Measuring the Fermi Surface of Quasi-One-Dimensional Metals

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We have discovered a new type of angular dependent magnetotransport which permits the measurement of the Fermi surface parameters of quasi-one-dimensional metals. Resistance measurements of $(TMTSF)_2ClO_4$ in the c (least conducting) direction show pronounced resonances when the field is rotated in the a-c plane near the a axis. At these resonances each electron trajectory across the warped Fermi surface sheets has an average velocity along c approaching zero. The resonance angles are determined by the bandwidths and allow us, for example, to extract t_b. For $(TMTSF)_2ClO_4$ in the anion ordered state, we measure $t_b = 0.012 \pm 0.001$ eV.

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The organic superconductors $(TMTSF)_2X$ have demonstrated the rich variety of physical phenomena possible in low-dimensional systems. Under different conditions of pressure, temperature, and magnetic field these materials can exhibit superconductivity, an antiferromagnetic (spin density wave) distortion, a cascade of magnetic field induced spin density wave transitions, and even the quantum Hall effect [1,2]. These highly anisotropic materials consist of stacks of TMTSF molecules along the high conductivity direction (a or x). The stacks assemble into sheets with lower conductivity in the (approximately) perpendicular (b or y) direction. The sheets are separated by an anion layers (X=ClO_4, PF_6, NO_3, ReO_4, etc.) in the c (or z) direction, forming the least conducting axis. The resulting anisotropy in conductivity is $\sigma_a : \sigma_b : \sigma_c \cong (t_a)^2 : (t_b)^2 : (t_c)^2 \cong 10^5 : 10^3 : 1$, where t_i is the tight binding transfer integral in the i direction [1]. The Fermi surface for the nearly one-dimensional band structure consists of two warped sheets at $k_x \sim \pm k_{\rm Fermi}$ (k_F) in the k_y-k_z plane. It is this *quasi-one-dimensional* structure that gives these materials their unique properties.

In this Letter we report resistance measurements along the least conducting direction (c axis) which exhibit a striking angular dependence as the magnetic field is tilted from the a to the c axis. We interpret these resonances in terms of orbital averaging of the c axis velocity. This model explains the new phenomena and allows direct evaluation of band parameters of these materials from the angular positions of resistance maxima.

An electric field causes electrons to redistribute among the states near the Fermi surface in such a way that there is a finite average velocity and current, and therefore a finite conductivity. In a material with a flat Fermi surface (t_b=t_c=0), the velocity in the z direction is zero for all **k** states. The average velocity is zero for any distribution or occupation of the states, and the conductivity (σ) is zero. If t_b and t_c are nonzero, there is a nonzero velocity, $v_z(\mathbf{k})$, and in equilibrium the **k** states are occupied so that $\langle v_z \rangle = 0$. The combined effect of an electric field and scattering shifts the momentum so that more **k** states with one sign of velocity are occupied than the other. The average velocity and conductivity will then be nonzero.

Quasiclassically, a magnetic field causes electrons to move over the open orbit sheets so that in effect each state on the Fermi surface has the average velocity corresponding to its particular trajectory. When the magnetic field is at certain angles with respect to the Fermi sheets, the trajectories are such that the average velocity in the z direction is zero for *all* of the states. Since each electronic state has zero velocity, any occupation of these states yields zero average velocity and zero conductivity. These special angles depend on the shape of the Fermi surface and particularly on t_b. Qualitatively, if each orbit oscillates across the Fermi surface with excursion $\approx n2\pi/c$ in the k_z direction, then $\langle v_z \rangle = \langle 2t_c c \sin(k_z c) \rangle \to 0$. For long scattering times the actual condition is that $J_0(\gamma_n) = 0$ where $\gamma_n = 2t_b c B_x / \hbar v_F B_z$ and $J_0(\gamma_n)$ is a Bessel function. For finite scattering times we numerically compute the conductivity and use the resonance peaks (in good agreement with the equation above) to measure $t_b = 0.012 \pm 0.001$ eV in the anion ordered state of ClO_4. The numerical results are in qualitative agreement with the complete angular dependence of the magnetoresistance (MR). Preliminary measurements of PF_6 and ClO_4 at high pressure confirm these results and support our understanding of the origins of this effect.

There have been other "magic angle" effects (known as Lebed oscillations [3–7]) observed for fields rotated in the b-c plane (as opposed to the a-c plane rotation here) that appear as resistance minima at special angles. The microscopic explanation for this effect is still controversial, but one explanation proposed by Osada [8] also involves averaging of the velocities along the z direction. However, Lebed's effect is related to the commensurate motion of electrons across the Fermi surface and is a purely geometrical resonance which measures the lattice parameters [e.g., $\tan\theta \sim (p/q)b/c$] rather than the band parameters.

