Charge-Density Waves Survive the Pauli Paramagnetic Limit

R. D. McDonald,[1] N. Harrison,[1] L. Balicas,[2] K. H. Kim,[1,*] J. Singleton,[1] and X. Chi[1]

[1]National High Magnetic Field Laboratory, LANL, Mississippi-E536, Los Alamos, New Mexico 87545, USA

[2]National High Magnetic Field Laboratory, Florida State University, 1800 E. Paul Dirac Drive, Tallahassee, Florida 32310, USA

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Measurements of the resistance of single crystals of $(\mathrm{Per})_2\mathrm{Au(mnt)}_2$ have been made at magnetic fields B of up to 45 T, exceeding the anticipated Pauli paramagnetic limit of $B_{\mathrm{p}} \approx 37$ T. The continued presence of nonlinear charge-density wave electrodynamics at $B \geq 37$ T establishes the survival of the charge-density wave state above this limit, and the probable emergence of an inhomogeneous phase analogous to that anticipated to occur in superconductors.

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Fundamental changes can occur within paired-electron condensates subjected to intense magnetic fields [1–3]. If the state is a spin-singlet (with electron spins opposed), as in charge-density waves (CDWs) [4] and s- and d-wave superconductors [5], the energy of the partially spin-polarized electrons of the uncondensed metal eventually becomes lower than the condensate energy above a characteristic magnetic field known as the Pauli paramagnetic limit [6–8]. Continued survival of the condensate requires the formation of a lower energy, spatially-inhomogeneous phase, in which pairing is between spin-polarized quasiparticles [8–12]. The existence of such a phase in superconductors becomes questionable owing to the field-induced kinetic energy of orbital currents, which often suppresses superconductivity more strongly [13,14]. By contrast, pure CDW systems are free from orbital currents, yet their high condensation energies increase the demand on magnetic field strength required to reach the Pauli paramagnetic limit [4]. $(\mathrm{Per})_2\mathrm{Au(mnt)}_2$ is a rare example where this limit (≈ 37 T) falls within reach of the highest available quasistatic magnetic fields of 45 T [15,16]. In this Letter, we use temperatures down to 25 mK (roughly one-thousandth of the energy gap) to show that the CDW state survives the anticipated Pauli paramagnetic limit, signalling the probable appearance of an inhomogeneous phase.

Both superconductivity [5] and CDWs [4] form as a consequence of electron-phonon interactions. Superconductors are ground states in which gauge symmetry is broken (where the spatial variation of the magnetic field is dependent on topology) [5], while CDWs exhibit a periodic charge modulation that breaks translational symmetry [4]. The BCS (Bardeen-Cooper-Schrieffer) formalism that applies to superconductivity [17], also conveniently describes the electronic structure of CDWs, with the gap in the electronic energy spectrum in the zero temperature limit being given by $2\Delta_0 = \zeta k_{\mathrm{B}} T_{\mathrm{c}}$, where T_{c} is the transition temperature. Whereas the ratio $\zeta = 3.52$ in weak-coupling BCS theory, $5 < \zeta < 10$ in CDWs owing to their strong coupling to the ionic lattice [4]. Upon lowering the temperature through T_{c}, a metal-insulator transition occurs, below which normal carriers must be thermally excited across the gap to conduct. The presence of a magnetic field B lowers T_{c} [8]; simple theory predicts $T_{\mathrm{c}} \rightarrow 0$ at the Pauli paramagnetic limit defined as [6]

$$B_{\mathrm{P}} = \frac{\Delta_0}{\sqrt{2} g s \mu_{\mathrm{B}}}, \tag{1}$$

where g is the electron g-factor, s is the electron spin and μ_B is the Bohr magneton. Equation (1) defines the field at which the paramagnetism of the electrons causes the free energy $F_{\mathrm{N}} = -D(\varepsilon_{\mathrm{F}})[g s \mu_{\mathrm{B}} \mathrm{B}]^2$ of the normal metal to become equivalent to that $F_{\mathrm{CDW}} = -D(\varepsilon_{\mathrm{F}})\Delta_0^2/2$ of the regular CDW phase, where $D(\varepsilon_{\mathrm{F}})$ is the density of electronic states of the normal metal at the Fermi energy.

