Commensurate Fine Structure in Angular-Dependent Studies of $(TMTSF)_2ClO_4$

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Clear fine-structure oscillations in magnetoresistance and torque magnetization are observed at low temperatures in the organic superconductor $(TMTSF)_2ClO_4$ as a function of sample orientation in a magnetic field. These fine structures appear as resistance minima and torque maxima at specific field orientations, with one-to-one correspondence. The angular positions of the features are independent of magnetic field, temperature, and cooling rate (disorder), while their magnitudes depend strongly on all three. We compare these observations with a recent prediction by Lebed' and Bak of resistance, but not magnetization, anomalies expected to arise at special "magic angles" in field.

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The anisotropic organic conductors $(TMTSF)_2X$ have proven to be an incredibly rich system in which to explore electron physics in reduced dimensions. The many conducting states observed in these charge-transfer salts include metallic, superconducting, antiferromagnetic [spin-density wave (SDW)] insulating, charge-density wave (CDW), semimetallic magnetic-field-induced spin-density wave (FISDW) with complex subphase structure, embodiments of the integral and fractional quantized Hall effects (QHEs), a reentrant metal state, nonlinear conduction, and possibly other phases and fine structures [1]. Many of these phenomena can be related to the low-dimensional nature of the electronic spectrum, with the conductivity and bandwidth anisotropy given by $\sigma_a:\sigma_b:\sigma_c=(t_a)^2:(t_b)^2:(t_c)^2=10^5:10^3:1$. The crystal structure consists of sheets of donors (TMTSF) and sheets of anions ($X=PF_6$, AsF_6, ClO_4, ReO_4, NO_3, and others) forming a-b planes, with a warped quasi-2D Fermi surface. The existence of spin-density-wave condensation is evidence for quasi-1D behavior, consistent with $t_a \gg t_b, t_c$. The FISDW transitions, however, are essentially orbital (2D) in nature, resulting from a nesting of the open-orbit Fermi surface in a magnetic field normal to the layers, consistent with $t_a, t_b \gg t_c$.

Magnetoresistance measurements have been used to demonstrate the (manifold) dimensionality of these materials. Early results showed deviations from behavior expected for an anisotropic 2D metal [2,3]. More recent anisotropy studies [4–6] have shown additional anomalous features somewhat consistent with a novel angular-dependent order parameter (threshold field) for FISDW formation [7], or possibly a new electronic phenomenon of "commensurability resonance" predicted to occur at special field angles in anisotropic three-dimensional metals [8]. In addition, there is a theory which predicts "fractional" Hall quantization phenomena to occur [9], while yet another finds suppression of the FISDW critical temperature [10], all for the same special orientations in field.

In this work, we describe the clear observation of fine structure in the angular dependence of the magnetoresistance and the torque magnetization of $(TMTSF)_2ClO_4$, several aspects of which are consistent with these essentially 3D effects. The angular positions of the observed features accurately obey an equation depending entirely on the crystal structure, leading to a hierarchy of apparent commensurate electron motion conditions. We also discuss the effect of disorder on the observed resistance oscillations, including the virtual disappearance of the effect for significantly disordered samples.

The experiments were done in a split-coil magnet, in the temperature range 0.1 to 4.2 K. Each sample ($\sim 5\times0.5\times0.3$ mm^3, $J\sim10^{-2}$ A/cm^2) was aligned with its a axis normal to the field direction, and the cryostat was rotated about an axis normal to the field, yielding rotations in the b^*-c^* plane. The cooling rate in the range 30 to 10 K, near an anion ordering at 24 K, was ~ 15 mK/min, yielding relaxed state samples.

Figure 1 shows angular-dependent resistance for our sample No. 1 at 5 T. The inset shows the experimental geometry. Note the broad but distinct minima at $\theta=\pm 90°$, the $\pm b'$ axes, and near $\theta=6°$, the c' axis. $(TMTSF)_2ClO_4$ is triclinic, so the rotation plane normal to a is the b^*-c^* plane, coplanar with b'-c', the projections of b and c onto the plane normal to a. Since $\alpha\approx 84°$ and $\beta\approx 88°$, c' is near $\theta=6°$, with c^* at $\theta\equiv0°$, orthogonal to a and b'. Note also in Fig. 1 the topic of this paper: the additional resistance oscillations which develop at low temperature. At 4.2 K, the features are relatively small, but nonetheless present. At 1.2 and 0.4 K, several structures are observable, and by 0.1 K, distinct oscillations appear superimposed on the smoothly varying, somewhat sinusoidal background resistance.

