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Rapid magnetic oscillations in an organic conductor: Possibility of a new type of quantum oscillation

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We report the existence of rapid magnetic quantum oscillations in the low-temperature metallic phase of the organic conductor tetramethyltetraselenafulvalenium perchlorate, $(TMTSF)_2ClO_4$, at magnetic fields lower than those associated with observed spin-density-wave (SDW) transitions. These resistance oscillations are seen at low field only for samples cooled extremely slowly through an anion ordering at 24 K, and become more pronounced at fields greater than 10 T. Their frequency remains unchanged from 4 to 30 T, through the magnetic-field-induced SDW transitions which occur from 5 to 8 T (at $T=1$ K). Angular studies reveal a two-dimensional nature. These results suggest an intrinsic magnetic periodicity which is unaffected by the SDW transitions, and require a new mechanism for their explanation.

INTRODUCTION

Two-dimensional electrons in a magnetic field have been studied extensively since the discovery of quantum Hall effect (QHE).[1] The Bechgaard salts tetramethyltetraselenafulvalene $(TMTSF)_2X$, where $X = PF_6$, ClO_4, ReO_4, etc., are a family of organic charge-transfer salts variously described as quasi-one- or quasi-two-dimensional conductors. Among other unusual properties they were widely studied as the first organic superconductors. However, their most striking properties are found at low temperature in the presence of a large magnetic field parallel to the least conducting c^* axis. Above a temperature-dependent threshold field there are a series of magnetic-field-induced phase transitions to several spin-density-wave (SDW) phases.[2]

These field-induced spin-density-wave (FISDW) transitions are characterized by plateaus in the Hall resistance[2,3] similar to the QHE, accompanied by sharp jumps in the magnetization[4] and cusps in the specific heat.[5] In contrast to the usual QHE, the ratios of the plateau values are nonintegral, depend on the temperature, and ρ_{xx} does not tend toward zero. These measurements demonstrate that these thermodynamic transitions correspond to a loss of carrier density[2] at the Fermi surface as the magnetic field is increased. Theoretically[6-10] it has been shown that the Fermi surface (FS) of a two-dimensional (2D) open-orbit metal is unstable against SDW formation in the presence of a magnetic field. The series of transitions result from competition between the SDW distortion wave vector and the magnetic length. The transitions leave the Fermi surface greatly altered with only small electron or hole pockets remaining.

Theoretically and experimentally the carriers in these pockets should be quantized into the lowest Landau level states ($n=0,1$) at any field above 10 T. It was therefore very surprising that a number of investigators have observed rapid Schubnikov–de Haas type (SdH*) oscillations (corresponding to $n \sim 10-20$) in this high field region.

In this paper, we report a detailed study of the SdH* oscillations in the extremely well-relaxed (very slowly cooled) state of ClO_4 salt. We demonstrate their two dimensionality by angular dependence, their thermodynamic nature via magnetization, and their appearance below, throughout, and above the FISDW transitions. The existence of the SdH* oscillations below the FISDW is especially unexpected since here the Fermi surface should be completely open,[11] allowing for no Landau quantization. Previous experiments on the magnetoresistance of the ReO_4 salt have also suggested the presence of these oscillations through the FISDW region,[12] but the FISDW has not been as clearly established in that system.

EXPERIMENTS

The resistance ρ_{xx} and Hall resistance ρ_{xy} of our samples were measured with current along the highly conducting a axis with a conventional four-probe ac technique. Six 25-μm gold wires were attached to the sample using DuPont silver paint. Care was taken to check the samples with dc two-probe and four-probe measurements at all stable temperatures. The signals were recorded throughout the entire temperature and field range both digitally and with an analog chart recorder. All the data shown were taken on samples where each room-temperature contact resistance was less than 2 Ω. Two samples were mounted on a rotatable platform[13] for the purpose of inverting the sample for complete Hall measurements, and additionally changing the orientation of the field with respect to the highly conduction a-b planes. Much of the data was taken with the hybrid magnet (to 30 T) at the Francis Bitter National Magnet Laboratory at MIT. A ^{3}He cryostat was used with 15-T superconducting magnet and later with 9-T superconducting magnet at the University of Pennsylvania. The temperature was determined by a combination of a Ga-As diode, a capacitance thermometer and ^{3}He vapor pressure. Temperature was controlled with a Lakeshore capacitance controller in the presence of the magnetic field.