Whenever a CDW is present, very low temperatures facilitate its observation by freezing out normal carriers that would otherwise be thermally excited across the energy gap [4]. Electrical conduction can then only take place via the CDW collective mode, requiring a threshold electric field E_{t} (or a threshold voltage V_{t} observed between voltage terminals) to depin it from impurities and defects in the crystalline lattice [4]. Once depinned, the CDW is able to slide and carry a current with only small incremental changes in electric field producing large increases in current. This gives rise to a distinctive current I-versus-voltage V behavior that has been observed experimentally in numerous CDW systems [4,18]. The size of the threshold electric field (or V_{t}) depends on the strength of the coupling between the charge modulation and pinning sites [4]. This coupling is known to become weaker once the CDW becomes more incommensurate or when the size of the energy gap is reduced. Both are expected to occur within the spatially-inhomogeneous phase [11,12].

The material described in this Letter, $(\mathrm{Per})_2\mathrm{Au(mnt)}_2$ belongs to a series of isostructural charge-transfer salts consisting of one-dimensional conducting chains of perylene molecules (in the $(\mathrm{Per})_2^+$ oxidation state) and insulating chains of maleonitriledithiolate (in the $M(\mathrm{mnt})_2^-$

oxidation state), with two formulas per unit cell giving rise to a 3/4-filled band [18]. CDWs occur for $M = \mathrm{Pt}$, Cu and Au, with the transition temperature being approximately 12 K in the $M = \mathrm{Au}$ salt. This brings the anticipated B_{P} comfortably within the range of the 45 T Hybrid Magnet at the National High-Magnetic Field Laboratory in Tallahassee [15,16]. Although a lower transition (8 K) occurs in the $M = \mathrm{Pt}$ salt, CDW formation there is compounded by the synchronous formation of a spin Peierls state involving localized spins on the Pt sites [15]. A pure CDW state occurs only in the case of the $M = \mathrm{Au}$ and Cu salts.

Previous experimental studies of $(\mathrm{Per})_2\mathrm{Au(mnt)}_2$ have shown the suppression of the transition temperature into the insulating state to be proportional to the square of the magnetic field (B^2) to leading order, in accordance with the predictions of mean-field theory [15]. The CDW energy gap is also suppressed with magnetic field, with excitations of normal carriers across the gap giving rise to a thermally activated resistance of the form $\rho \propto \exp(-\Delta/2k_BT)$ on entering the CDW phase, where Δ parametrizes the activation gap. Fits of the resistance to the thermal activation model enable one to anticipate gap closure of the uniform CDW phase at $B_{\mathrm{P}} \approx 37$ T[16]. Assuming $gs = 1$ and weak dispersion of the electronic bands orthogonal to the chains (see discussion below), this yields $\zeta \approx 6$, which falls within the range typical for CDW ground states [4]. Figure 1 compares plots of the B-dependence of the resistance R of a needle-shaped sample of $(\mathrm{Per})_2\mathrm{Au(mnt)}_2$ (of dimensions 3 mm $\times$ $30\mu\mathrm{m} \times 20\mu\mathrm{m}$), for different values of the current I (applied along the chains parallel to the **b**-axis) and for two orthogonal directions of B oriented perpendicular to the chains at 25 mK. The hysteresis between up and down B sweeps could be the consequence of a first order phase transition, compounded by CDW pinning effects [4]. The Pauli limit is expected to yield a first order phase transition [8,12].

In agreement with previous studies [16], the sample resistance R shown in Fig. 1, is observed to drop by roughly an order of magnitude between 28 and 37 T. This abrupt drop in resistance on surpassing B_{P} was recently interpreted (Ref.[16]) as the destruction of the CDW phase, followed by the recovery of metallic behavior. Unfortunately the experiments in Ref. [16] were limited to temperatures $T \gtrsim 0.5$ K; hence, the high-magnetic field region of non-linear conductivity could not be accessed in those experiments [16], preventing the observation of the true nature of the ground state at $B > B_{\mathrm{P}}$. In the present study, the continued strong dependence of R on I at $B > B_{\mathrm{P}}$ at dilution refrigerator temperatures ($T \ll 0.5$ K) in Fig. 1 is clearly uncharacteristic of a metal. It is, nevertheless, consistent with the continued presence of a CDW phase. The data in Fig. 1 display typical CDW non-linear I-versus-V electrodynamics (where $V = IR$) at all magnetic fields, characterized by