The new features present themselves as local resistance minima with respect to the background. A better view is afforded by observing derivatives. Figure 1(b) shows scaled second derivatives for the data in Fig. 1(a). Again, b' and c' are clearly marked by distinct maxima

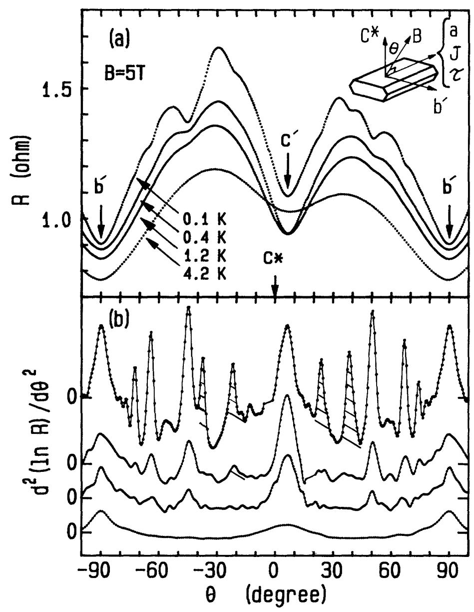

FIG. 1. (a) Resistance anisotropy for several temperatures. (b) Logarithmic derivatives. Hatched regions denote FISDW transitions. Inset: Sample geometry.

(i.e., resistance minima) at all temperatures, while the additional oscillations become more pronounced as temperature is reduced. In addition, several FISDW subphases are visible in the lower-temperature data (hatched regions).

We will briefly review the theoretical works which motivated this study. Initially, Lebed' [7] considered the anisotropic nature of $(TMTSF)_2X$ in the metal phase and noted that for a field aligned along certain directions in the b^*-c^* plane, the effect of the relatively small size of the c-axis bandwidth is eliminated. Here, the system loses its 3D character and becomes essentially 2D, resulting in a reduction (to $B=0$ at $T=0$) in the threshold field for FISDW. He reasoned that at these "magic" angles, semiclassical electron motion on the open Fermi surface along c^* becomes bounded and periodic, resulting in true 2D real-space motion. The angles are given by the condition $\tan\theta=(m/n)b'/c^*$, where m and n are integers, and b and c are unit-cell parameters. Earlier measurements of the angular dependence of the threshold field for $(TMTSF)_2ClO_4$ and $(TMTSF)_2PF_6$ found no features at the predicted angles [11,12], though in retrospect, there may be some deviation from 2D behavior in the data of Ref. [12]. In fact, those data [12] extended only to $\theta\sim 50°$, the smallest angle at which we observe new features in this work.

More recently, Lebed' and Bak (LB) [8] calculated the magnetoresistance of the $(TMTSF)_2X$ salts based on a quasi-two-dimensional tight-binding electron spectrum. They showed that the motion of such electrons includes tunneling between a-b layers leading to commensurate conditions between periodic motion along b^* and periodic motion along c^*, resulting in fine-structure "resonances" in the resistance at the same orientations as in the case of Ref. [7]. In particular, this formalism predicts enhanced scattering producing sharp local maxima in the resistance at commensurate orientations, with field and temperature dependence of the amplitudes of the new oscillations and of the angular position of the background resistance maximum.

Both theories [7,8] refer essentially to the condition of an electron completing m oscillations along b^* simultaneous to completing n along c^*. Lebed' predicts a phase transition (metal SDW) at each magic angle. Depending on T, B, θ, and the background resistance, it is possible to get a rise or drop in resistance for this case. LB, on the other hand, explicitly predict resistance maxima at the special angles. Both theories simplify for calculations the crystal structure, leading to symmetric conditions about b' and c^*. In our measurements, we observe clear nonsymmetry reflecting the true triclinic structure. The correct governing equation should read

$$\tan\theta=[2mb\sin\gamma-nc'\cos\alpha^*]/nc^* . \qquad (1)$$

Here, α^* is the angle between b^* and c^* ($\sim$95°–96°). This fact was pointed out by Osada *et al.* [6], and the above equation reduces to their expression, $2mb\sin\gamma/nc^*-\cot\alpha^*$. The factor of 2 in these expressions has been added for a more reasonable indexing of the features, as discussed later.

