magnet at the National Institute for Materials Science, Tsukuba, Japan (NIMS). Temperature was maintained at 1.5 K in pumped liquid ^4He . The interlayer resistance R_{zz} was measured by the conventional four-probe ac method using lock-in amplifiers. Hydrostatic pressure was generated in a BeCu clamp cell in which samples were mounted with silver paste. The values of pressure taken at room temperature were corrected to the low temperature value by separate calibration using the superconducting transition of 6N pure lead.

At ambient pressure, $(\text{TMTSF})_2\text{ReO}_4$ undergoes a metal-insulator transition at 180 K driven by an anion ordering with characteristic wave vector $(1/2, 1/2, 1/2)$. Pressurization suppresses the $(1/2, 1/2, 1/2)$ anion ordering and encourages the formation of anion ordering with wave vector $(0, 1/2, 1/2)$. According to the phase diagrams, the metallic state remains stable down to low temperature at pressures above 10.5 kbar and the superconducting transition occurs at $T_c \sim 1.6$ K.¹³ For the $(0, 1/2, 1/2)$ superlattice, the lattice parameters along the b and c axes are doubled and the effect of superlattice formation simply cancels in Eq. (1).

Figure 1 shows the measured angular magnetoresistance of $(\text{TMTSF})_2\text{ReO}_4$ at 12.2 kbar for various magnetic fields. The shapes of the angular magnetoresistance curves appear very complicated due to the Shubnikov–de Haas-like oscillations (also called rapid oscillations), which are well developed between -60° and $+60^\circ$. Although rapid oscillations are observed in most superconducting $(\text{TMTSF})_2X$ salts, $(\text{TMTSF})_2\text{ReO}_4$ is a special case in which they are clearly observed in both the angular magnetoresistance and the conventional magnetoresistance. The frequency of the rapid oscillations can be obtained by tracing the resistance as a function of $H_{c^*} = H \cos \theta$. For the curves in Fig. 1, the

frequencies of the positive (16° – 58°) and negative (-56° to -35°) parts are 319.5 T and 322.6 T, respectively.

In addition to the rapid oscillations, the angular magnetoresistance curves for $(\text{TMTSF})_2\text{ReO}_4$ show clear resonance dips. The largest dip appears at -24° , corresponding to $p/q = -1$, and a similarly large dip appears at $+33^\circ$, corresponding, to $p/q = +1$. Ignoring the rapid oscillations, the angular magnetoresistance between $\pm 40^\circ$ resembles that previously reported for $(\text{TMTSF})_2\text{PF}_6$ under low pressure (< 9 kbar).^{12,14} However, the $(\text{TMTSF})_2\text{ReO}_4$ curve continues to show sharp dips up to very large values of θ (more than 11 dips in each direction). The most striking feature in this set of data is that the magic angles appear only where the p/q values in Eq. (1) are odd integers. This behavior differs from that reported previously for $(\text{TMTSF})_2\text{ClO}_4$ and $(\text{TMTSF})_2\text{PF}_6$, both of which show magic angles when the p/q values in Eq. (1) are any integers.

When ReO_4 anions order alternately along the three axes, the TMTSF molecules adjust their positions accordingly, causing the molecular sites to become inequivalent. TMTSF molecules are mainly displaced along the c axis, with only slight displacements along the a and b axes; hence pairs of nearest-neighbor TMTSF molecules move apart or closer together laterally in the $b'c^*$ plane alternately.¹⁵ In the case of the $(0, 1/2, 1/2)$ ordering under pressure, the arrangements of TMTSF molecules in the $b'c^*$ plane can be regarded to be similar to those under the $(1/2, 1/2, 1/2)$ ordering because the anion ordering is suppressed only along the a axis. Figure 2(a) shows a simplified scheme of the arrangement of TMTSF molecules in $(\text{TMTSF})_2\text{ReO}_4$ projected in the $b'c^*$ plane. Arrows represent a pair of TMTSF molecules and their directions indicate two different molecular rearrangements.

