Origin of the split quantum oscillation wave form in α-(BEDT-TTF)$_2$KHg(SCN)$_4$

N. Harrison
National High Magnetic Field Laboratory, Los Alamos National Laboratory, MS-E536, Los Alamos, New Mexico 87545

N. Biskup, J. S. Brooks, and L. Balicas
National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310

M. Tokumoto
Electrotechnical Laboratory, Tsukuba, Ibaraki 305, Japan

(Received 28 November 2000; revised manuscript received 8 February 2001; published 11 April 2001)

We report the results of a detailed study of the field orientation dependence of the de Haas–van Alphen wave form in α-(BEDT-TTF)$_2$KHg(SCN)$_4$ over a wide range of angles and fields. By considering the field orientation dependence of the sign and phase of the fundamental α frequency, at fields both well above and below the kink transition field, it is found that the product of the effective mass with the electron g factor is approximately constant. This implies that spin splitting cannot occur within the low-magnetic-field phase until the angle between the magnetic field and the normal to the conducting planes is $\sim 42°$. This finding contrasts greatly with that recently published by Sasaki and Fukase. The results of the present study imply that the electron-electron interactions are largely field independent in this material, while a field dependence of the electron-phonon interactions is still tenable. The manner in which the amplitude of the wave form of the oscillations is damped within the low-magnetic-field phase is suggestive of a nonharmonically indexed reduction of the amplitude, thereby eliminating explanations in terms of magnetic breakdown or impurity scattering. Meanwhile, the presence of a large amplitude second harmonic within the low-magnetic-field phase that has a negative sign over a broad range of angles can be explained only by the frequency doubling effect.

DOI: 10.1103/PhysRevB.63.195102 PACS number(s): 74.70.Kn, 71.30.+h

I. INTRODUCTION

Charge-transfer salts of the form α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ (where $M=$ K, Tl, or Rb) exhibit a complex phase diagram that is very sensitive to both temperature T and the orientation of an applied magnetic field **B**.[1–5] Angle-dependent magnetoresistance oscillations[6] and the Shubnikov–de Haas (SdH) and de Haas–van Alphen (dHvA) effects have demonstrated[7,8] the existence of a reconstructed Fermi surface at low magnetic fields and temperatures below T_{p} ($T_{\mathrm{p}}\sim 8$ K for the $M=$ K salt[1] and ~ 10 K for the $M=$Tl and Rb salts); such a reconstruction is indicative of a density wave ground state. However, direct evidence for a lattice superstructure, which would unambiguously distinguish a charge-density wave (CDW) ground state from one that is a spin-density wave (SDW),[9] has not been forthcoming. Only very recently has sufficient indirect evidence accumulated so as to tip the balance of the arguments in favor of a CDW ground state. Notably, antiferromagnetism is either weak[10,11] or absent,[12] and T_{p} is strongly depressed by the application of a magnetic field.[3–5,13]

The electronic properties of the α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ salts then change abruptly on passing through the first order ''kink'' transition field[14] B_{k} ($B_{\mathrm{k}}\sim 23$ T in the $M=$K salt), above which they exhibit a critical state.[5] While the experimentally delineated phase boundaries (see Fig. 1) are consistent with this being a transition from a commensurate CDW$_0$ phase into a high-magnetic-field modulated CDW$_x$ phase,[3–5] as predicted by several recent theoretical models,[15,16] many of the experimental observations are difficult to reconcile with such a simple transition.[5] Nevertheless, for convenience, in the following discussion we shall refer to the low-temperature, low-field phase as the CDW$_0$ phase and the low-temperature, high-field phase as the CDW$_x$ phase (see Fig. 1).

Magnetic quantum oscillations are sensitive to the changes at B_{k}.[14] All signatures of a reconstructed Fermi surface are lost at high magnetic fields,[2,5,7,8,17,21] while the quasiparticle effective mass m^* corresponding to the dominant α quantum oscillation frequency F_α appears to

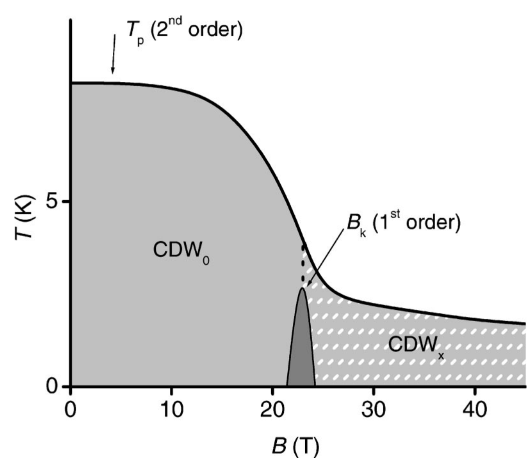

FIG. 1. A notional phase diagram of α-(BEDT-TTF)$_2$KHg(SCN)$_4$; the thick solid line represents the second order transition at T_{p} into the CDW ground state depicted in light gray. The vertical dotted line represents the first order kink transition field B_{k} beteween the CDW$_0$ (solid) and CDW$_x$ (hatched) regimes, with the region of hysteresis depicted in dark gray.

increase.[2,18–20] However, perhaps the most notable change is in the physical appearance of the wave form, from one that is strongly damped but displaying split maxima in the CDW_0 phase[10,22,23] to one that is almost triangular in the CDW_x phase.[5,24,25] The origin of the split wave form within the CDW_0 phase is a contentious issue. Several publications[10,22,23] suggest that it is due to the ''spin-splitting'' phenomenon. This occurs when the Zeeman splitting $\Delta\varepsilon = g\hbar eB/m_e$ (where g is the electron g factor and m_e the free electron mass) of the Landau levels becomes equal to an odd half-integer multiple of the cyclotron energy $\hbar\omega_c = \hbar eB/m^*$.[26] However, a split quantum oscillation wave form need not necessarily result from spin splitting; for example, a similar wave form occurs in the CDW compound $NbSe_3$,[27] but this was shown to be completely unrelated to the Zeeman effect.[28] The frequency doubling (FD) effect,[29] which occurs when an additional term proportional to the square of the oscillatory component $\tilde{\mu}$ of the chemical potential modulates the free energy of a CDW ground state, provides an alternative explanation.

The purpose of the present paper is therefore to investigate the importance of the spin splitting and FD effects in α-(BEDT-TTF)$_2$KHg(SCN)$_4$. This is accomplished by performing a detailed study of the magnetic field orientation dependence of the dHvA wave form in both the CDW_0 and CDW_x phases. In spite of the seemingly strong arguments in favor of spin splitting in the α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ salts,[10,22,23,30] no such thorough tests have been previously carried out to our knowledge. In this work, the product $\nu_0^* g$, where $\nu_0^* = m_0^*/m_e$, is determined by fitting the field orientation dependence of the sign and phase of the F_α oscillations. As described in Sec. III, this may be useful for determining the relevance of electron-electron (e-e) or electron-phonon (e-ph) interactions in the formation of the ground state. The validity of the canonical ensemble (in which the chemical potential is allowed to oscillate as the quasiparticle density of states changes with magnetic field) for describing the field orientation dependence of the wave form within the CDW_x phase is discussed in Sec. IV, while the anomalous behavior of the quantum oscillations within the CDW_0 phase is discussed in Sec. V. The frequency doubling effect is discussed in Sec. VI and, finally, all of the results are summarized in Sec. VII.

