Itinerant-Electron Antiferromagnetism Precursor to Superconductivity in an Organic Conductor

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(Received 8 June 1982)

Below 5.5 K minimally strained crystals of $(TMTSF)_2ClO_4$ (TMTSF: tetramethyltetraselenafulvalene) exhibit vanishing spin-resonance intensity and reduced conductivity at low microwave power. More intense microwave electric fields along the needle axis nonlinearly restore both the resonance signal and the conductivity, indicating the presence of charged spin-density waves. Very anisotropic antiferromagnetic resonances are observed at 1.6 K, confirming that an itinerant spin-density-wave state precedes the onset of superconductivity at 1.3 K.

PACS numbers: 76.50.+g, 72.15.Nj, 74.70.Lp, 76.30.Pk

Organic conductors containing segregated stacks of planar donor and/or acceptor molecules exhibit maximum electrical conductivity in the stacking direction and usually undergo charge-density-wave (CDW) transitions to semiconducting ground states when cooled to ~ 50–200 K.[1] The essentially isomorphous series of Bechgaard salts $(TMTSF)_2^+X^-$ (where TMTSF is the organic donor tetramethyltetraselenafulvalene and X is one of many inorganic complex monoanion groups such as PF_6, AsF_6, ClO_4) is remarkable, *inter alia*, in that the maximal conductivity along the stacks of $TMTSF^{0.5+}$ donors continues to improve down to much lower temperatures.[2] When $X = PF_6^-$ or AsF_6^- metal-semiconductor transitions do occur below ~ 12 K but these appear to result from weak pinning of charged spin-density waves (SDW) rather than CDW instabilities.[3-8] The most direct evidence for the SDW state of the AsF_6 salt is provided by the observation of antiferromagnetic resonance (AFMR) by Torrance, Pedersen, and Bechgaard.[9] Whether the SDW state is, or is not, suppressed before the onset of superconductivity (SC) near 1 K in the PF_6 and AsF_6 salts under pressures $\gtrsim 6$ kbar is of considerable interest.[10,11]

The discovery of superconductivity at ambient pressure[12] below ~ 1.3 K in $(TMTSF)_2ClO_4$, coupled with weak resistive indications of a SDW transition below ~ 6 K,[13,14] suggested that the perchlorate salt offered a unique opportunity to observe competing magnetic and superconducting interactions among the itinerant holes. Here we report the disappearance of the conduction-hole spin resonance of $(TMTSF)_2ClO_4$ below 5.5 ± 0.5 K and its nonlinear restoration accompanied by variations of the microwave conductivity.[15] These are qualitatively similar to the nonlinear microwave phenomena which signaled formation of the SDW states of the PF_6 and AsF_6 salts.[3] Even more striking, however, is our observation of highly anisotropic antiferromagnetic resonances at 1.6 K, qualitatively similar to the signals found in the AsF_6 salt.[9] Thus, in the perchlorate, we have unambiguous evidence of sequential transitions from a normal, albeit very anisotropic, metallic state above 5.5 K to an itinerant antiferromagnetic (SDW) state followed directly by superconductivity below 1.3 K.

Crystals of $(TMTSF)_2ClO_4$ were prepared electrochemically from distilled 1,1,2-trichloroethane (stored over alumina) by using twice-recrystallized tetrabutylammonium perchlorate as supporting electrolyte. The TMTSF donor was purified by successive gradient sublimations at 10^{-4} Torr. Growth at 1–2 μA over a 2–3 week period produced crystals of various sizes. Crystals having typical dimensions $6 \times 0.5 \times 0.2$ mm^3 in the $\hat{a}$, $\hat{b}'$, and $\hat{c}'$ directions,[16] respectively, yielded the clearest results when individually inserted *without adhesive* in a rectangular glass capillary tube which was then greased on the wall of a rectangular microwave cavity resonant at ~ 12 GHz (TE_{101}) and ~ 17 GHz (TE_{102}). The ef-

fects to be described were reproducibly observed with crystals from two growth batches but only during the initial cryogenic run for each crystal.[17] Superconductivity was verified in both batches via resistivity and Meissner-effect measurements.