Montambaux and Littlewood [9] have stressed that these large orbits in a tilted field can have integer areal quantization, which will lead to a fractional quantization of the number density, an interesting idea since it does not involve many-body effects as in fractional QHE. Chen and Maki [10] calculated the temperature for FISDW formation $T_c(H,\theta)$ and found local dips at 0° and $\tan^{-1}(b/c)\sim 30°$, but suggest this only is visible for fields $\sim$15 T.

Returning to Fig. 1(b), it is clear that we are observing resistance minima (derivative maxima) which become larger as T is reduced. This is in agreement with our earlier observations [4], as well as those of Ref. [6], where in both cases the picture was less clear (the Ref. [4] samples were cooled too rapidly, while the Ref. [6] data are at 1.5 K).

And what of the angular positions of these anomalies? In Fig. 2 we plot derivative data for sample No. 2 at 5 T. Here, the new oscillations are more pronounced, possibly due to the lack of microcracks on cooling as occurred in sample No. 1. We have indexed the peaks using the triclinic expression (1) above, finding very good agreement. We can identify and index accurately at least eight resonances corresponding to $-(m/n)=1$–6, 3/2, and 5/2. It is curious that we have no evidence in any measurement for resonances at subunity fractions, like $m/n=1/2$ or 1/3, even though there are features for $n>1$ ($\pm\frac{1}{2}$

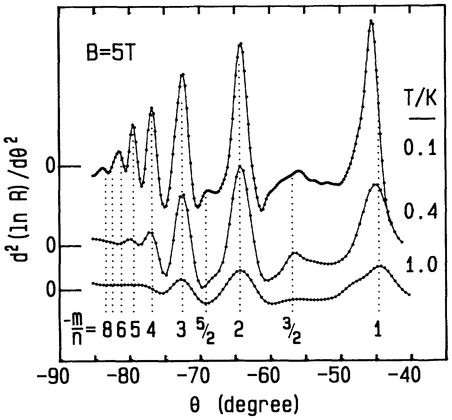

FIG. 2. Derivative data at low temperature, with rational fractions m/n indexed according to Eq. (1).

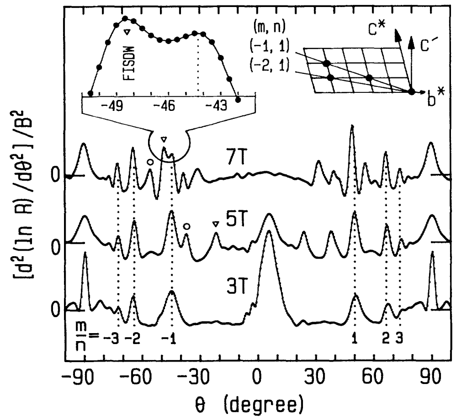

FIG. 3. Derivative data at 0.2 K and several values of magnetic field. Two FISDW states are marked (○ and ▽), with the left inset detailing coexistence of FISDW and new fine structure. Right inset: b^*-c^* plane showing two commensurate conditions.

should occur near $+32°$ and $-24°$). The fact that $t_b/t_c \sim 30$ suggests that an $m>1$ is much more likely than an $n>1$, if the features scale with the bandwidth as LB imply. This can explain why the $m/(n=1)$ features are larger than the $m/(n>1)$, but not the absence of $\frac{1}{2}$. The use of the factor of 2 in the indexing equation could be due to the b-axis doubling at anion ordering, with the primitive cell being $(a,2b,c)$.

The strong temperature dependence of the LB-type oscillations is also evident in Fig. 2. This may be due to the electron mean free path, since according to LB, the resonances result from a modification of the scattering rate at the magic angles. Ignoring for a moment the huge discrepancy of the sign of the effect (predicted maxima versus observed minima), there is further evidence opposing such an electron-scattering theory. In Fig. 3 are data for sample No. 1 at several values of magnetic field. These show the independence of the angular positions of the commensurate features on magnetic field, and the enhancement of their magnitudes with field. We have marked two FISDW transitions (○ and ▽). In the 5- and 7-T traces, these transitions occur for the same field component along c^*, owing to the orbital nature of FISDW. The left inset is an expansion of the 7-T data near $\theta = -45°$, and demonstrates explicitly that the FISDW and the new commensurate effects coexist. Unless the mean free path is unchanged in passing from the metal to the FISDW state, a phase transition which involves a near destruction of the Fermi surface, there should be no coexistence. It is possible that magnetic breakdown across an SDW gap could account for this [6]. It is also worth noting that Shubnikov–de Haas and de Haas–van Alphen–like oscillations are observed in all measurements on high-quality samples of $(TMTSF)_2ClO_4$, and these coexist with FISDW as well [13]. There is at present no accepted explanation for these so-called "fast oscillations," although magnetic breakdown [14], edge state quantization [15], and oscillatory scattering matrix elements due to interference effects have been proposed [16]. Perhaps there is a common solution to the two phenomena.