The low-temperature properties of these samples have previously been demonstrated to depend significantly on the rate at which the samples are cooled through the anion ordering transition at 24 K. For our studies, we first cooled the samples through this transition at a medium rate (0.3 K/min) and recorded the resistance. A sharp kink indicated the transition at 24 K. The samples were then heated to 30 K for 1 h, then cooled at a rate of 7 mK/min to 10 K. The samples show a sharp superconducting transition at 1.3 K and a large sign reversal in the low-temperature Hall resistance between 6.3 and 6.9 T (present only in such slowly cooled samples[3]). The positions of the series of transitions (FISDW) were consistent with previous results.[3-5]

In Fig. 1 we show our results for the magnetoresistance of $(TMTSF)_2ClO_4$ for two different temperatures. At magnetic fields above 8 T the SdH* oscillations are observed both at 6.5 and 1.5 K as in previous measurements (usually on less relaxed samples), but here the effect is larger, with a harmonic contribution at higher field values. The FISDW's are only visible in the 1.5-K data where the threshold field is ~6 T (H_t ~18 T at 6.5 K). The interesting new result is shown more clearly in the inset in Fig. 1, where a linear term has been subtracted from the magnetoresistance in the range 4–7 T. The strong SdH* oscillations are here seen to be present below the onset of the FISDW's.

In Fig. 2, we show the logarithmic derivative of the data of Fig. 1, plotted versus $1/H$. From this figure it is clear that the SdH* frequency (~255 T) is unaffected by the FISDW's although there is certainly an effect of these transitions on the amplitude of the faster SdH* oscillations. Note also that the FISDW's, which themselves have a vague resemblance to SdH* oscillations, have a very different frequency (~35 T). The field dependence of the oscillation amplitude is in the usual SdH* form for T=6.5 K, but is altered by the FISDW transitions as shown for T=1.5 K. Two important features need to be pointed out about the amplitude of the oscillations. One is the irregular temperature dependence, that is, the amplitude is seen to increase upon cooling at 15 T, while it decreases for cooling from 6.5 to 1.5 K at 10 T. The second is that a new envelope develops above the last FISDW transition, rather than continue the low-field dependence. From the amplitude dependence then, it is clear that there is some interaction between the two phenomena (SdH* and FISDW), but it has no effect on the oscillation frequency. This is seen in Fig. 3, which shows the usual indexing of the peak positions giving an SdH* frequency.

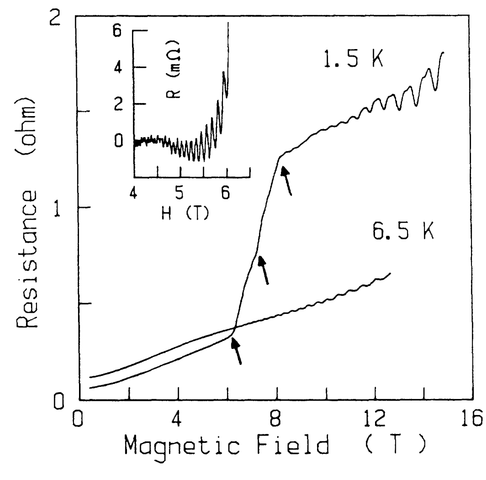

FIG. 1. Magnetoresistance of $(TMTSF)_2ClO_4$ in the very relaxed state. At 1.5 K, the SDW threshold appears at 6 T, followed by the FISDW transitions (arrows). The oscillatory resistance is seen to be enhanced above 10 T. Inset shows the oscillations below the threshold field. For T=6.5 K, H_t > 15 T.

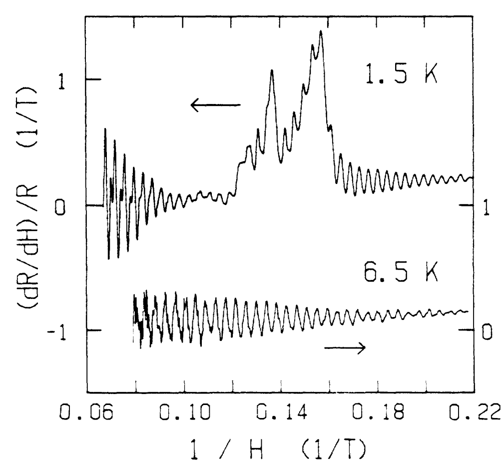

FIG. 2. The logarithmic derivative of the resistance vs inverse field, showing oscillations at all field values.