The g tensor and linewidth of the conduction-hole spin resonance (CHSR) determined at 12 GHz and temperatures of 295, 150, 80, and 20 K agreed with Scott's results.[15] At 4.2 K in minimally strained crystals no CHSR could be detected when using low microwave power (< 1 mW). When crystals were oriented with their $\hat{a}$ axis parallel to the weak microwave electric field near the cavity wall spin resonance could be restored ("resurrected," see Fig. 1) above a threshold field estimated to be ~ 30 mV/cm in the skin-effect region. The estimate is particularly crude because the microwave conductivity also changed significantly in the same range of microwave electric-field strength (see Fig. 1), becoming more conducting as the CHSR was restored. Above the transition region both the spin resonance susceptibility and microwave conductivity remained roughly constant. With use of a heated cavity it was found that these nonlinear effects

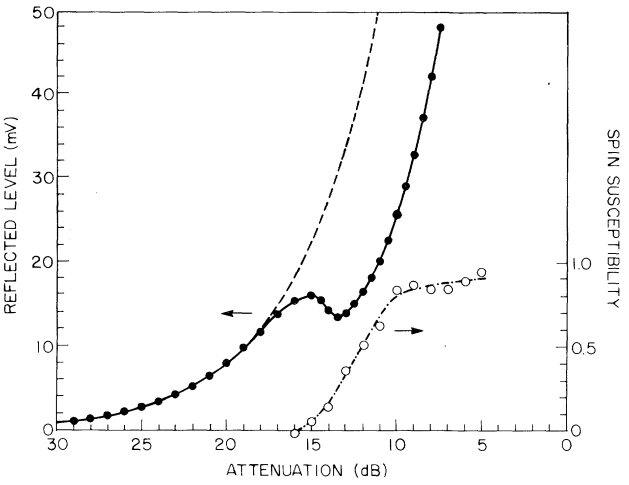

FIG. 1. Nonlinear response of a minimally strained crystal of $(TMTSF)_2ClO_4$ at 4.2 K to 12-GHz electric-field excitation along the $\hat{a}$ axis. The solid circles show the change in reflected level as a function of microwave power incident on the cavity; the deviation from square-law behavior above 1 mW is due to decreased loss. The open circles show the nonlinear "resurrection" of the donor-stack spin resonance susceptibility, undetectable below ~ 2 mW (16 dB), to its value above the onset of nonlinear behavior at 5.5 ± 0.5 K.

became undetectable above 5.5 ± 0.5 K, close to the temperature at which dc-conductivity evidence of SDW onset was reported.[13,14] Crystals believed to be strained did not display the relatively sudden recovery shown in Fig. 1 but some broad regions of nonlinearity in spin resonance intensity were often observed. It is important to emphasize, however, that *all* the spin signal disappears below threshold in minimally strained crystals. Thus all the spins and, therefore, all the carriers enter a collective state, presumably SDW, even though the conductivity decreases only a modest amount. Evidently the perchlorate is a truly itinerant-electron antiferromagnet.[18]

At lower temperature (1.6 K) we were unable to restore the normal-state spin resonance. However, a new signal linear in the microwave power was discovered. This resonance had roughly $\frac{1}{3}$ the intensity of the normal CHSR, was about 4 times broader (30 G full width at half maximum), and had an extremely "metallic" line shape, i.e., was nearly antisymmetric. The signal was strongly anisotropic both in the field for resonance and in its coupling to the microwave magnetic field, in a manner consistent with an orthorhombic antiferromagnetic resonance description.[9]