Various authors¹⁶ have suggested that the c axis conductivity at zero field can be regarded as the summation of contributions along all the possible interlayer hoppings. If a finite magnetic field rotates in the $b'c^*$ plane, electron motion along the field direction dominates, with electron motion along other directions being suppressed by the component of the field perpendicular to those directions. The dependence of the conductance ($\sigma_{zz} \sim 1/R_{zz}$) on the angle, shown in Fig. 3, exhibits peaks at magic angles and is negligibly small elsewhere. This behavior is in good agreement with previous results for $(\text{TMTSF})_2\text{PF}_6$,¹⁶ and provides support for the above-mentioned theory, namely, that the c axis conductivity at zero field can be regarded as the summation of contributions along all the possible interlayer hoppings.

Now, let us consider the interchain electron motion along some representative directions depicted in Fig. 2(a). When the magnetic field is applied in the direction of line A ($p/q = 1$), the electrons move along the TMTSF molecule pairs with the same lateral displacement, forming a uniform molecular chain. In the case of line B ($p/q = 2$), however, the electrons must move along TMTSF molecule pairs that are alternately displaced. TMTSF molecule pairs along this line form a dimerized molecular chain, which is vulnerable to the formation of a kind of Peierls gap. The formation of such a gap means that electrons can barely move along the line B at

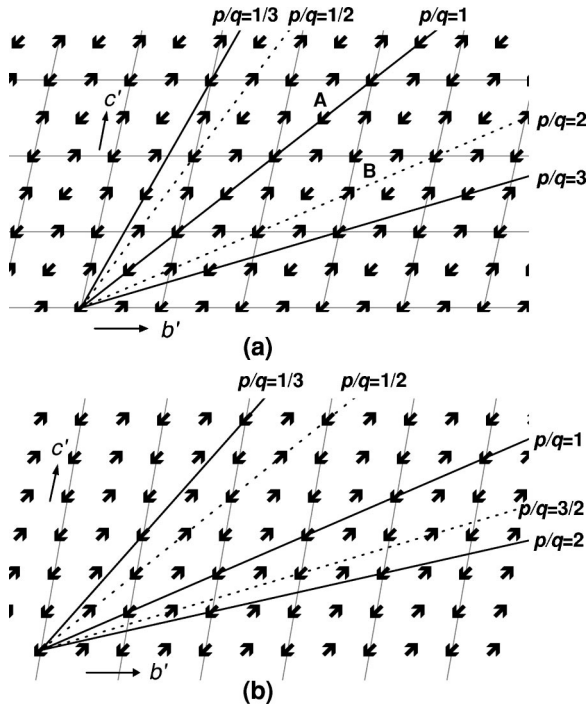


FIG. 2. Simplified schemes of molecular sites projected to the $b'c^*$ plane for (a) $(\text{TMTSF})_2\text{ReO}_4$ and (b) $(\text{TMTSF})_2\text{ClO}_4$ after $(0, 1/2, 1/2)$ and $(0, 1/2, 0)$ anion ordering, respectively. Each arrow indicates a pair of TMTSF molecules and its orientation represents the molecular displacement. There are two arrow types: (\swarrow) represents a pair of TMTSF molecules that are closer to each other, and (\nearrow) represents molecules that have moved apart laterally in the $b'c^*$ plane. Solid lines join molecules with the same displacements and dashed lines with alternating displacements.

low temperature, despite it being a major crystallographic orientation. As a result, the conductivity is significant only when the field is parallel to one of the lattice directions indicated by solid lines in Fig. 2(a), along which all the TMTSF molecular pairs are equivalent. Using the general convention that we have used for p and q in Eq. (1), the solid lines satisfy the condition that both p and q are odd integers.

