Destabilization of a Charge-Density Wave by an Oscillatory Chemical Potential

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The influence of an oscillatory chemical potential $\tilde{\mu}$ within the gap equation of a commensurate charge-density wave (CDW) is shown to lead to a new type of quantum oscillatory effect in the susceptibility of the nested one-dimensional sheets, with frequency exactly double that of the two-dimensional pocket from which oscillations in $\tilde{\mu}$ originate. On approaching the Pauli paramagnetic limit, $\tilde{\mu}$ further leads to a cascade of multiple first-order phase transitions between CDW and normal metallic phases. These ideas are applied to α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ charge-transfer salts.

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Recently, there has been renewed interest in the effect that oscillations in the chemical potential μ have on the de Haas–van Alphen (dHvA) effect of two-dimensional (2D) systems [1–4]. In such systems, the Landau levels are often very sharp at high magnetic fields, so that under the constraint of a constant particle number N, μ becomes pinned to individual Landau levels over extended regions of field, resulting in a large oscillatory component $\tilde{\mu}$. In all cases, the Lifshitz-Kosevich formalism that is usually used to interpret dHvA oscillations is rendered invalid [5].

The discussions of $\tilde{\mu}$ have thus far focused on conventional Fermi liquids; the potential effect of $\tilde{\mu}$ on the stability of a broken-symmetry ground state such as a spin-density wave (SDW) [6], charge-density wave (CDW) [7], or type-II superconductor [8], has not been studied. However, many classes of a 2D system possess a SDW or CDW state in which closed sections of the Fermi surface (FS) survive within (or are created by) the reconstructed band structure. Such closed 2D FS sections result in Landau quantization in a magnetic field, leading to a $\tilde{\mu}$ that can sometimes become comparable to the order parameter Δ of such ground states, potentially affecting their stability. In this Letter, I shall show that this effect is, in fact, rather significant, leading in both SDW and CDW systems to a new type of quantum oscillatory effect in the susceptibility of the nested one-dimensional (1D) sheets, which should then be visible in the dHvA effect as an unusually strong second harmonic component. In CDW systems, in particular, the influence of $\tilde{\mu}$ within the gap equation, on approaching the Pauli paramagnetic limit [9], leads prematurely to a destabilization of the CDW at certain fields, and, consequently, to a cascade of first-order phase transitions between consecutive CDW and normal metallic (NM) phases. These effects should be observable in a wide range of CDW systems. However, here, I shall restrict the application of these ideas to charge-transfer salts of the form α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ (with M = K, Tl, or Rb) [10], which have rather simple unreconstructed FSs composed of quasi-1D sheets and a quasi-2D pocket [11], and in which an unusually strong second harmonic is observed in the dHvA effect that has not been explained consistently using conventional theory, but that appears to be consistent with the model under discussion.

Let us first consider the effect of a magnetic field (on a CDW), written in reduced units as $h = \sigma g \mu_B \mu_0 H$, where σ is the electron spin, g is the Landé g factor, μ_B is the Bohr magneton, and Δ_0 is the zero temperature, zero field order parameter. As shown schematically in Fig. 1(b) for nested 1D FS sheets, h increases the tendency for quasiparticle excitations and eventually reduces the free energy gained by the formation of the CDW by Zeeman shifting each of the spin components of the gapped one-particle density of states (DOS) in opposite directions. The critical field $h_c = \Delta_0/\sqrt{2}$ [9], which is equivalent to that of singlet-paired strongly type-II superconductors [12,13], occurs when the free energy gained by formation of the CDW passes through zero. The α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ charge-transfer salts have been known for some time to transform either to a SDW or CDW ground state at low temperatures ($T_P \sim 8$ K in the M = K salt) [10], yet a number of more recent articles provide compelling arguments for these materials possessing either a CDW or a mixed CDW-SDW ground state in which the CDW component plays the dominant role [14–16]. This is inferred from the weak spontaneous magnetic moment [16,17] and the thermodynamic behavior of these materials in a strong magnetic field [14,15]. According to the BCS relation $2\Delta_0/k_B T_P = 3.52$, one should expect an upper critical field of $B_c \approx \mu_0 H_c \sim 16$ T in the M = K salt, while experimentally, a broadly hysteretic first-order "kink" transition to a high magnetic field regime with an unreconstructed FS is observed at $B_k \approx \mu_0 H_k \sim 23$ T [18,19]. B_c can be brought into agreement with B_k either by considering a lower g factor of $\sim$1.4 or, alternatively, by considering $2\Delta_0/k_B T_P \sim 5$; the latter (which I shall assume in this Letter) is not without precedent in other CDW compounds with highly anisotropic FSs [7]. The FSs of the α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ charge-transfer salts are certainly anisotropic [11].

