Thermodynamic evidence for bulk charge-density wave rigidity in $NbSe_3$

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(Received 14 January 2000)

We show that the split wave form of the magnetic quantum oscillations observed in $NbSe_3$ cannot be attributed to the Zeeman splitting of the Landau levels. Instead, the behavior of the pronounced second harmonic is consistent with the ''frequency doubling'' effect that occurs when the oscillatory chemical potential interferes with a commensurate charge-density wave. Since the charge-density waves in $NbSe_3$ are most definitely incommensurate, this low temperature rigidity must be caused by pinning mechanisms that involve the bulk of the sample.

The effects of orbital quantization on the thermodynamic properties of density waves have become well known in the Bechgaard (TMTSF) charge-transfer salts.[1] The adaptable nature of the field-induced spin-density waves (SDW's) in these materials is largely connected with their intrinsic incommensurability, with the optimum nesting vector **Q** being free to adjust itself in a continuous manner as the magnetic field B is varied, so as to minimize the total free energy. This is achieved by maintaining the chemical potential μ in the gaps between adjacent Landau levels of the residual closed pocket created by the imperfect nesting, giving rise to a manifestation of the bulk quantum Hall effect (QHE).[2] Transitions between consecutive Hall plateaus occur when **Q** undergoes discontinuous changes on shifting μ to the next Landau gap. Similar orbital mechanisms have been proposed to explain the origin of the bulk QHE in the incommensurate charge-density wave (CDW) compound η-Mo_4O_{11}.[3]

A qualitatively different behavior could, however, be expected in systems in which **Q** remains locked at a constant value, as can, for example, be realized in commensurate density wave systems.[4] Under such circumstances, μ is no longer preferentially located between Landau levels, but instead oscillates with $1/B$ so as to maintain a constant number of particles N.[5] The bulk QHE therefore does not occur, but the oscillations of μ do, however, interfere with the stability of the DW ground state. This interaction was recently shown to give rise to frequency-doubling (FD) effects in the quantum oscillation spectra and was proposed to be responsible for the strongly split de Haas–van Alphen (dHvA) wave form observed in α-(BEDT-TTF)$_2M$ Hg(SCN)$_4$ (with M = K, Tl or Rb) charge-transfer salts.[5]

Given that the CDW ground state in $NbSe_3$ is incommensurate,[6] we might expect it to behave similarly to $(TMTSF)_2ClO_4$ (Ref. 1) and η-Mo_4O_{11};[3] especially since these density wave systems are of comparable purity, as evidenced by the presence of large quantum oscillatory effects. However, rather than exhibiting a QHE,[7] instead, the Shubnikov–de Haas (SdH) oscillations in $NbSe_3$ display a strongly split wave form[8] in some ways resembling those observed in α-(BEDT-TTF)$_2M$ Hg(SCN)$_4$ salts.[5] While, in previous works, the split waveform in $NbSe_3$ has been attributed to the Zeeman splitting of the Landau levels in a magnetic field,[7,8] this was never actually proven. A rigorous proof would require a self-consistency check in order to verify that the same Zeeman splitting energy $\Delta\epsilon = g\mu_B B$ fits the quantum oscillatory data at all orientations of B.[9]

In this paper, we report new measurements of the field orientation dependence of the SdH oscillations in $NbSe_3$ and show rather conclusively that the persistence of the split wave form at all orientations of B cannot be explained by the Zeeman splitting model; i.e., the splitting persists against a change in the SdH oscillation frequency F and the effective mass m^* by more than a factor of 3.[10] The behavior of the second harmonic, that gives rise to the appearance of splitting, is, nevertheless, quantitatively consistent with the FD mechanism.[5] In view of the fact that the ground state of $NbSe_3$ consists of a pair of incommensurate CDW's,[6] the fact that the FD model is able to describe the angle dependence of the oscillations so well comes as a surprise. What this implies is that, unlike other incommensurate density wave systems[1–3] of comparable purity, the incommensurate CDW ground state in $NbSe_3$ is exceptionally ''rigid'' in that

