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Field-induced magnetic order in bis-tetramethyltetraselenafulvalenium perchlorate $(TMTSF)_2ClO_4$

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A microscopic study of the organic superconductor bis-tetramethyltetraselenafulvalenium perchlorate $[(TMTSF)_2ClO_4]$ has been undertaken with the use of nuclear magnetic resonance techniques. Proton and selenium resonances were recorded over the field range 60–120 kOe at a temperature of 1.5 K. The proton spin-lattice relaxation-rate measurements clearly reflect both the high-field phase transition and magnetotransport anomalies. The selenium resonance is strongly attenuated above the high-field transition which indicates the onset of field-induced magnetic order. These results and their bearing on the high-field electronic properties of the Bechgaard salts are discussed.

INTRODUCTION

The 2:1 organic conductors based on the tetramethyltetraselenafulvalenium (TMTSF) molecule and a monovalent anion X, and commonly known as Bechgaard salts, exhibit a variety of interesting phenomena including an insulating spin-density wave state, a highly conducting metallic state, and superconductivity. The ability to modify the physical properties by the application of pressure, temperature, and magnetic field renders these salts convenient materials for fundamental studies. Of particular interest has been the magnetic properties of these unusual systems. In the PF_6 salt, and probably in the ClO_4 derivative, the magnetic and electronic properties may be classified into two distinct field regimes. In the low magnetic field regime numerous studies[1,2] have shown that the transport is quasi two dimensional or three dimensional, depending upon the time frame of interest. At a particular value of magnetic field, depending upon the applied pressure, temperature, and field orientation, a transition occurs that signals the sudden appearance of de Haas–Shubnikov oscillations in the magnetoresistance.[3] The interpretation of these results has been that the Fermi surface is closed in this high-field regime and has pockets of electrons and holes that are compensated.[3] The field, temperature, and pressure dependence of this turn-on field have been studied via nuclear magnetic resonance of protons that are hyperfine coupled to the conduction electrons.[4]

Studies of the ClO^4 salt have had the added complication that the low-temperature properties are drastically affected by the rate of cooling at temperatures less than 30 K.[5] So-called "quenched samples" do not exhibit superconductivity while slowly cooled "relaxed" samples do.[6] X-ray studies have revealed that slow cooling establishes anion order while fast cooling freezes in anion disorder.[7] Even though the anion stacks do not play a direct role in determining the electronic properties of this material (i.e., the anion order and/or disorder does not cause a charge or spin-density wave transition), the disordered anion potential does affect the superconducting properties. A further complication regarding the perchlorate salt has been the observation[8] that the magnetoresistance anomalies do not appear to be fully periodic in $1/H$, i.e., hysteresis is observed in the oscillations and their positions in field are temperature dependent. Therefore the interpretation that the magnetotransport is exhibiting quantum oscillations is open to question.

The manner in which these results on the ClO_4 salt bear on the interpretation of magnetotransport in the PF_6 derivative is still an open question. If the same interpretation applies to both salts, questions arise concerning the interpretation of the PF_6 magnetotransport data in terms of quantum oscillations. Our motivation for the present study is to employ a local probe of the electronic system in the ClO_4 derivative in the metallic high-field regime in an attempt to better understand the high-field properties. Nuclear magnetic resonance (NMR) serves as an excellent probe in this case. Our results demonstrate that the ClO_4 salt in the high-field regime exhibits magnetic order.

EXPERIMENTAL DETAILS

Large single crystals ($0.3\times0.6\times7$ mm^3) were grown by constant current electrocrystallization techniques (Pt electrodes) using trichloroethane as the solvent and tetrabutylammonium perchlorate as the anion source. That the samples were single crystals was verified using single-crystal diffraction techniques. Great care was taken to ensure that the sample was cooled sufficiently slowly to be in the relaxed state. The cooling rate below 50 K was less than 0.5 K/min. Data were collected over a 30-day period. The sample was maintained within 0.1 of 1.5 K during the entire period. The temperature of 1.5 K is about 0.5 K above the superconducting transition temperature in zero field so that the sample was in the metallic state throughout the experiment. The refrigeration method employed a helium-gas-flow system.[9] Temperatures were measured either using a calibrated Ge thermometer or a calibrated Allen-Bradley resistor. The sample crystal was orientated in a superconducting Nb_3Sn magnet with the crystalline c axis (triclinic system, space group $P\bar{1}$) parallel to the field. In view of the fact that several investigators[8] have observed that the mag-

netotransport properties of the ClO_4 salt above the turn-on field display hysteresis, all relaxation-rate measurements reported here were performed with a field approach from zero field. The proton and selenium resonances were recorded with a pulsed spectrometer[10] capable of operating over the frequency range 2–1000 MHz. Both spin-echo and direct observation of the free-induction decay with a boxcar integrator were used to record the resonances.

EXPERIMENTAL RESULTS

In Fig. 1 we show the spin-lattice relaxation rate T_1^{-1} of the methyl protons in tetramethylselenafulvalenium perchlorate [$(TMTSF)_2ClO_4$] versus magnetic field from 60 to 122 kOe at 1.5 K. Each data point represents the average of at least six relaxation measurements (error bars are 2% unless otherwise noted). The c axis (lowest conducting direction and the direction in which magnetotransport oscillations are observed) of the sample was oriented parallel to the magnetic field. Several features are shown in the figure. First of all, the turn-on field is clearly seen as a large peak in T_1^{-1} at about 70 kOe. The same effect has been observed in the PF_6 salt under pressure[4] where the peak coincides with the onset of the magnetotransport oscillations.[3] Above the turn-on field, T_1^{-1} decreases and then exhibits small bumps at 80 kOe and possibly at 96 and 118 kOe. The sudden increase in T_1^{-1} at 80 kOe is real; T_1^{-1} increases about 20% within a field change of less than 500 Oe. Such abrupt changes in the relaxation rate are often seen at phase transitions. The relaxation rate is itself time dependent on the order of hours (at least) in the region of the increases at 80, 96, and 118 kOe. No time-dependent relaxation rate was observed outside these regions in field. The time dependence is such that T_1^{-1} slowly increases with time at constant field.