II. EXPERIMENT

The single crystal sample of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ of volume $\sim 0.8\ \mathrm{mm}^3$ used in this study was the same as that used for the magnetic torque measurements in Ref. 5. It was mounted on the moving plate of a phosphor-bronze capacitance cantilever, which was itself attached to a rotating platform for which the axes of torque and rotation were parallel to each other and both perpendicular to **B**. The angle between **B** and the normal to the capacitance plates was approximately the same as the angle θ between **B** and the normal **n** to the highly conducting planes of the sample. The capacitance, ~ 1 pF, was measured by means of a capacitance bridge energized with 30 V rms at 5 kHz

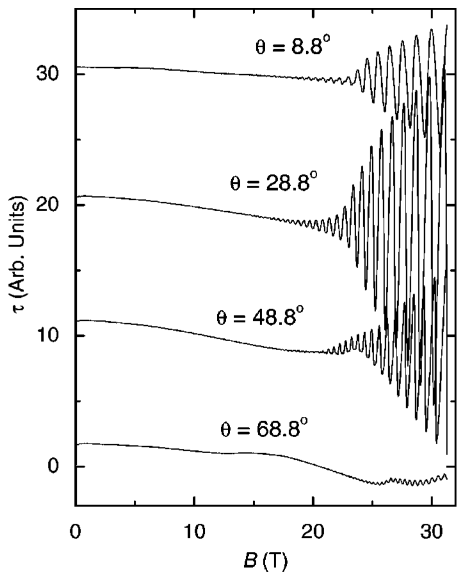

FIG. 2. Examples of the oscillatory magnetic torque at several different angles measured in α-(BEDT-TTF)$_2$KHg(SCN)$_4$ at 450 ± 20 mK throughout. The traces have been offset with respect to each other for clarity.

and was observed to change by less than 0.1%. Since this implies a maximum angular displacement of $\sim\frac{1}{20}°$, torque interaction effects were insignificant. Static magnetic fields extending to ~ 32 T were provided by the National High Magnetic Field Laboratory, Tallahassee, while a constant temperature of ~ 450 mK was obtained using a ^{3}He refrigerator.

As the interlayer transfer integral $t_\perp$ of α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ charge-transfer salts is immeasurably small compared to those within the planes, these materials provide good examples of almost ideally two-dimensional (2D) multilayered quasiparticle systems.[8,24] Consequently, the only significant component of the Landau diamagnetic susceptibility is that projected along **n**. Because $\boldsymbol{\tau} = \mathbf{M} \times \mathbf{B}$, the oscillatory component of the magnetic torque is

$$\tilde{\tau}_\theta = -\tilde{M}_{\perp,\theta} B \sin\theta, \qquad (1)$$

where $\tilde{M}_{\perp,\theta}$ is the oscillatory component of **M** parallel to **n**.

III. FIELD ORIENTATION DEPENDENCE OF THE DHVA PHASE

Examples of the oscillatory magnetic torque of α-(BEDT-TTF)$_2$KHg(SCN)$_4$, measured in static magnetic fields of up to 32 T and at several different field orientations, are shown in Fig. 2. Note that these data closely resemble earlier measurements made on the same material.[19,20] Fourier transformation of the data in the $1/B$ domain over a restricted range of B within the CDW_0 phase at $\theta \sim 8.8°$, shown in Fig. 3, reveals a plethora of harmonics, indicative of good sample quality.

A number of recent articles have shown that the presence of an oscillatory component of the chemical potential $\tilde{\mu}$ (in this and other 2D materials) invalidates a simplistic analysis

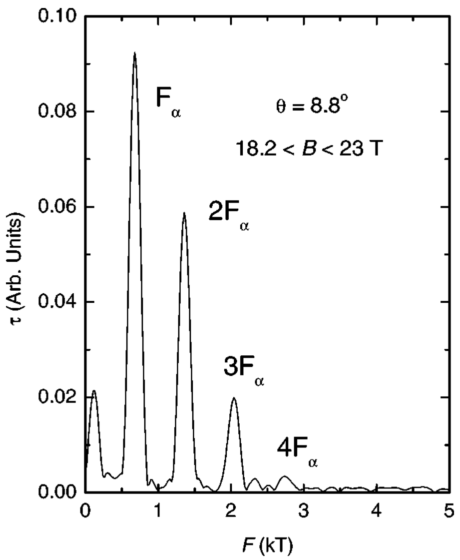

FIG. 3. Fourier transform of the data at $\theta \sim 8.8°$ in Fig. 2 over a restricted range of field $(18.2 < B < 23\ \mathrm{T})$.

of the dHvA oscillation data in terms of the Lifshitz-Kosevich (LK) formula.[8,24,31] The reasons for this are twofold. First, the LK formula is suited only to systems in which the Fermi surface is significantly curved in all three k-spatial dimensions.[24,26] Second, the presence of $\tilde{\mu}$ significantly perturbs the wave form of the oscillations so as to cause the amplitude and sign of each of the $p > 1$ harmonics to depart significantly from those predicted by the LK model.[24] The predictions of the LK model are further invalidated by other oscillatory phenomena, periodic in $1/B$, caused by the quasiparticle system itself; examples include magnetic breakdown,[32] the FD effect,[29] and induced currents. Induced currents, which contribute an additional oscillatory structure to the dHvA wave form, occur in the CDW_x phase of the α-$(\mathrm{BEDT\text{-}TTF})_2M\mathrm{Hg(SCN)}_4$ salts in both static magnetic fields[5] and pulsed magnetic fields.[25,33]

In spite of the fact that the wave form of the dHvA oscillations is significantly perturbed by $\tilde{\mu}$ in the canonical ensemble (in which the number of quasiparticles is kept constant and the chemical potential given complete freedom to vary), the underlying sign and phase of the fundamental frequency (labeled $p = 1$) are the same as those in the grand canonical ensemble (or LK model) for which $\tilde{\mu} = 0$.[24,26] The amplitude of the fundamental oscillations in the magnetic torque can therefore be written in the form

$$\tilde{\tau}_{1,\theta} \approx A_{1,B,T,\theta} \sin\left(\frac{2\pi F}{B}\right) S_{1,\theta} \sin\theta, \tag{2}$$

where $A_{1,B,T,\theta}$ is a monotonically varying prefactor (for which there is no simple algebraic form in the canonical ensemble) and F is the dHvA frequency. Note that $A_{1,B,T,\theta}$ contains no information about the sign and phase of the oscillations, both of which are determined entirely by the Zeeman term $S_{1,\theta} = \cos(\pi \nu_\theta^* g/2)$,[26] for which $\nu_\theta^* = m_\theta^*/m_\mathrm{e} = m_0^*/m_\mathrm{e} \cos\theta$.[8,35]

The magnitude $|S_{1,\theta}|$ becomes unity whenever $\Delta\varepsilon$ becomes commensurate with $\hbar\omega_\mathrm{c}$, or, equivalently, when the product $\nu_\theta^* g$ becomes equal to an even integer. Conversely, whenever $\nu_\theta^* g$ is equal to an odd integer, the amplitude of the fundamental oscillation frequency undergoes a node (often called a spin-splitting zero or spin zero).[26] The θ dependence of ν_θ^* then causes the amplitude of the fundamental to pass through a series of spin-splitting zeros upon rotation of the sample in a magnetic field. The experimentally determined positions of these nodes can then be identified with particular values of $\nu_0^* g/\cos\theta$, enabling an accurate estimate of $\nu_0^* g$ to be made.