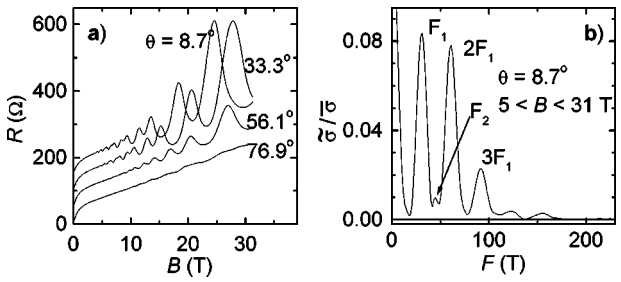

FIG. 1. (a) Examples of the magnetoresistance of $NbSe_3$ at several different angles θ at 500 ± 20 mK, offset for clarity. (b) An example of a Fourier transformation in reciprocal magnetic field for $\theta=8.7°$.

it resists the formation of soliton excitations. The nature of the pinning mechanism at low temperatures must therefore be significantly different from that in other metallic CDW systems that exhibit the QHE such as η-Mo_4O_{11},[3] or in the field-induced SDW systems.[1,2]

For the purpose of this study, single crystals of $NbSe_3$, with the usual needlelike morphology, were grown using the vapor transport technique.[11] Four gold wires were attached to the samples by means of electrically conductive silver paste, and low ac currents of $\sim10\mu$A at low frequencies of ~19 Hz were employed throughout the measurement process in order to ensure that the CDW was not depinned or transformed into a metastable CDW state.[12] Static magnetic fields extending to ~32 T were provided by the National High Magnetic Field Laboratory, Tallahassee, while stable temperatures of 500 ± 20 mK were obtained by means of a ^{3}He refrigerator. The sample was rotated between sweeps of the magnetic field with B in the **ac** plane.

Examples of the magnetoresistance measured at several different angles are shown in Fig. 1(a), having qualitatively the same form as those observed by other groups at high magnetic fields.[7,8,13] Here, θ refers to the angle by which the orientation of B is rotated off the **c** axis towards **a**. A Fourier transformation at $\theta=8.7°$ is shown in Fig. 1(b). The frequency F_1 of $\sim31.3\pm0.1$ T at $\theta=8.7°$, in Fig. 1(b), or $\sim$ 30.2 ± 0.1 T at $\theta=0°$, has the largest amplitude, together with its harmonics, and originates from an elongated ellipsoid of ellipticity $r\sim3.64$ that occupies $\sim0.10\%$ of the first Brillouin zone; as depicted by the polar plot of Fig. 2(a). A second much weaker frequency F_2 of $\sim45\pm1$ T is observed over a more limited range of angles, becoming ob-

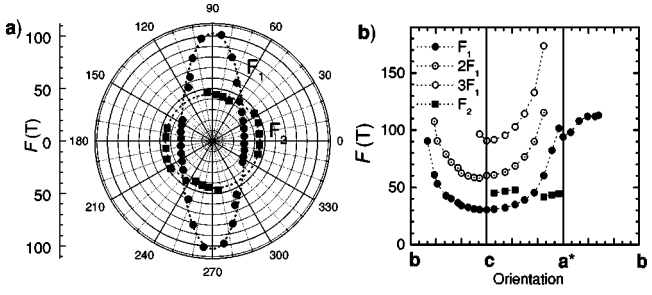

FIG. 2. (a) Polar plots of the F_1 and F_2 frequencies versus θ, illustrating their topologies. (b) Full orientation dependence of all of the frequencies measured in $NbSe_3$ in this work (in the **ac** plane) and by Monceau [7] (in the **ab** and **bc** planes).

scured by the much larger amplitude F_1 frequency for $40°<\theta<60°$. From the limited angular data on F_2 in Fig. 2(b), we can infer only that it originates from pocket of Fermi surface (FS) with either a spherical or pancakelike topology. As will be considered later in this paper, the weak amplitude of F_2 compared to F_1 implies that this piece of FS functions primarily as a charge reservoir.