We have also observed the new effect in a torque magnetization experiment. The measured torque is along **a** and so corresponds to orbits in the **b***-**c*** plane. As shown in Fig. 4 (sample No. 3), features occur at common angles in both resistance and magnetization. The torque was measured simultaneously to and independent of the resistance, showing that the effect does not require a transport current. While there are features in both traces between 0° and $-30°$, their angular positions are B and T dependent, and so are due to FISDW transitions. According to LB, the resonances arise from synchronized *open* orbits on the Fermi surface. While an open-orbit metal can provide a magnetic torque in certain orientations [17], this situation appears to be unique in that open orbits exist for all field directions. Periodic open orbits should give sharp torque maxima when the field is aligned normal to the open-orbit direction, as opposed to broad

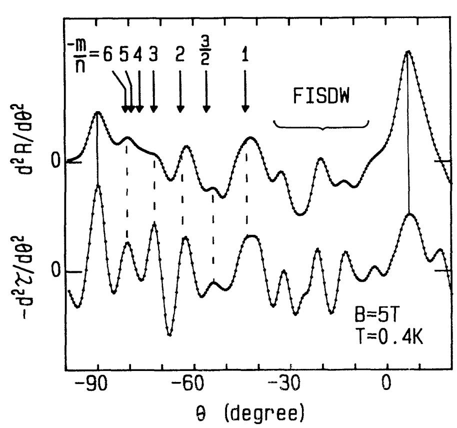

FIG. 4. Resistance (upper) and torque magnetization (lower) derivative traces showing 1:1 correspondence.

rises for aperiodic orbits. The observed torque, however, can also be thought of as arising from paramagnetic moments along c^*, as in the case of FISDW transitions, which give a sizable torque signal [18].

The fact that the resonance effects are seen in magnetization casts doubt on the validity of the LB model, and any other model which does not account for thermodynamic oscillations at the commensurate orientations, suggesting that the situation involves more than scattering matrix terms.

Finally, we wish to discuss the effect of cooling rate on the commensurate features. The 24-K transition involves orientational ordering of the ClO_4 anions [19]. The ground state can be a disordered insulator (cooling rate $\sim 10^2$ K/min), or a metal (superconductor) with a unit cell doubled along b ($\sim 10^{-2}$ K/min). Intermediate rates yield competition between the two ground states. Essentially, one can tune the mean free path by varying the cooling rate. So the new features should be very rate dependent. With the assumption of the factor of 2 due to the doubling of b, we would also expect the $m/n=1$ peak to shift to the $m/n=1/2$ position (24°). We indeed observe a reduction in the magnitude of the peaks with increased cooling rate, as well as a broadening in the angular width. For a 6-K/min cooling rate, the ground state was semiconducting. Nonetheless, the $m/n=\pm 1$ peak remained, with the peak height reduced by 90%, and no sign of the $\pm \frac{1}{2}$ peak.

In summary, we have observed a hierarchy of commensuratelike features in anisotropic torque magnetization, as well as in magnetoresistance, reflecting the 3D nature of $(TMTSF)_2ClO_4$. While a theory by Lebed' and Bak predicting such features in the resistance is consistent with some aspects of our data, there remain important discrepancies, such as the sign of the resistance peaks and the lack of subunity fractions, and unresolved questions, such as the origin of the torque oscillations. A numerical factor in the formula governing the angular positions of the observed oscillations, employed to sensibly index the peaks, needs to be clarified, as does the role played by the electron mean free path. One important study would be with the nitrate salt, which remains metallic and lacks FISDW effects in magnetic fields, while another would involve thermal measurements to detect phase transitions at the commensurate angles.

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Note added.— A recent model by Maki [20] obtains resistance dips at commensurate angles, and also suggests that fractional (nonintegral) resonances are unlikely. Again, however, no thermodynamic oscillations are expected.

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