Changes in $\tilde{\mu}$, on the other hand, can have two possible effects depending on whether or not the CDW is commensurate. In the incommensurate case, $\tilde{\mu}$ manifests itself simply as oscillations of the nesting vector $\mathbf{Q}$ (or

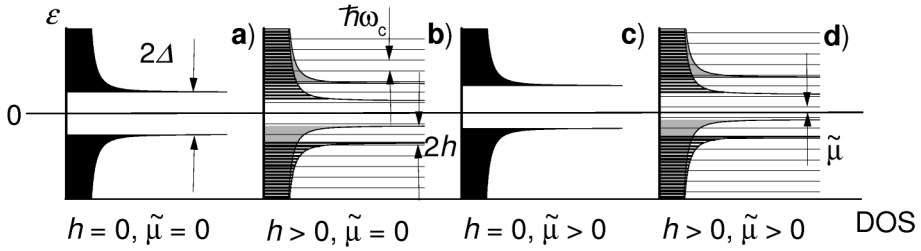

FIG. 1. An illustration of the one-particle DOS of the 1D sheets in the CDW regime with different combinations [(a)–(d)] of h and $\tilde{\mu}$. In (b) and (c) the positions of the Landau levels of the 2D pocket are indicated by thin lines.

soliton excitations). The alternative scenario, in which the CDW remains pinned to the crystal lattice, has more interesting implications. As shown in Fig. 1(c), changes in $\tilde{\mu}$ then have the same effect as doping with electrons or holes, with the carrier type depending on the sign of $\tilde{\mu}$. In contrast to h, $\tilde{\mu}$ shifts both spin components in the same direction. However, since both the gapped one-particle DOS and the derivative of the Fermi-Dirac (FD) distribution function are symmetric about $\tilde{\mu} \pm h$, both h and $\tilde{\mu}$ (irrespective of sign) have an equivalent detrimental effect on the stability of the CDW condensate. Given that the magnitude of $\tilde{\mu} \sim \frac{1}{2}\hbar\omega_c \sim 1$ meV [20,21] at fields of 23 T in the $M =$ K salt (where $\hbar\omega_c$ is the cyclotron energy of the 2D pocket) is directly comparable with $\Delta_0 \sim 1.2$ meV (estimated using the BCS relation), $\tilde{\mu}$ should clearly have quite a pronounced effect on these materials. Furthermore, a large body of papers, concerning measurements of quantum oscillatory effects and angular magnetoresistance oscillations within the low temperature, low magnetic field (LTLF) phase of these salts, support a picture in which the CDW (or SDW) is commensurate throughout [19,22,23]. Depinning a commensurate CDW from the lattice costs energy, with one possible form for the potential being $U(1 - \delta_{\mathbf{Q}-\mathbf{Q}_0})$, where $\mathbf{Q} - \mathbf{Q}_0$ is the degree of departure from commensurability and $\delta_0 = 1$. If U is sufficiently large then incommensurate CDWs become energetically unfavorable.