Of greatest interest in the present study, is the strongly split wave form, as clearly visible in Fig. 1(a). In a normal metal, such a wave form could only be realized when the Zeeman splitting energy $\Delta\epsilon$ becomes equal (or nearly equal) to an odd half-integer multiple of $\hbar\omega_c=\hbar eB/m^*$.[9] A simplified criterion for spin-splitting is obtained by taking the ratio of these two energies; i.e., spin-splitting can only occur when the product μ^*g is equal (or nearly equal) to an odd integer, where $\mu^*=m^*/m_e$ and m_e is the free electron mass. Conversely, no spin-splitting occurs whenever μ^*g is equal (or approximately equal) to an even integer, whereby the two spin polarities are degenerate. Since m^* changes by more than a factor of three upon rotation with respect to B,[10] while g does not, the spin-splitting condition should also change appreciably. So, were the split wave form at $\theta=0°$ really to originate from spin-splitting, this should then disappear for $60°\lesssim\theta\lesssim70°$ owing to the doubling of m^* at this angle (causing μ^*g to become even). The fact that this does not happen provides rather compelling evidence for the fact that the Zeeman splitting of the Landau levels is not the primary mechanism responsible for the pronounced second harmonic in this material. The lack of any appreciable change in the degree of splitting with angle in Fig. 1(a) (and Fig. 2 of Ref. 8) is, nevertheless, entirely consistent with the FD mechanism.[5]

Before continuing this discussion, it is instructive to refer to the Lifshitz-Kosevich (LK) formula[9] to assist in our understanding of the behavior of the angle dependence of the amplitudes of the various harmonics that are expected to originate from such a three-dimensional (3D) FS pocket, as observed in $NbSe_3$ within its low temperature CDW phase. While the LK theory was originally developed to explain the dHvA effect in 3D metals, which is purely thermodynamic in origin, the same formalism is known also to apply to the SdH effect in 3D systems.[14] The ratio of each harmonic p of the oscillatory component of the conductivity $\tilde{\sigma}_p$ to the monotonically varying background σ_0 has the form

$$\frac{\tilde{\sigma}_p}{\sigma_0}=-(-1)^p\frac{cB^{1/2}}{p^{1/2}A''^{(1/2)}}R_{T,p}R_{D,p}R_{s,p}, \tag{1}$$

where c is a constant.[9] Both the curvature factor $A''=\partial^2A/\partial k_z^2=2\pi(F/F_0)^3/r^2$ (Ref. 9) and the thermal damping factor $R_{T,p}$ (Ref. 9) at $T=500$ mK are well known, owing to the fact that the FS parameters of the pocket giving rise to F_1 have been determined.[8,10] Here, F_0 is F at $\theta=0°$, while A is the cross-section area of the FS in k space. Only the spin-damping and Dingle amplitude reduction factors, $R_{s,p}=\cos[p\pi g\mu_0^*(F/F_0)/2]$ and $R_{D,p}=\exp[p\gamma/B\cdot(F/F_0)^{1/2}]$, that originate from the Zeeman interaction and elastic scattering events respectively,[9] contain unknown parameters; namely g and γ. Again, μ_0^* is μ^* at $\theta=0°$, while the exponent of $\frac{1}{2}$ accounts for the variation of

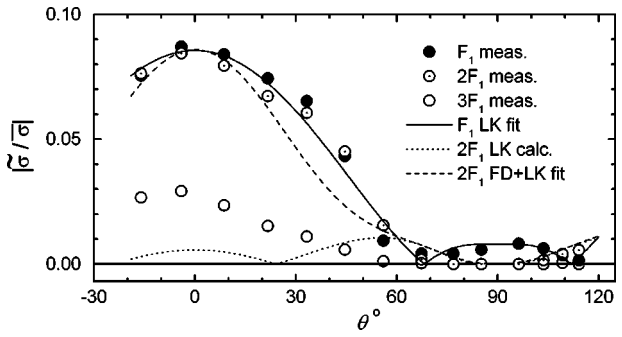

FIG. 3. The observed angle dependence of the Fourier amplitudes of the fundamental (solid circles), the second harmonic (dot-centered circles), and the third harmonic (open circles) for $5<B<31$ T. The solid line represents a fit to the fundamental using the LK model. The dotted line represents the expected LK amplitude of the second harmonic according to the LK fit to the fundamental. The dashed line represents a fit of the FD theory to the second harmonic (including the $p=2$ LK contribution) as described in the text.