Measurements were made on single crystals grown using standard electrochemical techniques. The mounted samples were immersed in liquid ^{3}He in a cryostat ca-

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pable of cooling to 0.5 K. Fields up to 8 T were generated using a split coil, horizontal bore superconducting magnet. The sample could be rotated through 4π sr using a goniometer above the magnet Dewar and a worm gear driven sample stage. Four probe resistance measurements were made with a low frequency lock-in. Eight contacts were made to the sample with 0.001 in. Au wire and silver paint such that the z and x directions could be probed simultaneously. Because the ClO_4 ion is not centrosymmetric there is a transition during which the ions orientationally order, the unit cell in the b direction is doubled [9], and the Brillouin zone (BZ) halved. The ClO_4 sample was cooled slowly through the anion ordering transition (<0.008 K/min from 32 to 16 K) to achieve a relaxed state.

The main experimental result of this Letter is shown in Fig. 1. The figure shows traces of the c axis resistance (R_{zz}) as the field is rotated in the a-c plane through a for different magnetic fields at 0.5 K. In the simplest picture, we expect no MR when the field is parallel to the current direction, maximum MR when current and field are perpendicular, and a smooth function between these limits. At high field we do see a maximum when the field is along a with the resistance dropping off to a minimum when the field is along c. The decrease is abrupt, though, with most of the decrease occurring in the first 20° of rotation away from a and with a nearly flat angular dependence near c. More surprisingly, when θ is less than some maximum angle we see two large peaks and a series of smaller peaks that sharpen as the field is increased and whose angular position is independent of field. At fields below 2 T, we see minima around $\theta = 0$ where the sample becomes superconducting. H_{c2} along a is much larger than along b or c [10]. Consequently, if the magnitude of field is below H_{c2} along a, the sample will become superconducting as it is rotated and the component along c falls below H_{c2} for that direction.

The Fermi surface (Fig. 2) for these materials consists of two sheets extended in the k_y-k_z plane whose k_x values are close to $\pm k_F$. There are weak modulations in k_y and k_z determined by the transfer integrals t_b and t_c, respectively. Taking a linear dispersion along x, the band structure near the Fermi surface is

$$E(\mathbf{k}) = \hbar v_F (|k_x| - k_F) - 2t_b \cos(k_y b) - 2t_c \cos(k_z c). \tag{1}$$

The orbits for the field oriented near a in the a-c plane are also shown in Fig. 2. When $\mathbf{H} \| \mathbf{a}$, there are a few orbits that close around the maxima and minima of k_x (orbit 1′), but most orbits are extended to infinity in k_z (orbit 1). As the field is tilted away from a, the orbits have large amplitude oscillations in k_z and are extended to infinity in k_y. The motion along k_y carries the electron over corrugations in the Fermi surface of amplitude $4t_b/\hbar v_F$ (along k_x). For an arbitrary angle, the average of v_z over the path need not be zero. Naively, at angles when the oscillation in k_z exactly covers an integer number of BZs, $\langle v_z \rangle$ will have equal positive and negative contributions over the path and will average to zero (orbits 2,3). At angles greater than those such that the oscillation in k_z can cover one BZ (orbit 3), v_z will not take on all possible values, and it can no longer average to zero. A rapid decrease of the MR with increasing angle is expected in this case. This tangent of this maximum angle (measured from a) is given approximately by the

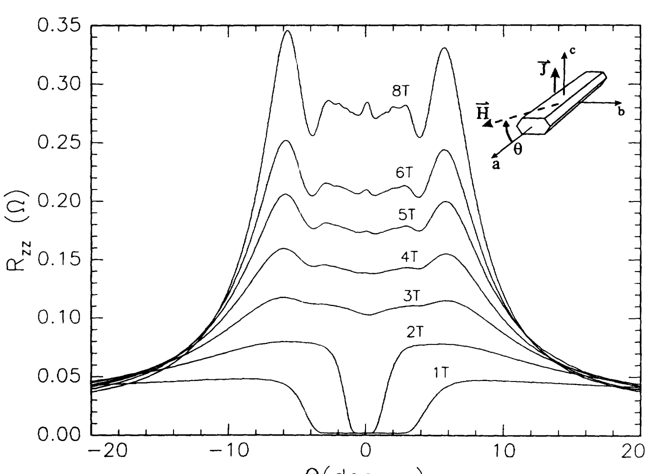

FIG. 1. Angular dependence of c axis resistance for rotations in the a-c plane at different fields for $(TMTSF)_2ClO_4$ at $T = 0.5$ K. The 2 T and 1 T traces exhibit superconductivity at smaller angles. Inset is a drawing of a crystal with axis, field, and current directions as shown.