For the purpose of this model, it is convenient to consider a simple FS that is topologically equivalent to that of the α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ charge-transfer salts [11]. The dispersion relation for the 1D sheets (which drive the CDW instability) can be considered to have the form $\epsilon = \hbar v_F(|k_x| - k_F)$ [7], where v_F is the Fermi velocity and k_x is the momentum vector in the highly conducting direction, while the 2D component of the FS (which generates $\tilde{\mu}$) can be considered to have an area in k space equal to the quasi-2D pocket of the unreconstructed FS in the $M =$ K salt, with an oscillation frequency of $F \sim 670$ T [10]. In the determination of Δ, one can also consider that the FS nesting affects only the 1D sheets and that the changes in the quasiparticle spectrum associated with the interconnection of the 2D pockets (as proposed by Kartsovnik *et al.* [22]) are relatively insignificant. At temperatures $T \ll T_P$ deep within the CDW phase (the same regime where $\tilde{\mu}$ is large), the number of quasiparticles associated with the 1D sheets is negligible. Hence the oscillations of $\tilde{\mu}$ are determined entirely by the conservation of N within the 2D pocket only; a situation that is now well understood [1–5]. Only when the CDW is destroyed so as to recover ungapped 1D states is $\tilde{\mu}$ modified by their presence [4]. Without including $\tilde{\mu}$, the gap equation is mathematically equivalent to that for a strongly type-II superconductor with suppressed orbital effects close to the paramagnetic limit [9,13,24]. On incorporating $\tilde{\mu}$ into the FD distribution, I obtain

$$\ln\frac{\Delta}{\Delta_0} = -2\sum_{n=1}^{\infty}(-1)^{n+1}\cosh\frac{n\tilde{\mu}}{t}\cosh\frac{nh}{t}\,\mathrm{K}_0\left(\frac{n\Delta}{t}\right), \quad (1)$$

where $t = k_B T$ is the reduced temperature and $\mathrm{K}_\nu(x)$ is the MacDonald function [24]. When the commensurability of the CDW is enforced by setting $U = \infty$, h and $\tilde{\mu}$ have equivalent effects within the gap equation. It is helpful to obtain a more simple expression for the case where $t = 0$ [25]; hence

$$\ln\frac{\Delta}{\Delta_0} = -\frac{1}{2}\sum_{m=\pm 1}\cosh^{-1}\frac{|h + m\tilde{\mu}|}{\Delta}, \quad (2)$$

where the $\cosh^{-1}x$ function assumes a value of zero when $x < 1$. At $t = 0$, Eq. (2) yields the solution $\Delta = \Delta_0$ only when $h + |\tilde{\mu}| < \Delta$. At high temperatures ($t \sim t_P$), $\tilde{\mu}$ is negligible and by setting $\Delta = 0$ in Eq. (1), one obtains a second-order phase transition [13] depicted as a heavy solid line in Fig. 2(a). It should be noted that there exist additional $\Delta = 0$ solutions for the order parameter that intersect the field axis at $h = h_c/\sqrt{2}$, although these states are energetically unfavorable [13]. Given that large finite solutions for Δ exist beyond this field (up to $h = \sqrt{2}\,h_c$), the transition becomes of first order at high fields for temperatures below $\sim 0.56 \times t_P$. The thermodynamic first-order phase boundary can then be obtained by equating the free energy gained by the CDW condensate to zero. Ignoring the small differences in the Landau quantum oscillation (LQO) free energies between the NM and CDW phases [4,26], the free energy of the condensate is given simply by

$$\Delta F \equiv F_{\mathrm{CDW}} - F_{\mathrm{NM}} = \int_0^{\Delta}\Delta^2 d\left(\frac{1}{|V|}\right). \quad (3)$$

Here, $|V|$ is the effective pairing interaction, such that $\Delta_0 = \hbar v_F k_F \exp(-1/g_{1D}|V|)$ and $g_{1D} = 1/2\hbar v_F k_F$ is

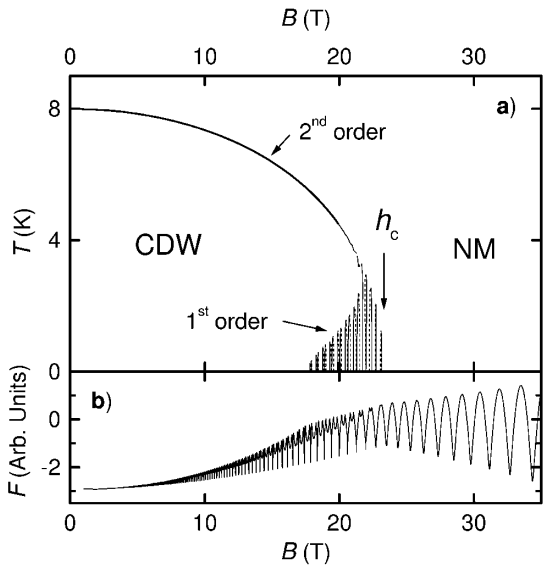

FIG. 2. (a) The proposed phase diagram of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ according to the model. (b) The total free energy calculated at 10 mK using the model, without considering the thermodynamic effects of domain boundaries.