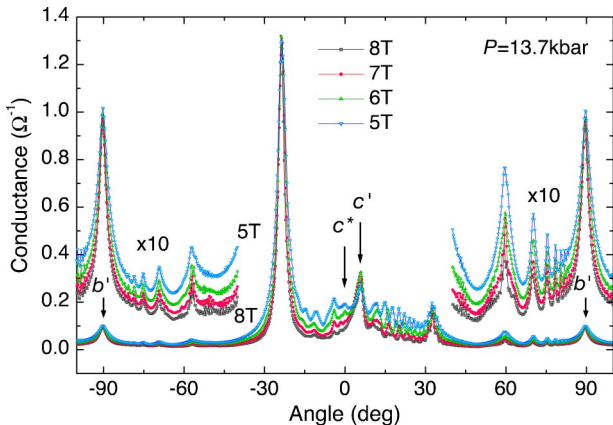


FIG. 3. (Color online) The angle-dependent magnetoconductance obtained by inversion of R_{zz} in Fig. 1. The conductance data at large angles are also shown magnified by a factor of ten.

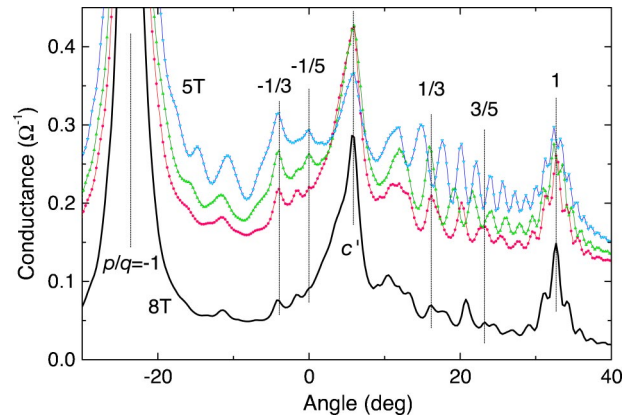


FIG. 4. (Color online) Plot of σ_{zz} between -30° and $+40^\circ$. Subresonances are distinguished from rapid oscillations by their fixed positions. A small offset is applied to the upper three curves to make the lowest curve clear.

This simple analysis explains successfully the absence of the Lebed resonance in $(\text{TMTSF})_2\text{ReO}_4$ when either p or q is an even integer.

The validity of our model can be tested by considering the angular magnetoresistance of $(\text{TMTSF})_2\text{ClO}_4$ system with anion ordering only along the b axis, shown schematically in Fig. 2(b). Again, dashed lines represent the directions in which electron motion suffers from a dimerization gap and therefore, the resonance effect is expected to be negligible. A local minimum in R_{zz} is anticipated when the magnetic field is aligned parallel to one of the solid lines. The q values for the solid lines, but not the dotted lines are always odd integers. When $q = 1$, the resonance effect can occur for all the integer values because both odd and even integers are possible for p , which agrees with previous experimental results.^{3,4} Although $(\text{TMTSF})_2\text{ClO}_4$ appears similar to $(\text{TMTSF})_2\text{PF}_6$ on replacing lattice parameter b with $2b$, the difference between the two samples is exposed when $p/q = \text{nonintegers}$. For instance, $p/q=1/3$ is allowed in $(\text{TMTSF})_2\text{ClO}_4$ but $p/q=1/2$ is not, whereas both are allowed in $(\text{TMTSF})_2\text{PF}_6$. Experimentally, it is difficult to discern the subresonances with $q > 1$ because the conductivity of $(\text{TMTSF})_2X$ along the c axis is about 1000 times smaller than that along the b axis.⁴ A substantial field is necessary to observe resonances for $|p/q| < 1$. However, $(\text{TMTSF})_2\text{ClO}_4$ enters in the FIDSW state above 6.1 T at 1.5 K and the magic angle effect with $|p/q| < 1$ becomes difficult to discern.³