A study of this type was recently made by Sasaki and Fukase at various magnetic fields both above and below B_k in α-$(\mathrm{BEDT\text{-}TTF})_2\mathrm{KHg(SCN)}_4$.[30] The interpretation of the positions of the nodes is not, however, entirely unambiguous.[26] Since the first spin zero could correspond to any odd integer value of $\nu_0^* g/\cos\theta = 1,3,5,7,\ldots$, part of the investigation involves determining which of these it is likely to be. The process of distinguishing these becomes trivial only when several nodes are observed. This is the case in our results within the CDW_x phase at $B \sim 26.5\ \mathrm{T}$ (i.e., for a Fourier transform of the interval in B between 23.0 and 31.25 T), presented in Fig. 4(a), which are in excellent agreement with those of Sasaki and Fukase.[30]

The phase in Fig. 4(a) is determined as follows. Having determined F by Fourier transformation, the in-phase and quadrature components of the dHvA signal are determined by multiplying the torque data by $\sin(2\pi F/B)$, and $\cos(2\pi F/B)$, respectively. Since the dHvA wave form in 2D metals can always be represented as a sum of sine functions,[24,26] the quadrature component is invariably zero. The phase of the oscillations is therefore either $\sim 0°$ or $\sim \pm 180°$, corresponding to a positive or negative sign, respectively.

For clarity, the data at 26.5 T are reproduced in Fig. 4(b), together with a solid line representing the functional form of $S_{1,\theta} \sin\theta$ best able to reproduce the correct sign of the oscillations and positions of the spin zeros. Note that the solid line is a fit only to the sign of the oscillations and not to the amplitude, yielding $\nu_0^* g = 3.67 \pm 0.02$.

In Fig. 4(a), we see that the apparent angular positions of the nodes appear to shift on lowering B through the transition field B_k, also in agreement with Ref. 30. However, in disagreement with the results of Sasaki and Fukase, our analysis fails to show any significant change in $\nu_0^* g$. Rather, at lower fields $(B \lesssim 18\ \mathrm{T})$, the positions of the nodes eventually shift back to approximately the same positions as those at $\sim 26.5\ \mathrm{T}$. Therefore, in contrast to Sasaki and Fukase,[30] we find that approximately the same value of $\nu_0^* g \approx 3.67 \pm 0.02$ is able to fit the field orientation dependence of the sign of the fundamental oscillation amplitude deep within both the CDW_0 and CDW_x phases. To illustrate this point more clearly, in Fig. 4(c) we have replotted the field orientation dependence of the oscillation amplitude in the magnetic torque at 16.5 T (i.e., for B between 15.0 and 18.2 T), together with a solid line representing the functional form of

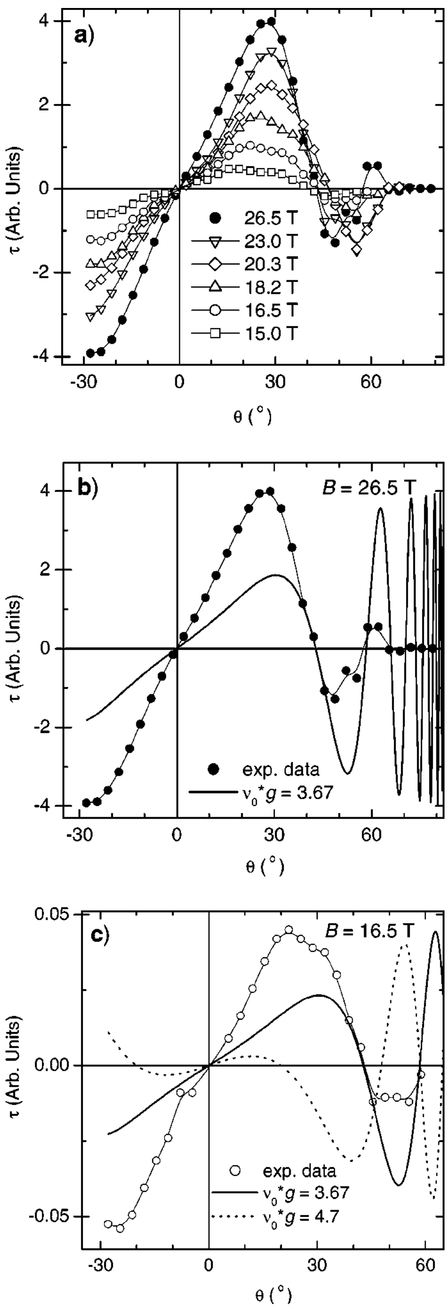

FIG. 4. (a) Field orientation dependence of the Fourier amplitudes at different magnetic fields in α-(BEDT-TTF)$_2$KHg(SCN)$_4$. Bezier fits between the points are shown for clarity. Each of the given values of magnetic field (26.6, . . . ,15 T) corresponds to the reciprocal of the midpoint of a 0.012 T^{-1} interval in $1/B$ over which the Fourier transform was performed. (b) The field orientation dependence of the quantum oscillations at $B\sim26.5$ T together with the functional form of $S_{1,\theta}\sin\theta$ best able to reproduce the correct positions of the nodes drawn as a solid line. (c) The field orientation dependence of the quantum oscillations at $B\sim16.5$ T, with the functional form for $S_{1,\theta}\sin\theta$ shown with $\mu_0^*g\sim3.67$ (solid line) and 4.7 (dotted line).

$S_{1,\theta}\sin\theta$ for $\nu_0^*g=3.67$ (i.e., the same as that within the CDW$_x$ phase). Clearly, this value of ν_0^*g is able to reproduce the positions of the nodes quite adequately. In contrast, when the value of $\nu_0^*g\sim4.7$ quoted by Sasaki and Fukase[30] is inserted into $S_{1,\theta}\sin\theta$, as indicated by the dashed line, the positions of the nodes are not accurately reproduced.