the density of 1D states. Following Maki and Tsuneto [13], the differential $d(1/|V|)$ can be obtained from Eq. (1), and after substitution into Eq. (3) one obtains

$$\Delta F = -g_{1D}\left[\frac{\Delta^2}{2} - 2\sum_{n=1}^{\infty}(-1)^{n+1}\frac{t^2}{n^2}\cosh\frac{\tilde{\mu}}{t}\cosh\frac{nh}{t} \times \int_0^{n\Delta/t} \mathrm{K}_1(x)x^2\,dx\right]. \quad (4)$$

Making use of the relation $\int_0^{n\Delta/t}\mathrm{K}_1(x)x^2\,dx = 2 - \int_{n\Delta/t}^{\infty}\mathrm{K}_1(x)x^2\,dx$, one obtains at low temperatures,

$$\Delta F \simeq -g_{1D}\left[\frac{\Delta^2}{2} - \frac{\pi^2 t^2}{3} - h^2 - \tilde{\mu}^2\right]; \quad (5)$$

the equivalent expression for the free energy of a SDW is obtained by removing the h^2 term.

With the exception of the $\tilde{\mu}^2$ term in Eq. (5), all of the terms vary monotonically with t or h. It is helpful to consider a simple scenario in which the oscillations of $\tilde{\mu}$ are purely sinusoidal (i.e., $\tilde{\mu} \sim (\hbar\omega_c/\pi)\sin(2\pi F/B)R_T R_D R_s$, where R_T, R_D, and R_s are the conventional thermal, Dingle, and spin damping factors [5]), which will certainly be the case at low magnetic fields. It then follows trigonometrically that the $\tilde{\mu}^2$ term is also sinusoidal, but with a frequency of $2F$. Since the susceptibility of the CDW (or SDW) phase is given by $\chi_{CDW} = -\partial^2 F_{CDW}/\partial B^2|_T$, this therefore leads to a new $2F$ oscillation frequency in the susceptibility of the nested 1D sheets; the CDW thus operates as a frequency-doubling device. The harmonic ratio in the susceptibility between this $2F$ "frequency-doubled" oscillation (FDO) and the conventional $1F$ LQO originating from the 2D pocket is

$$\frac{\chi_{2F}}{\chi_{1F}} = 4\frac{g_{1D}}{g_{2D}}R_T R_D R_s, \quad (6)$$

where g_{2D} is the field-averaged DOS of the 2D pocket. This expression demonstrates that, for a clean system, the amplitude of the $2F$ FDOs can be larger than the $1F$ LQOs. When superimposed on top of the conventional LQOs, the FDOs should appear to resemble the "spin-splitting" effect that occurs when the Zeeman splitting is near to an odd half integer multiple of $\hbar\omega_c$ (i.e., $R_s \sim 0$). The FDO effect can be easily distinguished from the conventional Zeeman effect, however, by observing the wave form of the oscillations as the magnetic field is rotated by an angle θ away from the direction normal to the 2D planes. The $2F$ FDOs should have their largest amplitude at the *same* angle where the $1F$ LQO amplitude is maximized; in a near-spin degenerate system ($R_s \sim 1$), this occurs at $\theta \sim 0$ because of the increase in the effective mass at higher angles. Consequently, at the angle at which the largest $2F$ amplitude occurs, there should be no minimum (or $R_s \sim 0$ "spin zero") observed for the $1F$ LQO, as one would expect occur with the conventional Zeeman splitting effect. Another notable difference is that the $2F$ FDOs should always remain phase locked to the $1F$ oscillations upon rotation; i.e., the interval in reciprocal magnetic field $1/B$ between the split dHvA maxima (or minima) should remain proportional to the fundamental $1F$ LQO period, which varies as $(\cos\theta/F)$. In contrast, the equivalent interval $1/B$ between the split maxima (or minima) in the conventional Zeeman splitting effect should be independent of θ. Indeed, there have been several reports of an anomalous behavior of the angle dependence of the split wave form in the M = K and Tl BEDT-TTF salts [22,27] that have not been definitively explained, but appear to be reconcilable with the above effects.