Contrary to the behavior of $(\text{TMTSF})_2\text{ClO}_4$ and $(\text{TMTSF})_2\text{PF}_6$, the resonance effects for $p/q = \text{nonintegers}$ are readily detected in $(\text{TMTSF})_2\text{ReO}_4$. Although the peaks due to subresonance effects are small and overwhelmed by rapid oscillations, those peaks that are out of phase with the rapid oscillations, and whose positions do not move with increasing field, can be easily distinguished from the rapid oscillations in the conductance plot (Fig. 4). An increasing number of subresonances can be distinguished as the magnetic field is increased. At 13.5 T, the highest field used in this study, subresonances with $|p/q| > 1$ as well as those with $|p/q| < 1$ were observed even in the $R_{zz}(\theta)$ plot (Fig. 5). In Fig. 5, the subresonances are marked with arrows together

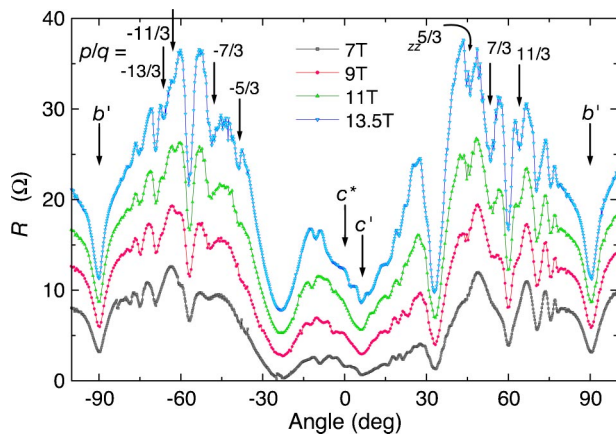


FIG. 5. (Color online) Angular magnetoresistance of a $(\text{TMTSF})_2\text{ReO}_4$ sample above 7 T under 12.0 kbar and at 1.5 K. Successive curves are shifted by 2.5Ω for clarity. Only some sub-resonance dips for $|p/q| > 1$ are indicated, where both p and q are again odd integers.

with the corresponding p/q values. These sub-resonances provide further confirmation that the magic angle peaks appear only when both p and q are odd integers for the $(0, 1/2, 1/2)$ anion ordering superlattice.

Here, it is necessary to point out that the molecular chains are far apart when there are resonances with $|p/q| \gg 1$ or $|p/q| \ll 1$. The two nearest chains are separated by as much as 200 \AA for $p/q = 13$, making it difficult to apply the semiclassical hopping model of independent electrons. Instead,

we require a mechanism that turns on the conducting states at the Fermi level whenever the magnetic field is aligned along a resonance direction and that switches them off if the field is not appropriately aligned.¹⁶

In summary, the Lebed resonances observed in the present study of the angular magnetoresistance of $(\text{TMTSF})_2\text{ReO}_4$ showed obvious differences from those previously reported for $(\text{TMTSF})_2\text{ClO}_4$ and $(\text{TMTSF})_2\text{PF}_6$. The angular magnetoresistance of $(\text{TMTSF})_2\text{ReO}_4$ showed a remarkably large number of resonances and subresonances, enabling us to make a detailed study of these features. The key finding of this work was that, unlike other organic conductors of the form $(\text{TMTSF})_2X$, $(\text{TMTSF})_2\text{ReO}_4$ exhibits Lebed magic angles only when both p and q are odd integers. We accounted for this effect using a simple model that considered the very small but finite molecular displacements due to anion ordering. When electrons move along the direction of alternating TMTSF molecular displacements, a type of dimerization gap prevents coherent motion. As a result, coherent interlayer electron motion survives only in those directions for which both p and q are odd integers, and hence the molecular displacements are identical. The observation of well-developed resonances at angles as large as 83° ($p/q = 13$) indicates that the Bechgaard salts are electronically extremely clean systems and that the electron-electron correlation is very important in these systems.

The stay of H. K. at the NIMS was supported by the Japan-Korea Foundation through the Eighth Winter Institute program. This work was supported by the Korea Research Foundation under Grant No. 2001-015-DP0175.

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