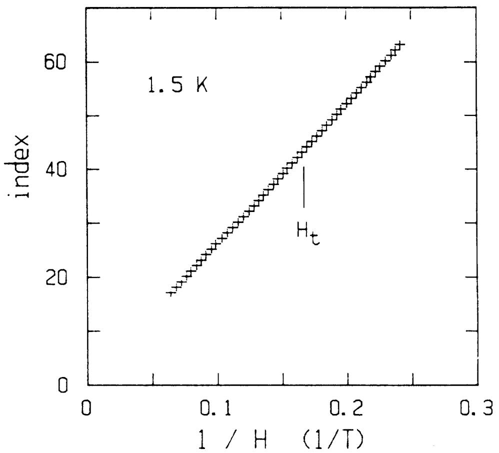

FIG. 3. Indexed peaks vs $1/H$, from resistance data at 1.5 K, giving the SdH* frequency. H_t marks the FISDW threshold.

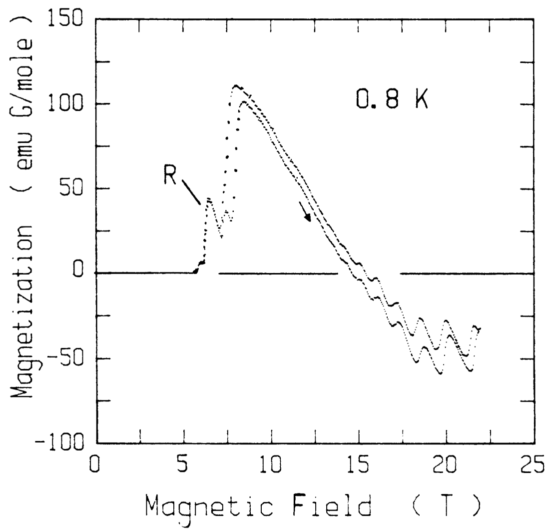

FIG. 4. Magnetization in very relaxed state, showing FISDW transitions and dHvA-type oscillations. R marks the extra step corresponding to the Hall sign reversal.

This plot is constructed such that $n=0$ at $1/H=0$.

The amplitude of the low-field SdH* oscillations is dependent on the cooling rate, which is probably why it has not been reported before. Our investigations show that only samples cooled slowly enough to exhibit the Hall sign reversal will show the oscillations below the FISDW region. As first shown by Ribault,[3] progressively slower cooling below 24 K yields a larger negative Hall step. However, not all samples which show the Hall reversal show low-field oscillations (slow cooling appears to be a necessary but not sufficient condition).

Field sweeps taken with $\mathbf{H} \perp c^*$ show no evidence of oscillations or FISDW, showing the same 2D orbital nature of both phenomena. The angular dependence of the SdH* oscillations was measured by rotating the c^* axis away from the field direction. These studies are in agreement with similar results at fields above the FISDW,[14] where $H_{\mathrm{eff}}=H/\cos\theta$ and the oscillations have the form $\Delta R/R=F(H_{\mathrm{eff}})$.

We have also measured the magnetization on samples with the same cooling conditions discussed, using a torque magnetometer.[15] Some results are shown in Fig. 4. With a small linear background term removed, one sees positive magnetization jumps followed by slower relaxation back toward $M=0$. Each jump corresponds to a different FISDW phase,[4] with the last jump around 8 T. This last phase is much more irreversible than the others, as evidenced by the hysteresis above 8 T. The magnetization jump labeled "R" corresponds to the "Ribault step," or negative Hall-effect region discussed earlier. A puzzling aspect of the data in Fig. 4 is that the magnetization appears to cross $M=0$ at ~ 15 T. This crossing occurs only for this very relaxed state,[4] and has been seen in every sample tested. Some authors[14] have attributed a resistance anomaly near 15 T to an unexplained phase transition, through we find only weak evidence for such a transition.