A visual inspection of the raw data in Fig. 3 of Ref. 30 suggests that the above inconsistencies have more to do with the analysis procedure than with the experimental data. One notable flaw in the analysis procedure of Sasaki and Fukase is that they attempt to obtain ν_0^*g by fitting a straight line through the $1/\cos\theta_n$ positions of the nodes (plotted versus the node index $2n+1$ in Fig. 5 of Ref. 30) without actually verifying whether the condition $1/\cos\theta_n=(2n+1)/\nu_0^*g$ is adequately satisfied. For example, if we instead extract ν_0^*g from the periodicity of the nodes [i.e., $\nu_0^*g=2(1/\cos\theta_n-1/\cos\theta_{n-1})$] in Fig. 5 of Ref. 30, we obtain quite a different value of $\nu_0^*g\sim4.2$. Given the apparent uncertainty in determining the positions of the nodes in Fig. 5 of Ref. 30, it is debatable whether the line corresponding to $\nu_0^*g=4.7$ provides a better fit to the data than one corresponding to $\nu_0^*g=3.67$ [making the appropriate adjustment of $(2n+1)$ by -2]. Serious problems with the analysis of Sasaki and Fukase become especially apparent in our Fig. 4. In particular, the reported value of $\nu_0^*g=4.7$ within the CDW$_0$ phase requires the existence of a node at $\theta\sim20°$ that has never actually been observed. In Secs. V and VI we will show that the field orientation dependence of the dHvA wave form within the CDW$_0$ phase can be quite adequately reproduced using $\nu_0^*g=3.67$ but not 4.7. This proves beyond any doubt that the value of $\nu_0^*g=4.7$ and therefore the conclusions reached in Ref. 30 are most definitely incorrect.

A reliable extraction of ν_0^*g is helpful for determining the relative importance of e-e and e-ph interactions. According to Landau Fermi liquid theory, e-e and e-ph interactions affect ν_0^* and g differently.[26] In most metals, e-ph interactions perturb and broaden the Landau levels at energies very close to μ. It follows that an increase in ν_0^* is approximately offset by a reduction in g, making the overall adjustment in the product ν_0^*g very small. For the same reasons, e-ph interactions do not generally contribute to the Pauli paramagnetic susceptibility of a metal.[36] The same is not true, however, in the case of e-e interactions. In heavy fermion materials, for example, the enhancement of ν_0^* can reach values of order ~100, while the changes in g remain relatively moderate.[37] It has been suggested that g (at least in organic metals) is more representative of the Wilson ratio[38] (a number that is used to quantify the ratio of the Pauli paramagnetic susceptibility to the electronic coefficient of the specific heat).

Because ν_0^*g (plotted in Fig. 5) does not change significantly with field, we can conclude that the e-e interactions also do not change significantly with field; this is in contrast to the conclusions of Sasaki and Fukase.[30] Thus, either the effective electron density is not a significant factor in determining the relative strengths of the effective Coulomb interaction between the two regimes, or, alternatively, e-e interactions do not play a very significant role in the formation of the CDW ground state. This is not unexpected, since CDW ground states are commonly thought to involve e-ph interactions rather than e-e interactions.[9] It could be argued that the

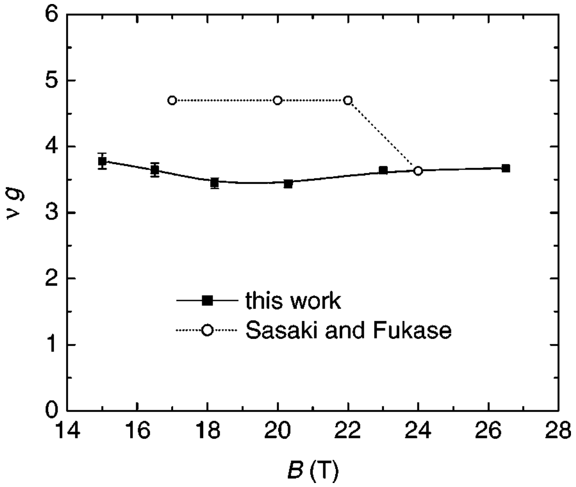

FIG. 5. A comparison of the field dependence of product $\nu_0^* g$ obtained in this work (solid squares inclusive of error) with those quoted by Sasaki and Fukase (circles).

apparent drop in $\nu_0^* g$ in the vicinity of B_k in Fig. 5 is an artifact of the Fourier transform being affected by the presence of one or more first order phase transitions.[29] This will likely be the case if these transitions occur within the interval in $1/B$ over which the Fourier transform is performed. We also note that at higher angles, $|\theta| \gtrsim 45°$, another phase, CDW_y, has been proposed,[4] which might complicate matters further.

While e-e interactions appear not to change significantly, a change in the strength of e-ph interactions is still tenable. The latter would manifest itself as a change in the effective mass. This matter, whether the apparent change in the effective mass of the α frequency on crossing B_k is genuinely related to a change in the strengh of the e-ph interactions,[2,18–20] or whether it is an artifact of the temperature dependence of some other property of the quasiparticle system,[32] remains unresolved. Effective mass estimates have a history of being unreliable in this family of salts.[2,8,18–20,25] Within the CDW_0 phase, for example, different values of m^* are obtained depending on whether one analyzes SdH or dHvA data.[18] Under normal circumstances, dHvA data are more reliable owing to the fact that they are derived from a thermodynamic function of state. However, there also exists the possibility that gaps of order 2Δ in the energy spectrum resulting from the formation of the CDW state lead to breaks in the α orbit trajectory that then have to be overcome by magnetic breakdown in a magnetic field.[20] It has been argued that since 2Δ falls with increasing temperature, this should lead to an additional temperature-dependent term in the quantum oscillation amplitude that could potentially cause the effective mass within the CDW_0 phase to appear artificially low.[32] In Sec. V, however, we will show that magnetic breakdown appears not to be the dominant form of damping within the CDW_0 phase. This eliminates explanations involving a temperature-dependent magnetic breakdown gap.

Having eliminated magnetic breakdown effects, the reported difference in the degree to which the effective mass is enhanced between the CDW_0 and CDW_x phases, $\delta\nu_0^* \sim 0.5$, is too large to be ignored. Within the CDW_0 phase, dHvA measurements all agree that $\nu_0^* \sim 1.5$.[2,8,18–20,39] Within the CDW_x phase, however, only one estimation of $\nu_0^* \sim 2.0$ has been made that properly accounts for the effects of induced currents, now shown to occur in both static and pulsed magnetic fields.[5] Since α-(BEDT-TTF)$_2$KHg(SCN)$_4$ is now believed to possess a CDW ground state of some form,[3–5,12,16] changes in ν_0^* between CDW subphases could be expected. A common observation in all CDW materials is that gaps open in the phononic density of states as well as in the electronic density of states.[9] Since the mass enhancement due to e-ph interactions is determined by an integration over both the phononic and electronic densities of states,[26] an increase in the effective mass is expected on passing into a phase within which 2Δ is lower. A change in ν_0^* is therefore not unexpected.