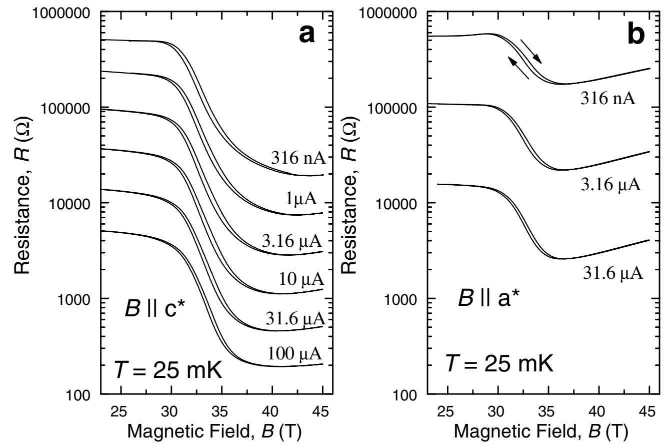

FIG. 1. Electrical resistance of a single crystal of $(\mathrm{Per})_2\mathrm{Au(mnt)}_2$ measured in a portable-dilution-refrigerator at 25 mK for fields between 23 and 45 T, for two different orientations c^* (a) and a^* (b) of B perpendicular to its long axis b, at several different applied currents. The lowest resistance for a given current occurs for B parallel to c^*, which is perpendicular to a^*. The dependence of the resistance on current signals nonohmic behavior (see Fig. 3). Hysteresis between rising and falling magnetic fields (shown by arrows) is the consequence of a first order Pauli phase transition between low-magnetic-field uniform CDW and high-magnetic-field inhomogeneous CDW phases. Orbital effects involving neighboring perylene chains are proposed to account for the field orientation dependence of the resistance [16].

an almost order of magnitude drop in R for an order of magnitude increase in I. This becomes particularly clear on comparing the I-versus-V plots at 26 and 44 T in Fig. 2. The only qualitative change between high and low-magnetic field regimes at 25 mK is that the I-versus-V curve is shifted to lower voltages at magnetic fields above B_{P}, corresponding to a drop in the threshold voltage V_{t} of more than one decade. We can therefore state that the CDW ground state survives the anticipated B_{P}, but with its pinning to the lattice becoming considerably weakened. Such weakening is likely to be a consequence of the CDW becoming increasingly incommensurate on accommodating Zeeman contributions to the modulation vector(s) [8,11,12], combined with a greatly reduced energy gap $2\Delta_\lambda$ [11,12] (see discussion below). In the case of the former, pinning is reduced because harmonics of the CDW ordering vector no longer match with the periodicity of the crystalline lattice [4]. In the case of the latter, a reduced gap gives rise to a weaker charge modulation, thereby having weaker Coulomb interactions with impurities and defects [4].

Evidence that $\Delta_\lambda \ll \Delta_0$ is obtained by repeating the I-versus-V plot at $T = 900$ mK in Fig. 2. This elevated temperature is approximately 60 times lower than $2\Delta_0$ and is therefore unable to excite significant numbers of carriers across the gap within the uniform low-magnetic field CDW phase [4]. It is, however, sufficiently high to