The structure seen in the high-field region is very similar to a textbook example of quantum oscillations in a 2D electron gas in a magnetic field. The frequency and angular dependence of these oscillations is the same as seen in the magnetoresistance measurements of the preceding figures. Since the magnetization is the derivative of thermodynamic potential, these oscillations and sharp jumps signify that the effects are thermodynamic in origin. We note that we have not as yet seen the de Haas–van Alpen oscillations below the FISDW region. This may be due to the fact that the magnetometer sensitivity scales with the magnetic field squared.[15]

DISCUSSION

The SdH* oscillation frequency is ~ 255 T and independent of temperature, corresponding to a Fermi surface area of approximately 3.4% of the Brillouin-zone a-b plane, similar to that observed in the ReO_4 salt. Could the experiments be explained by a small hitherto undiscovered section of the Fermi surface that is not affected by the FISDW's? The answer is yes, but it would be extremely unlikely. If there were a pocket of the requisite area it would contribute to the magnetoresistance and Hall resistance and would yield a Hall resistance that is more than an order of magnitude too small (i.e., many more carriers than are actually observed). However, there is a way around this argument. If there were two pieces of Fermi surface with precisely the same area but one with electrons and the other with holes their effects on the Hall coefficient would cancel while their contribution to the SdH* oscillations might not. We feel that this interpretation is highly unlikely. Moreover, it has often been noted that the SdH* frequency is that which one would expect from a Fermi surface nesting of $\mathbf{Q}=(2k_F,0,0)$ using the known values for the band parameters. Although this does not indicate such a nesting actually takes place (we do not believe this nesting is relevant), it does indicate that the oscillations may be related to another mechanism using the known Fermi surface.

Recently Yamaji[16] has proposed two different mechanisms to explain the high-field SdH* oscillations. In the first instance he noted that the wave functions for a two-dimensional open orbit metal in the presence of a magnetic field acquired an oscillatory phase factor. When scattering matrix elements are calculated the oscillatory term survives. The original calculation was made in the absence of the FISDW's. Although the frequency for these oscillations corresponds nicely with the experimental observations (within 10%), it is difficult to understand why the frequency would not change with the drastic change in the Fermi surface accompanying the FISDW's. Moreover, the modulation of the scattering matrix elements would not readily explain the thermodynamic oscillations which are evident from the magnetization measurements. In a more recent paper, Yamaji has shown that a second series of gaps (which accompany the larger Landau gaps from the FISDW) may arise in the energy spectrum from a combination of umklapp scattering and SDW nesting. However, the magnetoresistance should then only show oscillations when the system is in the FISDW state. This possible explanation is excluded by the main observation in this paper of oscillations below the threshold field for the FISDW.

What is required to explain our observation is a mechanism which is largely independent of the FISDW transition but otherwise mimics two-dimensional SdH* oscillations in their effect on both transport and magnetization. A model which may have some of these features has been proposed by Azbel and Chaikin.[17] It involves the quantization of edge states which result from open orbit electron trajectories which intersect the sample boundaries. These states cannot participate in the SDW pairing since their wave functions are strongly perturbed from the bulk states and, hence, should be relatively unaffected by the FISDW. The predicted frequency from the Landau levels arising from these states is approximately what we observe in our experiments, and they give rise to similar thermodynamic behavior as conventional two-dimensional quantum oscillations. However, they depend strongly on the nature of the sample boundaries (which may explain why different samples show these oscillations with greatly varying amplitude) and their effect on the magnetoresistance has not yet been calculated. We are performing experiments with samples that have modified boundaries to test these ideas.

CONCLUSIONS

We have observed SdH*-type oscillations in extremely slowly cooled $(TMTSF)_2ClO_4$ samples at field values below and throughout, as well as above the FISDW transitions. Magnetization jumps confirm the thermodynamic nature of the oscillations. The present experiments rule out several previous interpretations of these oscillations and strongly suggest that they require an explanation which is largely independent of the magnetic-field-induced spin-density waves, but is an intrinsic property of a system with a two-dimensional open orbit Fermi surface. One possible explanation consistent with our observations is the quantization of open orbit edge states, which would constitute a new mechanism for quantum oscillations in this and similar systems.

ACKNOWLEDGMENTS

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