Scans in the a-b' plane [Fig. 2(a)] at 17 GHz yielded a roughly sinusoidal anisotropy pattern whose minimum and maximum resonance fields occurred ~ 30° from the $\hat{a}$ and $\hat{b}'$ axes, respectively. No such signal could be detected at 12 GHz. Scans made in the a-c' plane yielded no signals at either frequency. However, when the sample was rotated ~ 15° out of the magnetic field plane around the c' axis the extremely anisotropic pattern shown in Fig. 2(b) was readily observed at 12 GHz (but not at 17 GHz despite repeated efforts). When the data are plotted for both θ and $-\theta$ measured from the minimum resonance field, H_{min}, their average follows $H_{min}/\cos\theta$ quite accurately. The minimum position occurred 15 ± 2° from $\hat{a}'$, the projection of the crystalline $\hat{a}$ axis on the scanning plane. The signal could be followed out to $\theta = \pm 75°$ where the anisotropy was so rapid (> 800 G/deg) that the line broadened and weakened below detection, presumably due to ~ 0.2° of mosaic spread.

These anisotropies differ qualitatively from those observed by Torrance *et al.* in the AsF_6 salt but also prove to be consistent with an orthorhombic antiferromagnetic Hamiltonian with rather similarly oriented axes.[9] The apparent differences arise primarily from our use of lower microwave frequencies lying near Ω_- in the

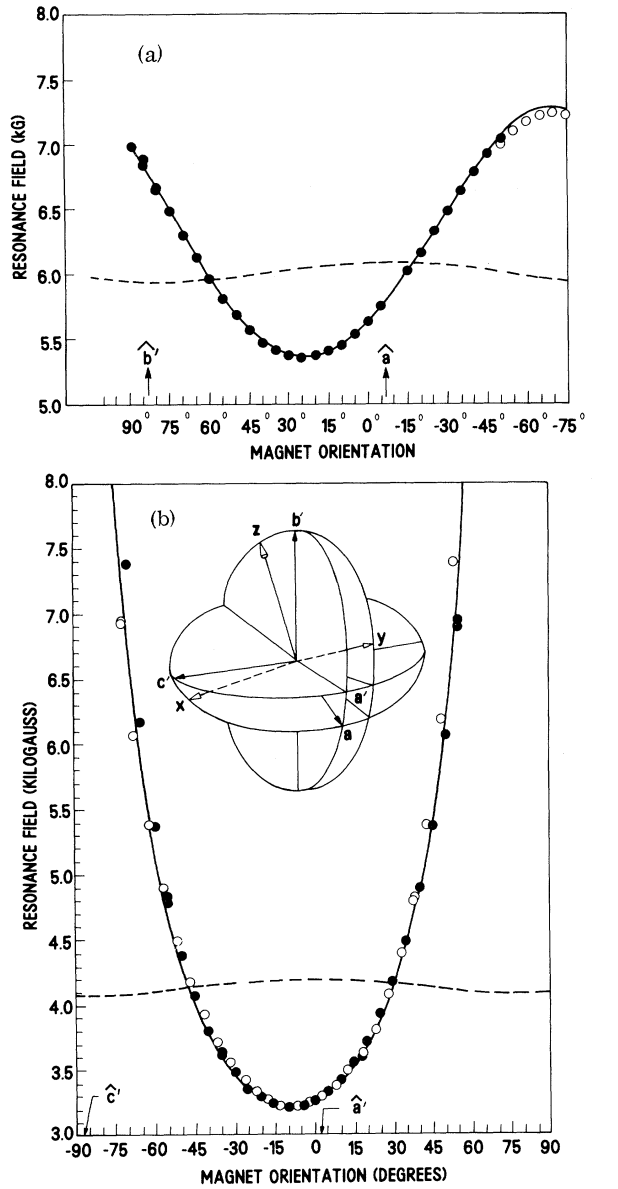

FIG. 2. Antiferromagnetic resonance anisotropies observed at 1.6 K in minimally strained $(TMTSF)_2ClO_4$ crystals. (a) In the a-b' plane at 16.99 GHz a roughly sinusoidal variation greatly exceeds the normal CHSR anisotropy (dashed curve) and shows the projections of the intermediate (y) and easy (z) axes to be rotated $\sim 30°$ from $\hat{a}$ and $\hat{b}'$. (b) An 11.4-GHz scan of the plane a'-c' rotated $\sim 15°$ out of a-c' (see inset) reveals an inverse cosine anisotropy relative to the projection of $y \sim 15°$ from a'. The divergences result from proximity to the magnetic hard axis (x). The open circles are the experimental points (solid circles) replotted reversed in angle to emphasize the slight asymmetry.