IV. DHVA WAVE FORM WITHIN THE CDW_X PHASE

The fact that the conventional form of $S_{1,\theta}$ is obeyed well in both in the CDW_0 and CDW_x regimes of α-(BED-TTF)$_2$KHg(SCN)$_4$ (with the exception of a narrow field interval immediately below B_k), implies that this material has, at all times, a well defined set of Landau levels characteristic of a normal Fermi liquid in a magnetic field. Given, also, that the product $\nu_0^* g$ is close to an integral value (i.e., 4), it is no surprise that the high-magnetic-field phase closely resembles a canonical ensemble of electrons for which the spins are approximately degenerate.[24] On inserting more exact parameters $\nu_0{}^* \approx 2.0$,[25] $\gamma \approx 0.68$,[5,40] and $\nu_0^* g \approx 3.67$ (this work) into the numerical model of Ref. 24, the canonical ensemble [calculated in Fig. 6(b)] is able to reproduce the experimentally observed magnetic torque in Fig. 6(a) rather well. The data in Fig. 6(a) were taken in a dilution refrigerator at $T \approx 27$ mK and $\theta \approx 7°$. Note that the parameters F, ν_0^*, γ, and $\nu_0^* g$ are constants specific to the material that have been determined experimentally and cannot be arbitrarily adjusted as fitting parameters. Only the scattering rate $\tau^{-1} \approx (0.6 \pm 0.1) \times 10^{12}\ \mathrm{s}^{-1}$, which is always sample dependent, is adjusted in order to obtain the best representation of the experimental data.

These same parameters, when inserted into the numerical canonical ensemble calculation, are also able to reproduce the correct field orientation dependence of the fundamental ($p=1$) amplitude of the magnetic torque in Fig. 7(a), at least for $|\theta| \lesssim 45°$. The same numerical model also predicts the correct sign of the second ($p=2$) harmonic; however, the field orientation depedence of its amplitude is less accurately reproduced. By ''sign'' we refer to the sign of the prefactor a_p that correctly represents the wave form of the oscillations when it is fitted by a Fourier expansion

$$\tilde{M} \approx \sum_p \frac{a_p N \beta^*}{\pi p} \sin\left(\frac{2\pi p F}{B}\right). \tag{3}$$

Here, $\beta^* = \hbar e/m^*$ is the double effective Bohr magneton, N is the density of carriers giving rise to the α frequency quantum oscillations, and $|a_p| < 1$ represents the degree to which

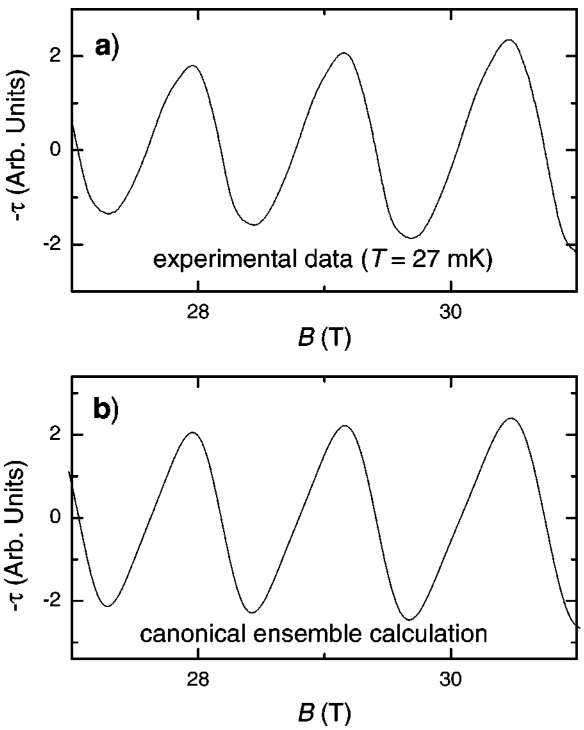

FIG. 6. (a) An example of the oscillations in the magnetic torque measured in α-(BEDT-TTF)$_2$KHg(SCN)$_4$ at low temperatures ($T\sim27$ mK), having subtracted the induced currents as described in Ref. 5. (b) The calculated wave form of the oscillations using the canonical ensemble as described in the text.

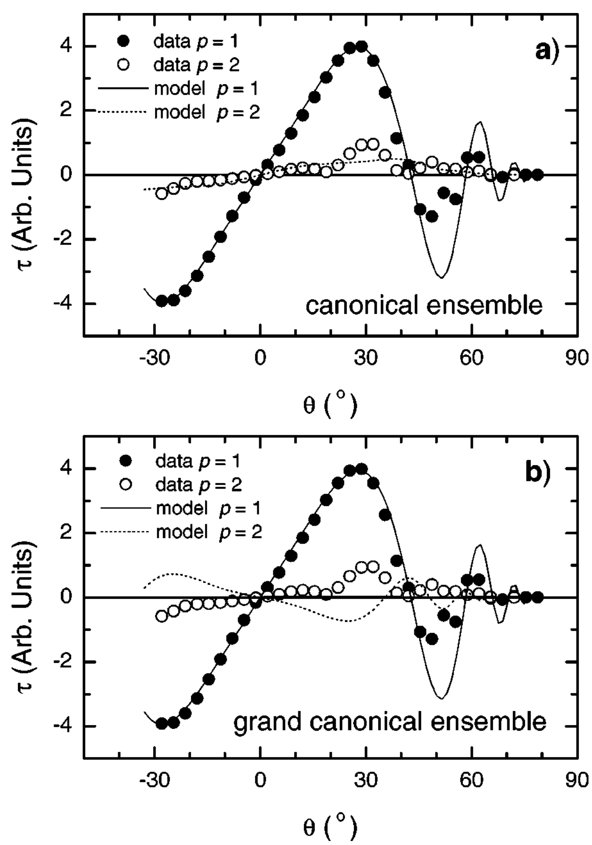

FIG. 7. (a) Field orientation dependence of the amplitude of the fundamental $p=1$ and second harmonic $p=2$ in α-(BEDT-TTF)$_2$KHg(SCN)$_4$ at 26.5 T, together with those calculated using the canonical ensemble. (b) The same data but with the fundamental and second harmonic calculated using the grand canonical ensemble (i.e., the LK model).

the amplitude of each harmonic is attenuated due to the combined effect of impurities, spin, and temperature. In the canonical ensemble, there is no simple way to separate each of these contributions;[24] the expression must be evaluated numerically. An important detail is that the field orientation dependence of the sign of the second harmonic is expected[24] to remain positive in the canonical ensemble for all angles when $\gamma>0.5$ (i.e., when the density of states of the 2D Fermi surface pocket is larger than that of the quasi-one-dimensional sheets). In Fig. 7(b) we can see that, while the grand canonical ensemble (i.e., the LK model which assumes a fixed chemical potential) is equally well able to explain the behavior of the fundamental, it fails to account for the positive sign of the second harmonic. This illustrates the hazards associated with fitting the LK model to a 2D system for which it does not apply.[18–20,34] In Sec. V we will show that this issue becomes particularly important when attempting to understand the oscillations within the CDW$_0$ phase.