Finally, by setting $\Delta F = 0$ at $t = 0$ in Eq. (5), one obtains the critical field(s) for a CDW,

$$h = \sqrt{\tfrac{1}{2}\Delta^2 - \tilde{\mu}^2}, \quad (7)$$

where, at $t = 0$, Δ is obtained from Eq. (2). Rather than describing only a single transition, the contribution of the $\tilde{\mu}^2$ term in Eq. (7) leads to a cascade of first-order transitions, and since $\tilde{\mu}$ is squared, these repeat at a frequency of $2F$. In Fig. 2(a) I have calculated a phase diagram based on this model [21], with the free energy of the LQOs included [26]; within the NM phase, the free energy of the LQOs is slightly modified by the presence of 1D states [4]. The thin solid lines represent transitions from the CDW phase into the NM phase with increasing field and the dashed lines correspond to reentrant transitions from the NM phase back into the CDW phase. Given that a full self-consistent evaluation of Δ as a function of t, h, and $\tilde{\mu}$ represents a formidable calculation, I have made use of the following approximations: close to the absolute critical field h_c at which the cascade of transitions occurs (i.e., the Clogston critical field at $\tilde{\mu} = 0$), $\Delta F \sim -g_{1D}[\Delta_0^2(1 - 0.788t^2/t_P^2 - 0.212t^4/t_P^4)/2 - h^2 - \tilde{\mu}^2]$. This expression is exact in the limit $t \to 0$. While it has been shown

that solutions for Δ vanish whenever $h + |\tilde{\mu}| > \Delta$, this occurs only within the NM phase and therefore does not modify the positions of the first order transitions shown in Fig. 2(a). A well-known property of first-order transitions is that there is some region in parameter space over which the two phases coexist, characterized by the hysteresis of many physical properties [28]. A complete thermodynamic calculation, nevertheless, requires a knowledge of the surface free energy between the CDW and NM domains, which is presently an undetermined quantity. In the α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ salts, the hysteresis is particularly pronounced within a few tesla of B_k [29]; the same interval in magnetic field over which the cascade of first-order transitions occur in Fig. 2(a).

While the present model does not include the thermodynamic effects of domain formation [28], it is nevertheless instructive to calculate the total free energy on the assumption that the phase with the lower energy prevails. Figure 2(b) shows the free energy calculated in this way at $T = 10$ mK. Above $B_c \sim 23$ T, the free energy corresponds almost entirely to that of the NM phase, in which there are no FDOs [4]. On passing below B_c, a notable second harmonic (i.e., $2F$ frequency) appears gradually. This occurs in spite of the fact that the effective mass and the Landé g factor are assumed to remain constant throughout [21]. Note that the field dependence of the oscillations on passing between the NM and CDW phases closely resembles experimental observations made on $M =$ K, Tl, and Rb α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ salts [10].

In summary, the oscillations of $\tilde{\mu}$ originating from 2D FS sections within a CDW ground state are shown to lead to two novel effects; the first being a new type of quantum oscillatory effect in the Pauli paramagnetic susceptibility with a frequency exactly twice that of the 2D pocket (occurring in both CDW and SDW systems), and the second being multiple first-order transitions between reentrant CDW and NM phases on approaching the Clogston critical field h_c (occurring only in CDW systems). The former effect may account for the anomalous split wave form effects that are observed within the LTLF phase of certain α-phase BEDT-TTF salts, while the latter may account for the extensive hysteresis observed in the vicinity of the kink transition field [18,29]. The FDO effect, in particular, should be observable in a wider variety of systems. Indeed, a distinct split wave form effect is observed in the archetypal CDW compound $NbSe_3$ [30], with the field orientation dependence of the splitting being proportional to the fundamental LQO period exactly as expected for the FDO effect. A pronounced $2F$ frequency is also observed in the final ($n = 0$) field-induced SDW phase of $(TMTSF)_2ClO_4$, over a restricted range of temperature [31], indicative of a prominent $\tilde{\mu}^2$ term in the free energy.

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