Charge-density Waves Survive the Pauli Paramagnetic Limit

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Measurements of the resistance of single crystals of (Per\textsubscript{2}Au(mnt))\textsubscript{2} have been made at magnetic fields \( B \) of up to 45 T, exceeding the Pauli paramagnetic limit of \( B_{P} \approx 37 \) T. The continued presence of non-linear charge-density wave electrodynamics at \( B \geq 37 \) T unambiguously establishes the survival of the charge-density wave state above the Pauli paramagnetic limit, and the likely emergence of an inhomogeneous phase analogous to that anticipated to occur in superconductors.

PACS numbers: 71.45.Lr, 71.20.Ps, 71.18.+y

Fundamental changes can occur within paired-electron condensates subjected to intense magnetic fields \[ 1, 2, 3 \]. If the state is a spin-singlet (with electron spins opposed), as in charge-density waves (CDWs) \[ 4 \] and \( s \) and \( d \)-wave superconductors \[ 7 \], the energy of the partially spin-polarized electrons of the uncondensed metal eventually becomes lower than condensate energy above a characteristic field known as the Pauli paramagnetic limit \[ 4, 7 \]. Continued survival of the condensate requires the formation of a lower energy spatially-inhomogeneous phase, in which pairing is between spin-polarized quasiparticle states \[ 6, 9, 10, 11, 12, 13 \]. 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 \[ 10, 11, 12 \]. 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 \[ 4 \]. (Per\textsubscript{2}Au(mnt))\textsubscript{2} is a rare example where this limit (\( \approx 37 \) T) falls within reach of the highest available quasi-static magnetic fields of 45 T \[ 10, 11, 12 \]. In this paper we use temperatures down to 25 mK (roughly one-thousandth of the energy gap) to show that the CDW state surpasses the Pauli paramagnetic limit, signalling the likely appearance of an inhomogeneous phase.

Both superconductivity \[ 2 \] and CDWs \[ 4 \] form as a consequence of electron-phonon interactions. Superconductors are ground states in which gauge symmetry is broken (where the variation of the magnetic field is dependent on topology) \[ 10 \], while CDWs exhibit a periodic charge modulation that breaks translational symmetry \[ 4 \]. The BCS (Bardeen-Cooper-Schrieffer) formalism that applies to superconductivity \[ 10 \], also conveniently describes the electronic structure of CDWs, with the gap in the electronic energy spectrum in the zero temperature limit being given by \( 2\Delta_{0} = \zeta\mu_{B}T_{c} \), where \( T_{c} \) is the transition temperature. Whereas the ratio \( \zeta \approx 3.52 \) 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 \( T_{c} \); simple theory predicts \( T_{c} \to 0 \) at the Pauli paramagnetic limit defined as \( B_{P} = \Delta_{0}/\sqrt{2g\mu_{B}} \), where \( g \) is the electron \( g \)-factor, \( s \) is the electron spin and \( \mu_{B} \) is the electron Bohr magneton.

Apart from the above energetic considerations \[ 6 \], Zeeman splitting of the electronic bands by \( B \) provides another fundamental reason why uniform CDWs cannot exist for \( B \gtrsim B_{P} \). At \( B = 0 \), the optimum modulation vector \( \mathbf{Q}_{0} \) of the CDW is equal to the wave vector \( 2\mathbf{F} \) separating states with opposing momenta \( \pm \hbar \mathbf{k} \) and Fermi velocities \( \pm \mathbf{v}_{F} \) at the Fermi energy \( \varepsilon_{F} \) (the energy to which the electronic bands are filled) \[ 10 \]. A model of the density of electronic states gapped upon CDW formation is sketched in Fig. 1a. The Zeeman energy \( \pm g\mu_{B}B \) causes \( 2\mathbf{F} \) to differ by for spin-up and spin-down electrons, causing the spin-up and spin-down energy gaps (formed by \( \mathbf{Q}_{0} \)) to shift with respect to \( \varepsilon_{F} \), as depicted in Fig. 1a, 12, 13. At fields above \( \sqrt{2}B_{P} \) (depicted in Fig. 1a), \( \varepsilon_{F} \) can no longer reside within the gap \[ 10 \].

One possible outcome is that the CDW phase is simply destroyed, reverting to a normal metallic state \[ 10, 17 \]. Another more interesting possibility is that the \( \mathbf{Q}_{0} \) becomes modified so as to include incommensurate components proportional to the Zeeman energy so as to create a new gap at \( \varepsilon_{F} \), as depicted in Fig. 1b, 12, 13. Hence \( \mathbf{Q}_{0} \) becomes \( \mathbf{Q}_{0} \pm 2g\mu_{B}\mathbf{v}_{F}/h|\mathbf{v}_{F}| \), for the spin-up and spin-down components respectively, giving rise to spin-up and spin-down CDWs that are mutually incommensurate which each other as well as the crystalline lattice. 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 \( \lambda = \pi|\mathbf{v}_{F}|/2g\mu_{B}B \), giving rise to possible nodes. While a detailed theoretical model of this complex inhomogeneous phase has not been made, the modified energy gap \( 2\Delta_{0} \) is expected to be significantly smaller than \( 2\Delta_{0} \) \[ 12 \] requiring lower temperatures for its observation.