gap between the two zero-field AFMR modes and intersecting only the lower AFMR branch.[19] As shown in the inset of Fig. 2(b) the experimental a-b' and a'-c' scans were near the y-z and y-x principal magnetic planes. The divergent resonance fields of Fig. 2(b) mark the close approach to the hard $\hat{x}$ axis. The minimum resonance fields in each scan occur along the projections of the intermediate $\hat{y}$ axis where $\gamma H_{min} = (\omega^2 - \Omega_-^2)^{1/2}$. The maximum field of Fig. 2(a) lies along the projection of the easy $\hat{z}$ axis where $\gamma H_{max} = (\omega^2 + \Omega_-^2)^{1/2}$. Approximately correcting the observed extrema for the misorientations we deduce $\Omega_-/\gamma = 3.1 \pm 0.1$ kG for the lower zero-field AFMR frequency, quite comparable to the value 4.4 kG in the AsF_6 case.[9]

While it is not possible to determine Ω_+/γ from the data of Fig. 2 a lower bound of 10 kG is required to avoid marked deviations from the observed anisotropies. Clearly further experiments at higher frequencies and other temperatures will be required to measure the $T \to 0$ values of Ω_+ and Ω_-. As is evident from the discussion of the measured anisotropy fields of the AsF_6 salt, however, quantitative interpretation of these parameters will be difficult, particularly so in view of the very appreciable rotation of the principal magnetic axes with respect to those of the ClO_4 crystal.

It is more important at this time to emphasize that the $\hat{a}$-axis conductivity of $(TMTSF)_2ClO_4$ mains of order 10^{+6} $(\Omega\ cm)^{-1}$ in the temperature range where the AFMR is observed. Thus a very itinerant form of antiferromagnetism has been verified. It is quite distinct from the electron-hole annihilation of major sheets of Fermi surface as occurs in chromium metal where residual conductivity below the ordering temperature results from other carriers. In $(TMTSF)_2ClO_4$ the entire mobile carrier population enters a charged spin-density-wave ground state which is barely less conducting than the normal metallic state. Even more surprising is the unambiguous intersection of such a magnetic phase observed at 1.6 K with superconductivity below 1.3 K.[20] The possible coexistence of two such forms of electronic order is now the most interesting open question.[21,22]

We have benefited from discussions with numerous colleagues, especially W. F. Brinkman, M. C. Cross, E. Fenton, P. A. Lee, G. A. Thomas, and L. R. Walker.

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[16]These orthogonal axes are defined relative to the crystal morphology: $\hat{a}$ along the needle axis (donor stacking direction), $\hat{c}'$ normal to the broadest growth face (alternating sheets of donors and acceptors), $\hat{b}'$ orthogonal to the a-c' plane.

[17]Temperature cycling or the use of appreciably thicker samples even on initial cooling produced only weak indications of magnetic ordering. The fragility of the perchlorate cannot be overemphasized.

[18]The itinerant nature of the antiferromagnetic state in the PF_6 and AsF_6 salts should also be noted as their *microwave* conductivites remain $\gtrsim 10^5\ (\Omega\ \mathrm{cm})^{-1}$ well below their Néel temperatures.

[19]The frequency-field diagrams shown in Figs. 1–3 of H. J. Gerritsen, Physica (Utrecht) 21, 639 (1955), are helpful in visualizing these anisotropies.

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