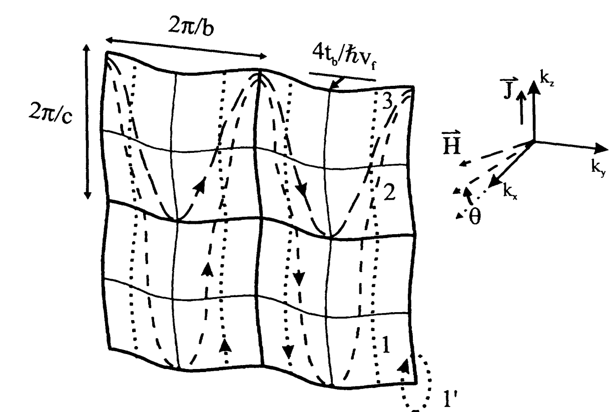

FIG. 2. The Fermi surface for $(TMTSF)_2ClO_4$. Orbits 1 and 1′ (dotted) show the approximate paths for electrons when the field is parallel to a for closed (1′) and open (1) orbits. Orbits 3 (long dashed) and 2 (short dashed) show the paths when the angle of the magnetic field is near the primary maxima and the first secondary maxima of the data, respectively.

height of the corrugations in k_x over the length of the BZ in k_z, or $(4t_b/\hbar v_F)/(2\pi/c)$.

We can make this result more quantitative by calculating v_z and integrating over the electron path. We use the equations of motion for an electron in a uniform magnetic field,

$$\hbar\frac{d\mathbf{k}}{dt} = e\left(\frac{\mathbf{v}}{c_l}\times\mathbf{B}\right), \quad \mathbf{v} = \frac{1}{\hbar}\nabla E(\mathbf{k}), \tag{2}$$

and integrate to get $v_z(t)$. If one assumes $v_F B_z \gg v_z B_x$ then the solution for v_z can be obtained analytically as

$$v_z(t) = \frac{2t_c c}{\hbar}\sin\left[\gamma\cos\left(\omega_b t + k_{y0}b\right) + k_{z0}c\right], \tag{3}$$

where

$$\gamma = \frac{2t_b c}{\hbar v_F}\frac{B_x}{B_z}\ , \qquad \omega_b = \frac{ev_F B_z b}{\hbar c_l}\ , \tag{4}$$

k_{y0}, k_{z0} determine the initial positions on the Fermi surface, and b, c are the lattice constants. The average of (3) over one period $(2\pi/\omega_b)$ can be written as

$$\langle v_z\rangle \propto \int_0^{2\pi}\sin[\gamma\cos(\theta)]d\theta. \tag{5}$$

This integral has the same zeros as the Bessel function $J_0(\gamma)$. In the absence of scattering, the average velocity of an orbit originating anywhere on the Fermi surface is zero for the values of γ_n giving $J_0(\gamma_n) = 0$. By using these zeros and the angles at which the maximum in resistance occurs, we can measure the value of t_b. The difference between the condition $\tan\theta_n = 2t_b c/\gamma_n\hbar v_F$ and the naive condition $\tan\theta_n = 2t_b c/n2\pi\hbar v_F$ is that the motion along k_z is a sinusoidal rather than a sawtooth function of time. As a result the electron remains in certain regions of its orbit longer than other regions, and the averaging reflects this. The complete equation for the conductivity can be expressed using a relaxation time approximation [11] as

$$\sigma_{ij} = e^2\int\frac{d\mathbf{k}}{4\pi^3}\tau v_i(\mathbf{k})\bar{v}_j(\mathbf{k})\left(-\frac{\partial f}{\partial E}\right), \tag{6}$$

where f is the Fermi function, τ is the scattering time, and

$$\bar{v}_j(\mathbf{k}) = \int_{-\infty}^{0}\frac{dt}{\tau}e^{t/\tau}v_j(\mathbf{k}(t)). \tag{7}$$