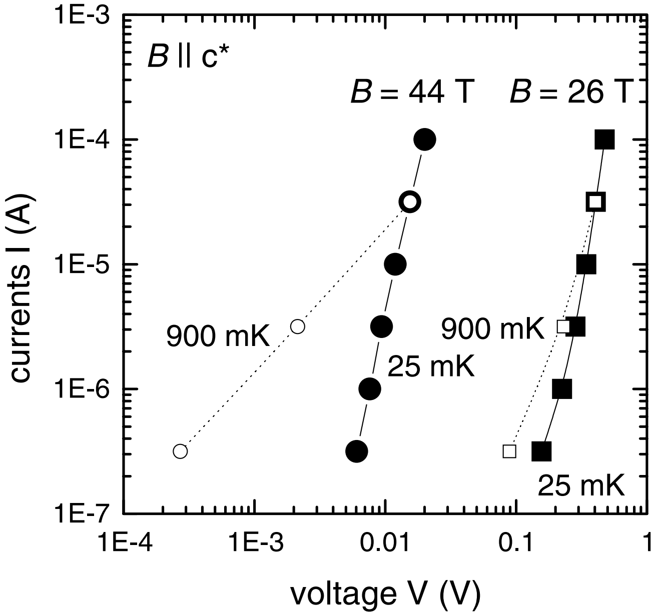

FIG. 2. Non-linear current-versus-voltage characteristic of $(Per)_2Au(mnt)_2$ plotted on a log-log scale, for selected magnetic fields (26 and 44 T) above (circles) and below (squares) B_P. Filled symbols connected by solid lines represent data taken at 25 mK while open symbols connected by dotted lines represent data taken at 900 mK. A strong increase in current for a small increase in voltage (or electric field) is the characteristic electrodynamic behavior of CDWs at very low temperatures where normal carriers are frozen out [4]. The threshold depinning voltage V_t is usually defined as the lowest voltage at which non-linear I-versus-V behavior is observed, yet attempts to drive currents of 100 nA or smaller through the sample were unsuccessful at 25 mK for $B < 37$ T: hence, we loosely define $V_t \approx 150$ mV at $B = 26$ T and ≈ 6 mV at $B = 44$ T for voltage contacts $\sim$1 mm apart.

restore Ohmic ($I \propto V$) behavior above B_P. Ohmic behavior is restored whenever the gap is destroyed or when a significant number of carriers are thermally excited across a gap that has become considerably reduced. The data are therefore consistent with mean-field theory, which predicts $2\Delta_\lambda \ll 2\Delta_0$ [11].

Apart from the above energetic considerations that give rise to $B_P = \Delta_0/\sqrt{2}gs\mu_B$ [6], Zeeman splitting of the electronic bands by B provides another fundamental reason why uniform CDWs cannot exist for $B \gtrsim B_P$ [7]. At $B = 0$, the optimum modulation vector $\mathbf{Q}_0$ of the CDW is equal to the wave vector $2\mathbf{k}_F$ separating states with opposing momenta $\pm\hbar\mathbf{k}$ and Fermi velocities $\pm\Delta_0$ at the Fermi energy ε_F (the energy to which the electronic bands are filled) [4]. A schematic of the density of electronic states gapped upon CDW formation is sketched in Fig. 3(a), which has been rounded for visual clarity. We have used the generic mean-field expression [4]

$$D(\varepsilon) = \left|\frac{\varepsilon \pm b}{\sqrt{(\varepsilon \pm b)^2 - \Delta_0^2}}\right| D_0(\varepsilon \pm b) \qquad (2)$$

where the density of states $D_0(\varepsilon)$ in the absence of CDW formation is assumed to be a smoothly varying function, again, for the purposes of visual clarity. In the presence of a magnetic field, the Zeeman energy $b = gs\mu_B B$ causes $2\mathbf{k}_F$ to differ by $\pm b/\hbar v_F$ for spin-up and spin-down electrons. While the optimum nesting vectors for the separate Fermi surface spin components become different, it is still energetically more favorable for the CDW to maintain a single nesting vector $\mathbf{Q}_0$ for $B < B_P$ [8,9,19]. This causes the spin-up and spin-down energy gaps to shift with respect to ε_F, as depicted in Fig. 3(b) [11,12]. At fields above $\sqrt{2}B_P$ (depicted in Fig. 3(c) whereupon $b > \varepsilon$), however, ε_F can no longer reside within the gap [7].

One possible outcome is that the CDW phase is simply destroyed, reverting to a normal metallic state [16,19]. Another more interesting possibility is that the $\mathbf{Q}_0$ becomes modified so as to include incommensurate components proportional to the Zeeman energy, creating a new gap

$$D(\varepsilon) \approx \int \left|\frac{\varepsilon \pm b}{\sqrt{\varepsilon^2 - \Delta_\lambda(\mathbf{r})^2}}\right| D_0(\varepsilon \pm b) \mathrm{d}V \qquad (3)$$

at ε_F, as depicted in Fig. 3(d) [11,12], where $\mathrm{d}V$ is the volume integration element. Hence $\mathbf{Q}_0$ becomes $\mathbf{Q}_\lambda = \mathbf{Q}_0 \pm 2gs\mu_B B\mathbf{v}_F/\hbar|\mathbf{v}_F|^2$, for the spin-up and spin-down components, respectively, giving rise to spin-up and spin-