Very low temperatures facilitate CDW 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 $E_t$ to depin it from impurities and defects in the crystalline lattice (or a threshold voltage $V_t$ observed between voltage terminals). Once depinned, the CDW is able to slide and carry a current with only small incremental changes in electric field required for large increases in current. This gives rise to a distinctive current $I$-versus-voltage $V$ behaviour that has been observed experimentally in numerous CDW systems. The size of the threshold electric field (or $V_t$) depends on the strength of the coupling between the charge modulation and pinning sites. 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.

The material described in this paper, $(\text{Per})_2\text{Au(mnt)}_2$ belongs to a series of isostructural charge-transfer salts consisting of one-dimensional conducting chains of perylene molecules (in the $(\text{Per})_2^+$ oxidation state) and insulating chains of maleonitriledithiolate (in the $M(\text{mnt})_2^-$ oxidation state), with two formula units per unit cell giving rise to a $3/4$-filled band. CDWs occur for $M = \text{Pt, Cu and Au}$, with the transition temperature being approximately $12$ K in the $M = \text{Au}$ salt. This brings $B_P$ comfortably within the range of the $45$ T Hybrid Magnet at the National High Magnetic Field Laboratory in Tallahassee. Although a lower transition (8 K) occurs in the $M = \text{Pt}$ salt, CDW formation there is compounded by the synchronous formation of a spin Peierls state involving localized spins on the Pt sites. A pure CDW state occurs only in the case of the $M = \text{Au}$ and $\text{Cu}$ salts.

Previous experimental studies of $(\text{Per})_2\text{Au(mnt)}_2$ 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. The CDW energy gap is suppressed in a qualitatively similar manner 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. Fits of the resistance to the thermal activation model enable one to anticipate gap closure of the uniform CDW phase at $B_P \approx 37$ T. Assuming $g_s = 1$, this yields $\zeta \approx 6$, which falls within the range typical for CDW ground states. Figure 2 compares plots of the $B$-dependence of the resistance $R$ along the chains of a needle-shaped sample of $(\text{Per})_2\text{Au(mnt)}_2$, (of dimensions $3 \text{ mm} \times 30 \text{ \mu m} \times 20 \text{ \mu m}$), for different values of the current $I$ 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. The Pauli limit is expected to yield a first order phase transition.

![FIG. 1: 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 $\varepsilon_F$. (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 the uniform CDW phase cannot be stable. (d) Possible gap formation due to incommensurate CDW state for $B \gg B_P$. If the gap stays pinned to $\varepsilon_F$, the Pauli paramagnetic magnetization of this state is equivalent to that of the normal metal.](image1)

![FIG. 2: Electrical resistance of a single crystal of $(\text{Per})_2\text{Au(mnt)}_2$ measured in a portable dilution refrigerator at $25$ mK for fields between $23$ and $45$ T, for two different orientations $\epsilon^* (a)$ and $\epsilon^* (b)$ of $B$ perpendicular to its long axis $\epsilon$, at several different applied currents. The lowest resistance for a given current occurs for $B$ parallel to $\epsilon^*$, which is perpendicular to $\epsilon^*$. The dependence of the resistance on current signals non-ohmic behaviour (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 neighbouring perylene chains are proposed to account for the field orientation dependence of the resistance.](image2)
followed by the recovery of metallic behaviour. Unfortunately the experiments in Ref. 17 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 17, preventing the observation of the true nature of the ground state at $B > B_p$. In the present study, the continued strong dependence of $R$ on $I$ at $B > B_p$ at dilution refrigerator temperatures ($T \ll 0.5$ K) in Fig. 3 is clearly uncharacteristic of a metal. It is, nevertheless, quite consistent with the continued presence of a CDW phase. The data in Fig. 2 display the typical CDW non-linear $I$-versus-$V$ electrodynamics (where $V = IR$) at all magnetic fields, characterised by 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. 3. 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 $B_p$, 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, 12, 13, combined with a greatly reduced energy gap $2\Delta$ 12, 13.

Evidence for the reduced value of $\Delta$ is obtained by repeating the $I$-versus-$V$ plot at $T = 900$ mK in Fig. 3. 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 14. It is, however, sufficiently high to restore ohmic ($I \propto V$) behaviour above $B_p$. Ohmic behaviour 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 $2\Delta_\lambda \ll 2\Delta_0$ 12.

The survival of CDW electrodynamics to fields far above the Pauli limit of (Per)$_2$Au(mnt)$_2$, 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 behaviour 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 incommensurate 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

![FIG. 3: Non-linear current-versus-voltage characteristic of (Per)$_2$Au(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 electrodynamical behaviour 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-$V$ behaviour 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 $\approx 6$ mV at $B = 44$ T for voltage contacts $\sim 1$ mm apart.

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