We assume the scattering time is a constant and perform the integrations numerically (it is therefore not necessary to assume that $v_F B_z \gg v_z B_x$). The results are shown as the solid lines in Fig. 3. The qualitative agreement with the data is excellent. The resistivity ($\cong 1/\sigma_{zz}$) at large angles is nearly independent of angle, and for angles closer to zero we see a series of peaks. The amplitude of these peaks increases as field is increased (at fixed τ), but their angular position is field independent. For angles less than that of the primary peak, the resistivity falls off sharply and displays the secondary maxima and the peak at $\theta = 0$. The position of the primary peak as well as the amplitude of the structures is sensitive to the value chosen for t_b. The value of t_b determines the special angle for the maxima, as seen from the geometric argument earlier. It also determines the magnitude of the y velocity, which affects the speed along the path used in the averaging. From this calculation, we determine that the best agreement with the data comes from a value $t_b = 0.012$ eV. This should be $\sim 1/2$ the room temperature value (because of the anion ordering) and would give a bandwidth $4t_b = 0.096$ eV at room temperature. This is consistent with previous estimates. We can also obtain some information about t_c from this calculation (broken lines in Fig. 3). These curves show the results when t_c is varied around the assumed value of $t_b/15$; note that the peak at zero disappears as t_c is reduced. When the field is directly along a there is a small band of closed orbits near the extrema of the Fermi surface, and all other orbits extend to $\pm\infty$ in k_z. The closed orbits are more effective in averaging the velocity to zero than the extended orbits, resulting in an enhanced resistance. The enhancement will decrease as the closed orbits are destroyed by rotating the field away from a. The number of closed orbits is set by the warping of the Fermi surface, and hence t_c. The results of this calculation are consistent with the previously measured value for $t_c \approx t_b/15$ [1]. Although the calculation is in qualitative agreement with the data, some of the quantitative features are not. The calculation shows a stronger field dependence for the peaks than does the data. We have tried incorporating higher harmonics in k_y into the band structure, as well as adding series and parallel background resistances to

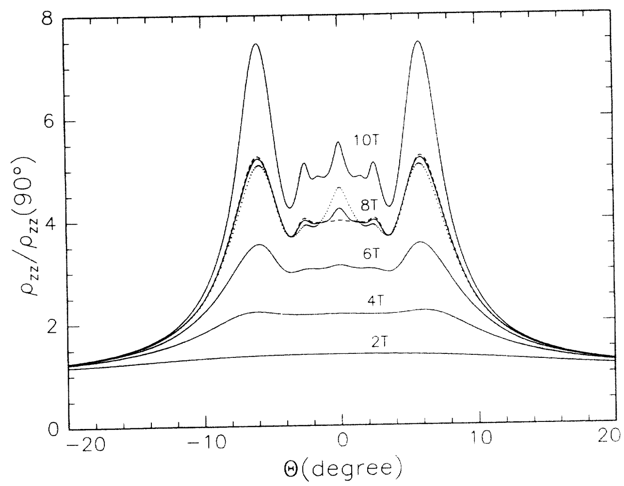

FIG. 3. Solid lines are the angular dependence of the calculated ρ_{zz} for different fields at fixed $\tau = 4.3\times10^{-12}$ s. These curves use values of $t_b = 0.012$ eV and $t_c = t_b/15$. The broken lines are for the same parameters as the 8 T solid line, except the dashed line uses $t_c = t_b/7.5$ and the dotted line uses $t_c = t_b/60$.

the results of the calculation. Neither of these solutions adequately corrected these defects. More complicated models incorporating a **k** dependent scattering time or a mechanism to give small angle scattering may give more quantitative agreement, but we have not pursued these possibilities here.

This technique can be used to measure the different Fermi surfaces of quasi-one-dimensional compounds. Preliminary measurements of PF_6 and ClO_4 at high pressure show similar effects but with values of t_b approximately 2 times larger than in this experiment. Pressure suppresses the anion ordering in ClO_4 [2, 12], and PF_6 is centrosymmetric and does not undergo an anion ordering transition. The reduced bandwidth measured here is consistent with the anion ordered state of the crystal. There is another family of organic superconductors based on BEDT-TTF (or ET) [13]. $(ET)_2KHg(SCN)_4$ has a Fermi surface consisting of a pair of 1D warped sheets in the k_y-k_z plane as well as warped cylinders extending along k_z [14]. There have been observations of anomalous angular magneto-oscillatory phenomena at low temperature that appear to depend only on the component of the field in a plane perpendicular to the 1D sheets [15, 16]. This experimental geometry is analogous to that described here, and it is suggestive that the effects may be related to the resonance phenomenon discussed above.

A closely related effect to this work is found in the Yamaji [17–20] resonances in closed orbit, quasi-two-dimensional compounds (also based on ET). In a tilted field the electron follows an elliptical orbit around the warped cylindrical Fermi surface. At special angles determined by the zeros of Bessel functions, the z velocity averages to zero. The mean diameter of the 2D cylinder can be measured in this way. Mathematically, the effects are similar because they involve sinusoidal averaging of the velocity along the narrow tight binding bands in the least conducting direction. We have introduced a new method for gaining quantitative information about the Fermi surface parameters of a quasi-one-dimensional metal. Using this novel angular MR resonance effect, we have measured values for t_b in anion ordered ClO_4. This effect makes possible detailed studies of phenomena related to the dimensionality and transverse bandwidths of low-dimensional systems where transition temperatures and different phases are often controlled by pressure, anion ordering, and magnetic fields.

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