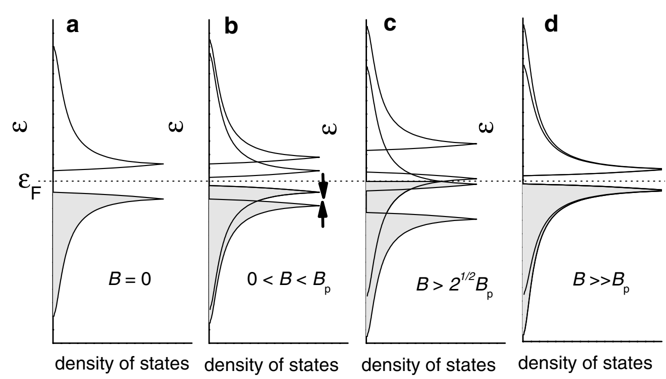

FIG. 3. The CDW gap in the electronic density of states (DOS) for different magnetic field strengths B. (a), the DOS at $B = 0$, with the shaded region representing occupied states below the Fermi energy ε_F. (b), the same DOS for $0 < B < B_P$, showing closing of the gap. The Pauli paramagnetic magnetization is zero since the proportion of spin-up and spin-down states (shown by arrows) is unchanged from that at $B = 0$. (c), the same DOS showing complete closure of the gap at $B > \sqrt{2}B_P$, in which case uniform CDW phase cannot be stable. (d), possible gap formation due to incommensurate CDW formation for $B \gg B_P$. For the purposes of contructiung this Figure, we have simply assumed $\Delta_\lambda(\mathbf{r})^2$ to take an average value $|\Delta_\lambda(\mathbf{r})^2| < \Delta_0^2$ If the gap stays pinned to ε_F, the Pauli paramagnetic magnetization of this state is equivalent to that of the normal metal.

down CDWs that are mutually incommensurate which each other as well as the crystalline lattice.

Were only a single spin component to nest [20,21], imperfect nesting of the other spin component would result in field-induced CDWs that incorporate orbital quantization. These would manifest themselves by way of quantized Hall plateaux and ohmic longitudinal edge-state transport by normal quasiparticles along the length of the needlelike samples at the lowest temperatures. The absence of a quantized Hall effect across Hall contacts together with the non-linear *I*-versus-*V* behavior in the longitudinal transport in Fig. 2 at the lowest temperatures indicates that such a scenario does not occur in $(Per)_2Au(mnt)_2$. Given the absence of significant electronic dispersion orthogonal to the chains (which enables the nesting to be perfect at $B = 0$), there is also no thermodynamic reason to expect field-induced CDW phases to exist at fields significantly lower than B_P. The same absence of significant electronic dispersion orthogonal to the chains also favors a scenario at $B > B_P$ where both spin components simultaneously nest [12]. A simple superposition of spin-up and spin-down modulations would lead to a combined charge and spin modulation, with the amplitude further modulated with a very long period $\lambda = \pi\hbar|\mathbf{v}_F|/2gs\mu_B B$, giving rise to possible nodes in $\Delta_\lambda(\mathbf{r})$, where $\mathbf{r}$ is the spatial coordinate. While a detailed theoretical model of this complex inhomogeneous phase has not been made [12], the average value of the modified energy gap $2\Delta_\lambda$ is expected to be significantly smaller than $2\Delta_0$ [11] (see Fig. 3d) requiring lower temperatures for its observation. In the absence of additional interactions, this inhomogeneous state should survive to fields as large as $B = \hbar(\mathbf{v}_F \cdot \mathbf{Q}_0)/2gs\mu_B$, whereupon the Fermi surface becomes spin polarized.

In summary, the survival of CDW electrodynamics to fields far above the anticipated Pauli limit of $(Per)_2Au(mnt)_2$ in Fig. 2, in a region where the uniform phase cannot exist, indicates the likely development of an inhomogeneous CDW phase that is stable only at high-magnetic fields. The weakened threshold electric field for depinning the CDW is consistent with such a fragile incommensurate phase. This finding, combined with the restoration of ohmic behavior at 900 mK (a temperature that is still low for the uniform CDW), is consistent with a greatly reduced gap $2\Delta_\lambda$. One distinct advantage of the inhomogeneous phase of a CDW, over that anticipated in superconductors, is that the long range incommensurate charge and spin modulations can be verified directly by means of x-ray and neutron diffraction techniques [4]. Until such techniques become available in fields of $B > 30$ T, however, nuclear-magnetic-resonance may provide an alternative means for probing incommensurate structures [4]. A direct verification of the inhomogeneous CDW phase would greatly enhance our understanding of the generic properties of singlet-paired condensates in high-magnetic fields. It would also provide an essential precedent for understanding proposed inhomogeneous phases in *s*- and *d*-wave paired superconductors [9,10,13,14].

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*Present address: CSCMR & School of Physics, Seoul National University, Seoul 151-742, Korea.

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