In spite of the fact that the models are able to predict the correct form of the fundamental amplitude of the dHvA oscillations at small angles, they cannot account for their rapid attenuation at larger angles, $|\theta|\gtrsim45°$, in Fig. 7. One possible explanation is that the scattering rate $\tau^{-1}(\mathbf{k})$ is strongly dependent on $\mathbf{k}$, with ''hot spots,'' or possibly even ''hot bands,'' occurring at certain values of k_z (the lattice vector parallel to $\mathbf{n}$). Such effects have been suggested to be important in some of the Bechgaard salts.[41] Since a dHvA experiment senses only a weighted average of $\tau^{-1}(\mathbf{k})$, the number of orbits that intersect hot regions of the Fermi surface could increase for large θ. It was noted in Ref. 42 that the experimentally observed scattering rate appears to increase roughly in proportion to tan θ.

V. DHVA WAVE FORM WITHIN THE CDW$_0$ PHASE

Thus far, we have shown that at least two parameters associated with the α frequency appear not to change significantly on traversing B_k; namely, its fundamental frequency $F\sim670$ T and the product ν_0^*g. The same cannot be said with confidence about the effective mass parameter ν_0^*, the γ parameter (which characterizes the effect of unnested quasi-one-dimensional sheets[24]), or the scattering rate τ^{-1}. A number of groups have reported an apparent increase in the scattering rate within the low-magnetic-field CDW$_0$ phase with respect to that within the high-magnetic-field phase.[2,18,19] Others have attributed the loss of amplitude of the α frequency within the CDW$_0$ phase to magnetic breakdown effects.[20,32] While the latter might be expected following the introduction of an additional periodic potential $2\Delta_0$ within the CDW$_0$ phase,[6,7] neither of these two possibilities can satisfactorily explain the experimental data. For either of them to be true, the field dependence of the amplitude of each harmonic p (having corrected for its temperature depen-

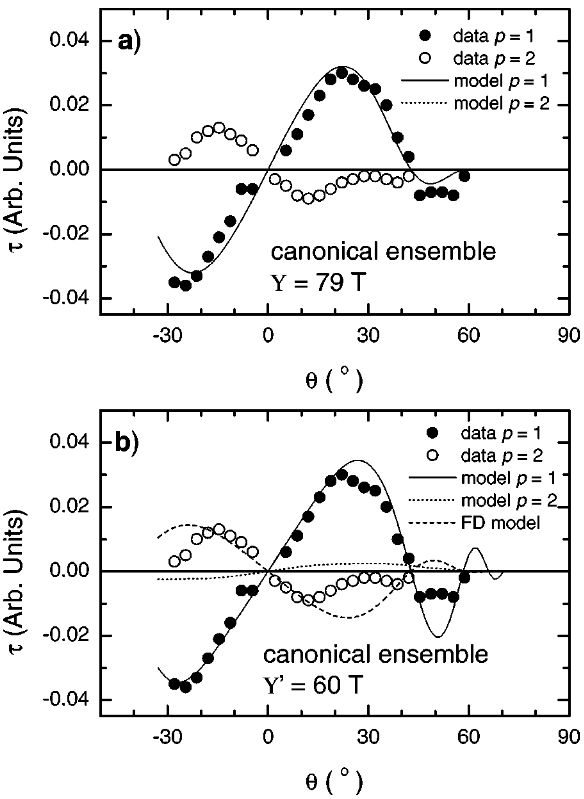

FIG. 8. (a) Field orientation dependence of the amplitude of the fundamental $p=1$ and second harmonic $p=2$ in α-(BEDT-TTF)$_2$KHg(SCN)$_4$ at 16.5 T, together with those calculated using the canonical ensemble with $\Upsilon=79$ T, which equates to an effective scattering rate of 2.9×10^{12} s^{-1}. (b) The same data with the fundamental and second harmonic calculated using the same scattering rate as within the CDW$_x$ phase, but with $\Upsilon'=60$ T.

dence) would have to be proportional to $R_{p,B}\approx\exp(-\pi p/\omega_c\tau-pB_0/B)$. The first term within the exponent accounts for scattering due to impurities[26] while the second accounts for magnetic breakdown, having assumed that no Bragg reflection takes place on the α orbit (as is commonly assumed[6–8]). Because the field dependence of both of these terms is the same, there is no way to distinguish them experimentally. We can therefore write this in the more generic form $R_{p,B}\approx\exp(-p\Upsilon/B)$, where Υ represents the total degree of damping inclusive of both effects. In Fig. 8(a), the experimentally observed fundamental amplitude of the oscillations within the CDW$_0$ phase, at $B\sim16.5$ T, can be approximately reproduced using the numerical model by setting $\Upsilon\sim79$ T. This is equivalent to a scattering rate of $\tau^{-1}\sim2.9\times10^{12}$ s^{-1}, comparable to that obtained in Ref. 18, or, alternatively, to a characteristic magnetic breakdown field of $B_0\sim79$ T. Implicit to either of these explanations, however, is the reduction of the amplitude of the second ($p=2$) harmonic with respect to that of the fundamental by another factor of approximately $R_B\approx\exp(-\Upsilon/B)\sim10^{-2}$. However, experimental results lend no support to either of these explanations. For example, when we calculate the wave form using the numerical model (with $\Upsilon\sim79$ T), the amplitude of the second harmonic in Fig. 8(a) is roughly two orders of magnitude smaller than that detected experimentally. This would also be the case were we to calculate the wave form using the grand canonical ensemble, or were we to take into consideration FD effects (see Sec. VI). Clearly, the presence of a second harmonic with an amplitude that is measured to be an appreciable fraction of that of the fundamental is inconsistent with a harmonically indexed damping factor of the form $R_{p,B}\approx\exp(-p\Upsilon/B)$ with Υ being as large as 79 T. We can therefore eliminate both impurity scattering and magnetic breakdown as dominant mechanisms for the damping of the dHvA oscillations observed within the CDW$_0$ phase, since both of these lead to harmonically indexed damping factors. The only alternative explanation, therefore, is that the quantum oscillations within the CDW$_0$ phase are uniformally suppressed in amplitude in a manner that is not indexed to the harmonics. Evidence for a nonharmonically indexed reduction of the amplitude has already been published.[18] In Ref. 18, the Dingle plots of the fundamental and second harmonic were found to have approximately the same slope, indicating the existence of an amplitude reduction factor that is not indexed to p. In order to account for these experimental observations, we can notionally introduce a damping factor of the form $R'_B\approx\exp(-\Upsilon'/B)$ within the CDW$_0$ phase that is independent of p but that operates in addition to the conventional damping that occurs within the high-magnetic-field phase. An exponential form for R'_B is required in order to account for the fact that the Dingle plots are approximately linear.[18]

The most trivial interpretation of a nonharmonically indexed damping factor is that where the effective volume of the sample contributing to the dHvA signal is reduced by a factor $R'_B\approx\exp(-\Upsilon'/B)$. A volume reduction factor of this type might be expected were the CDW$_0$ phase composed of two coexisting phases spatially separated over distances larger than the cyclotron length, only one phase of which yields dHvA oscillations of the α frequency, with their composition then changing with field. When the dHvA wave form in Fig. 8(b) is calculated using the same material parameters as within the CDW$_x$ phase, but with an additional empirical damping term of the form $R'_B\approx\exp(-\Upsilon'/B)$, setting $\Upsilon'\sim60$ T, the model is able to reproduce the experimentally observed amplitudes much better than Fig. 8(a). In particular, the model now predicts the second harmonic to have the correct order of magnitude, albeit with the wrong sign. We will return to a discussion of the sign of the second harmonic in Sec. VI where we consider FD effects.