In order to further elucidate the transitions at 80 and 96 kOe, we performed the following experiment. The apparatus was tuned so that ^{77}Se would be resonant at 68 kOe (55.291 MHz). A $\pi/2$-π pulse sequence was employed with the width of the boxcar detection gate positioned in time

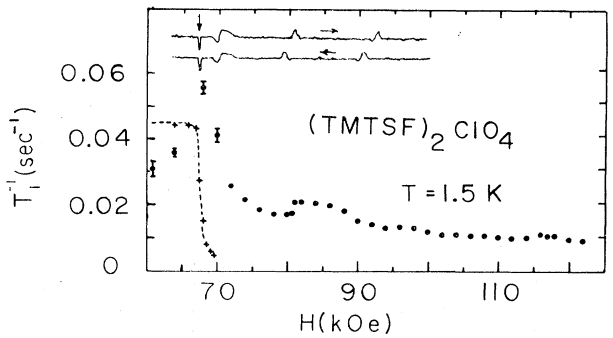

FIG. 1. Field dependence at 1.5 K of the proton spin-lattice relaxation rate for the magnetic field parallel to the cyrstalline c axis (dots) and nuclear susceptibility of the ^{77}Se (crosses). Proton measurements were made with a field approach from zero. Sample is in the relaxed state. At the top of the figure a boxcar trace is shown depicting the ^{77}Se resonance at 68 kOe, the turn-on field, and two signals that display hysteresis in field. The turn-on field shows no such hysteresis.

where the echo would occur. A field sweep of the boxcar output is shown at the top of the figure. If a resonance is being detected, then the output is directly proportional to the number of resonant spins or the nuclear susceptibility. The arrow on the figure depicts the selenium resonance. The remaining signals above 68 kOe are not associated with resonances as they are not dependent on the first pulse of the sequence and, indeed, their positions in field are independent of the rf frequency. We conclude therefore that these signals must correspond to a field-dependent absorption of rf energy. Possible mechanisms could include dielectric or magnetic transitions that are macroscopic in nature. Note that the positions of the signals correspond to the turn-on field and anomalies in the proton relaxation rates. Also note that the higher-field anomalies display hysteresis similar to that observed in the magnetotransport.

Also plotted in the figure is the ^{77}Se resonance amplitude versus applied field. A flat line on this figure would indicate a constant number of spins observed. Note that there is a sharp decrease in the amplitudes at the turn-on field. We observe that the amplitude of the selenium resonance decreases while the linewidth (on the order of 50 Oe) remains constant.

INTERPRETATION

We first discuss the turn-on field behavior. Several effects need to be understood: the enhancement of the proton spin-lattice relaxation rate, the absorption of rf energy, and the decrease of the selenium susceptibility at the turn-on field. We are confident that the protons are relaxed by electron spins based on earlier work on the PF_6 derivative[1] and the observation that at this low-temperature phonon and other relaxation mechanisms such as methyl group rotations are very small. The only interpretation can be that a large magnetic field of hyperfine origin must be present at the selenium site for a time longer than the inverse of the Larmour frequency. Since the ^{77}Se is a spin-$\frac{1}{2}$ nucleus, electric quadrupole effects cannot shift or broaden the resonance, therefore the mechanism must be magnetic in origin. At the transition, an increasing fraction of the selenium nuclei are "wiped out" in the sense that the hyperfine field is so large as to make the resonance extremely wide or to strongly shift the resonance. After a careful search for shifted resonances over our available field range and taking our sensitivity under consideration, we can conclude that this hyperfine field must be greater than 1 kOe.

The field-induced magnetic order is also responsible for the enhancement of the proton relaxation rate, but in this case the proton resonance is observed throughout the transition since the hyperfine field is localized at, or near, the selenium sites. As the applied magnetic field induces order there is a critical slowing down of the fluctuating magnetic moments causing the enhancement of the proton relaxation rate. This transition is also detected in the absorption of rf energy at the turn-on field.

If the picture of $(TMTSF)_2ClO_4$ were simply a quasi-two-dimensional or three-dimensional metal, there would be no reason to expect magnetic order at any field. The effect of the magnetic field would be simply to polarize the conduction electrons with a resulting Knight shift. It is reasonable to conclude, therefore, that some other mechanism is

responsible for these effects. One possibility is a spin-density wave (SDW) since it is well known that the SDW exists in these materials in the insulating state. We do not as yet have enough information regarding the magnetic symmetry of the ordered state to confirm this speculation. Experiments to ascertain the symmetry are underway.

We next turn to a discussion of the anomalies observed in the proton relaxation rates and rf absorption at 80 and 96 kOe. Here we can associate these effects with the observation of the magnetoresistance oscillations observed by several groups.[8,11] The anomalies that we observe correspond closely in field with the magnetotransport oscillations in which hysteresis is also noted. These effects are typically associated with magnetic transitions in ferromagnets, which also display hysteresis. It is difficult to understand a series of transitions as a function of magnetic field, but one possibility could be a magnetic field dependent wavelength of the SDW. Another mechanism for these effects might be due to a field-induced nesting of the Fermi surface[12]; however, it is difficult to account for magnetic order in this picture. Earlier work on the Se resonance in the PF_6 salt[13] also shows evidence for field-induced magnetic order. Obviously, the correct picture must account for these effects. To our knowledge, at present no theories account for field-induced magnetic order.

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