Having shown that neither impurity scattering nor magnetic breakdown can account for the strong damping within the CDW$_0$ phase, it could be argued that both of these explanations are unphysical for other reasons. For example, a scattering rate is usually determined by the number of defects and impurities in a metal, and this number is not expected to change across a phase transition. The product $m_0^*\tau^{-1}$ invariably remains constant.[43] Similarly, the estimated value of $\Upsilon\sim79$ T significantly exceeds the magnetic breakdown field[26] $B_0\approx n\varepsilon_{\rm gap}^2 B/2\varepsilon_{\rm F}\hbar\omega_c\sim20$ T that should be expected for $n\sim6$ magnetic breakdown nodes of size $\varepsilon_{\rm gap}\approx2\Delta_0\approx4$ meV,[5] $\varepsilon_{\rm F}=\hbar eF/m^*$ being the Fermi energy.

VI. FREQUENCY DOUBLING

The most distinguishing feature of the oscillations in the magnetic torque within the CDW_0 phase is the presence of a strong second harmonic. (The ratio of the harmonics is unaffected by the uniform nonharmonically indexed reduction in the amplitude of the oscillations discussed in the preceding section.) Another important feature of the dHvA oscillations within the CDW_0 phase, which has not been addressed by earlier publications, is that the sign of the second harmonic is negative compared to one that is positive above B_k. The change in sign of the second harmonic between the low- and high-magnetic-field phases gives rise to a node at B_k as observed by Uji *et al.*[20]

The negative sign of the second harmonic within the CDW_0 phase is clearly unexpected in the canonical ensemble. It is also inconsistent with spin splitting in the grand canonical ensemble (or LK model), for which a positive sign should also be expected. In fact, the negative sign of the second harmonic over a wide range of angles $0° < |\theta| < 42°$ is inconsistent with any model of the dHvA effect. As will become clear below, it is, however, expected to be negative when frequency doubling effects are taken into consideration.

The FD effect has been proposed to operate in CDW or SDW ground states for which the nesting vector **Q** is commensurate.[29] Fermi surface studies have suggested that the CDW_0 phase is commensurate,[7] and this is also expected to form the basis of theoretical models describing the phase diagram.[15,16] It should be noted that the effects described in Ref. 29 are expected to occur within the CDW_0 phase irrespective of the nature of the phase at fields above B_k. The FD effect is not expected to operate within the CDW_x phase, however, because this phase is proposed to be incommensurate.[15,16]

In order to model the extent to which the FD effect can affect the wave form within the CDW_0 phase, it is useful to consider the proportionality $\tilde{\mu} = B\tilde{M}/N$,[24,44] which, when combined with Eq. (3), enables the oscillations in the chemical potential to be written as a series expansion of the form

$$\tilde{\mu} \approx \sum_p \frac{a_p \hbar \omega_c}{\pi p} \sin\left(\frac{2\pi p F}{B}\right). \tag{4}$$

According to the frequency doubling model, oscillations in the chemical potential give rise to an additional term in the free energy of the form $\tilde{\Phi}_{FD} = g_{1D}\tilde{\mu}^2$ where g_{1D} is the density of quasi-one-dimensional states that become nested.[29] If we assume the limit $a_1 \gg a_2$ and count only oscillatory terms, this free energy can be written as

$$\tilde{\Phi}_{FD} \approx -\frac{g_{1D}(a_1 \hbar \omega_c)^2}{2\pi^2} \cos\left(\frac{4\pi p F}{B}\right). \tag{5}$$

The resulting frequency doubling term in the magnetization, $\tilde{M}_{FD} = -\partial\tilde{\Phi}_{FD}/\partial B$, thus has the form

$$\tilde{M}_{FD} \approx -\frac{2a_1^2 N \beta^* g_{1D}}{\pi g_{2D}} \sin\left(\frac{4\pi p F}{B}\right), \tag{6}$$

where $g_{2D} = N\beta^*/F$ is the total density of 2D states. Note that the sign of $\tilde{M}_{FD}$ is negative and it can have an amplitude as much as four times larger than the amplitude of the conventional dHvA contribution to the second harmonic. On inserting $g_{1D}/g_{2D} \sim 1$ into the expression

$$\frac{\tilde{M}_{FD}}{\tilde{M}_1} \approx -2a_1 \frac{g_{1D}}{g_{2D}} \tag{7}$$

for the harmonic ratio, the correct amplitude and sign of the second harmonic can be approximately reproduced in Fig. 8 over a wide range of angles. While there exists some departure from the predictions of the FD model in the range $15° < \theta < 40°$, a similar departure from the predictions of the quantum oscillation model is also observed for the fundamental. Nevertheless, it should be noted that *only* the FD model can account for the negative sign of the second harmonic within this range of angles.

VII. CONCLUSION

In summary, we have shown that similar values of $\nu_0^* g$ account for the field orientation of the sign and phase of the dHvA oscillations deep within both the CDW_0 and CDW_x phases above and below B_k. The implications of this are twofold: (1) the split wave form that occurs within the CDW_0 phase for field orientations $|\theta| < 42°$ cannot be attributed to spin splitting, and (2) the role of e-e interactions does not change significantly between the two phases.

The field orientation dependence of the wave form within the CDW_x phase is entirely consistent with the predictions for a canonical ensemble of electrons with a background reservoir of quasi-one-dimensional states. However, the behavior of the wave form within the CDW_0 phase is suggestive of an amplitude reduction factor that is not indexed to the harmonics. We can therefore eliminate both impurity scattering and magnetic breakdown as dominant mechanisms for the reduction of the amplitude within the CDW_0 phase. It is shown that the negative sign of the second harmonic that occurs within the CDW_0 phase over a large range of angles can be explained only by the frequency doubling effect.

ACKNOWLEDGMENTS

This work was supported by the Department of Energy, the National Science Foundation (NSF), and the State of Florida. J.S.B. acknowledges support from NSF Grant No. DMR-99-71474 and L.B. from FSU. N.H. would like to thank John Singleton for useful suggestions.

[1] M. Tokumoto, N. Kinoshita, and H. Anzai, Solid State Commun. **75**, 93 (1990).
[2] T. Sasaki, A.G. Lebed, T. Fukase and N. Toyota, Phys. Rev. B **54**, 12 969 (1996).
[3] M.V. Kartsovnik, W. Biberacher, E. Steep, P. Christ, K. Andres, A.G.M. Jansen, and H. Müller, Synth. Met. **86**, 1933 (1997); P. Christ, W. Biberacher, M.V. Kartsovnik, E. Steep, E. Balthes, H. Weiss, and H. Müller, Pis'ma Zh. Éksp. Teor. Fiz. **71**, 437 (2000) [JETP Lett. **71**, 303 (2000)].
[4] J.S. Qualls, L. Balicas, J.S. Brooks, N. Harrison, L.K. Montgomery, and M. Tokumoto, Phys. Rev. B **62**, 10 008 (2000).
[5] N. Harrison, L. Balicas, J.S. Brooks, and M. Tokumoto, Phys. Rev. B **62**, 14 212 (2000).
[6] M.V. Kartsovnik, A.E. Kovalev, and N.D. Kushch, J. Phys. I **3**, 1187 (1993).
[7] For a review of the Fermi surface topology, see N. Harrison, E. Rzepniewski, J. Singleton, P.J. Gee, M.M. Honold, P. Day, and M. Kurmoo, J. Phys.: Condens. Matter **11**, 7227 (1999).
[8] For a more recent review, see J. Singleton, Rep. Prog. Phys. **63**, 1111 (2000).
[9] G. Grüner, *Density Waves in Solids, Vol. 89 of Frontiers in Physics* (Addison-Wesley, Reading, MA, 1994).
[10] T. Sasaki, H. Sato, and N. Toyota, Synth. Met. **41-43**, 2211 (1991).
[11] F.L. Pratt, T. Sasaki, N. Toyota, and K. Nagamine, Phys. Rev. Lett. **74**, 3892 (1995).
[12] K. Miyagawa, A. Kawamoto, and K. Kanoda, Phys. Rev. B **56**, R8487 (1997).
[13] A. Kovalev, H. Mueller, and M.V. Kartsovnik, Zh. Éksp. Teor. Fiz. **113**, 1058 (1998) [JETP **86**, 578 (1998)].
[14] T. Osada, R. Yagi, A. Kawasumi, S. Kagoshima, N. Miura, M. Oshima, and G. Saito, Phys. Rev. B **41**, 5428 (1990).
[15] D. Zanchi, A. Bjélis, and Montambaux, Phys. Rev. B **53**, 1240 (1996).
[16] R.H. McKenzie, cond-mat/9706235 (unpublished).
[17] J. Caulfield, S.J. Blundell, M.S.L. du Croo de Jongh, P.T.J. Hendriks, J. Singleton, M. Doporto, F.L. Pratt, A. House, J.A.A.J. Perenboom, W. Hayes, M. Kurmoo, and P. Day, Phys. Rev. B **51**, 8325 (1995).
[18] N. Harrison, A. House, I. Deckers, J. Caulfield, J. Singleton, F. Herlach, W. Hayes, M. Kurmoo, and P. Day, Phys. Rev. B **52**, 5584 (1995).
[19] P. Christ, W. Biberacher, H. Müller, K. Andres, E. Steep, and A.G.M. Jansen, Physica B **204**, 153 (1995).
[20] S. Uji, J.S. Brooks, M. Chaparala, L. Seger, T. Szabo, M. Tokumoto, N. Kinoshita, T. Kinoshita, Y. Tanaka, and H. Anzai, Solid State Commun. **100**, 825 (1996).
[21] A.A. House, S.J. Blundell, M.M. Honold, J. Singleton, J.A.A.J. Perenboom, W. Hayes, M. Kurmoo, and P. Day, J. Phys.: Condens. Matter **8**, 8829 (1996).
[22] M. Tokumoto, A.G. Swanson, J.S. Brooks, C.C. Agosta, S.T. Hannahs, N. Kinoshita, H. Anzai, and J.R. Anderson, J. Phys. Soc. Jpn. **59**, 2324 (1990).
[23] T. Sasaki and N. Toyota, Phys. Rev. B **48**, 11 457 (1993).
[24] N. Harrison, R. Bogaerts, P.H.P. Reinders, J. Singleton, S.J. Blundell, and F. Herlach, Phys. Rev. B **54**, 9977 (1996).
[25] M.M. Honold, N. Harrison, J. Singleton, H. Yaguchi, C. Mielke, D. Rickel, I. Deckers, P.H.P. Reinders, F. Herlach, M. Kurmoo, and P. Day, J. Phys.: Condens. Matter **9**, L533 (1997).
[26] D. Shoenberg, *Magnetic Oscillations in Metals* (Cambridge University Press, Cambridge, 1984).
[27] P. Monceau, Solid State Commun. **24**, 331 (1977).
[28] N. Harrison, L. Balicas, J.S. Brooks, J. Sarrao, and Z. Fisk, Phys. Rev. B **61**, 14 299 (1999).
[29] N. Harrison, Phys. Rev. Lett. **83**, 1395 (1999).
[30] T. Sasaki and T. Fukase, Phys. Rev. B **59**, 13 872 (1999).
[31] N. Harrison, C.H. Mielke, D.G. Rickel, J. Wosniza, J.S. Qualls, J.S. Brooks, E. Balthes, D. Shweitzer, I. Heinen, and W. Strunz, Phys. Rev. B **58**, 10 248 (1998).
[32] T. Sasaki, W. Biberacher, and T. Fukase, Physica B **246-247**, 303 (1998).
[33] N. Harrison, A. House, M.V. Kartsovnik, A.V. Polisski, J. Singleton, F. Herlach, W. Hayes, and N.D. Kushch, Phys. Rev. Lett. **77**, 1576 (1996).
[34] A number of earlier publications were able to obtain ''good'' fits of the 3D LK model to dHvA and Shubnikov–de Haas wave forms by allowing field or temperature dependences of the g factor and/or Dingle temperature or by introducing an arbitrary phase adjustment factor into the argument of the sine time in the LK formula. The latter, in particular, is fundamentally incorrect and also obscures important phase information that would otherwise be available in the wave form of the oscillations.
[35] J. Wosnitza, *Fermi Surfaces of Low-Dimensional Organic Metals and Superconductors*, Vol. 134 of Springer Tracts in Modern Physics (Springer-Verlag, Berlin, 1996).
[36] N.W. Ashcroft and N.D. Mermin, *Solid State Physics* (Saunders College Publishing, Philadelphia, 1976).
[37] A.C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, 1993).
[38] J. Merino and R.H. McKenzie, Phys. Rev. B **62**, 2416 (2000).
[39] A.A. House, C.J. Haworth, S.J. Blundel, M.M. Honold, J. Singleton, W. Hayes, S.M. Hayden, P. Meeson, M. Springford, M. Kurmoo, and P. Day, J. Phys.: Condens. Matter **8**, 10 361 (1996); **8**, 10 371 (1996).
[40] The quantity γ represents the fraction of states in the material that compose the 2D α pocket. The other states are quasi-one-dimensional, functioning primarily as a charge reservoir.
[41] P.M. Chaikin, Phys. Rev. Lett. **69**, 2831 (1992).
[42] J. Symington *et al.*, Physica B (to be published).
[43] N. Toyota, E.W. Fenton, T. Sasaki, and M. Tachiki, Solid State Commun. **72**, 859 (1989).
[44] M.A. Itskovsky, T. Maniv, and I.D. Vagner, Phys. Rev. B **61**, 14 616 (2000).