the cyclotron length with F. For convenience, we have assumed that the scattering cross section between quasiparticles and static impurities is not significantly angle dependent for a closed 3D pocket, in which case the quasiclassical mean free path l is constant and $\gamma=\pi m_0^* v_{\mathrm{F},0}/el$ ($v_{\mathrm{F},0}=\sqrt{2e\hbar F_0}/m_0^*$ being the Fermi velocity). With all of these effects taken into consideration, fitting to the amplitude of the fundamental $p=1$ harmonic requires the adjustment of only three parameters: g, γ and c. Evidently, the LK model, as described by Eq. (1), is able to fit the behavior of the fundamental rather well in Fig. 3, with $g=1.53\pm0.06$,[15] $\gamma=4.7\pm0.1$ T (or $l\sim1320$ Å) and $c\sim0.094\pm0.005$. The most notable detail of this fit is that the fitted g factor is significantly lower than that of ~2.45 obtained by Monceau.[8] Rather than occurring at $\theta=0°$, this fit reveals that *real* spin-splitting is only realized at $\theta\approx68°$.

It follows from the LK theory of 3D metals that the parameters, g, γ and c, as determined above, should reproduce the correct angle-dependence of the amplitudes of all harmonics equally well. On inserting $p=2$ into Eq. (1) in Fig. 3, however, we find that the LK formula (depicted by the dotted line) grossly underestimates the amplitude of the second harmonic and incorrectly determines the angular positions of the nodes. The fact that the observed second harmonic does not undergo a node at $\theta\sim24°$, but instead closely follows the amplitude of the fundamental over a broad range of angles ($-20°<\theta<70°$), indicates quite clearly that the dominant contribution to the second harmonic is not of LK origin.

Because of the enormous difference in free energy $\sim ng_{1\mathrm{D}}\Delta^2/2$ between the normal metallic and CDW states,[5] where n is the number of pairs of one-dimensional (1D) FS sheets of density $g_{1\mathrm{D}}$ that become gapped on formation of the CDW, the destabilizing effect of the oscillatory chemical potential $\tilde{\mu}$ can result in an equally enormous FD effect with an oscillation amplitude that greatly exceeds that of the conventional $p=2$ LK contribution.[5] Consequently, the FD effect can be quite significant, even in the case of a 3D pocket for which $\tilde{\mu}$ is $\Gamma_{3\mathrm{D}}=(4A''F/\pi B)^{1/2}$ times smaller than that which would originate from a 2D pocket of the same cross section.[9] While the original FD model focused entirely on thermodynamic effects,[5] the quantum oscillations in $NbSe_3$ have only been observed in the magnetotransport. In this case, the FD mechanism manifests itself as oscillations in the density of states in the vicinity of μ and quasiparticle excitations across the gap. The theoretical arguments for expecting the FD effect to occur in the magnetotransport are therefore similar to those for expecting the SdH effect to occur.[9,14] If we assume that the ratio $\tilde{\chi}_{2F}/\tilde{\chi}_{1F}=\tilde{\sigma}_{2F}/\tilde{\sigma}_{1F}$ applies equally to the FD effect, as it does to regular quantum oscillations,[9] we then obtain

$$\frac{\tilde{\sigma}_{2F}}{\tilde{\sigma}_{p=1}}\sim\frac{\tilde{\chi}_{2F}}{\tilde{\chi}_{p=1}}\approx4\frac{ng_{1\mathrm{D}}}{\Gamma_{3\mathrm{D}}g_{3\mathrm{D}}}R_{T,1}R_{\mathrm{D},1}R_{\mathrm{s},1}R_{\mathrm{res}}^2 \tag{2}$$

for the ratio between the amplitude of the $2F$ oscillations that originate from the FD effect and the fundamental LK amplitude.[5,16] Equation (2) is merely an adaptation of Eq. (6) of Ref. 5, with $g_{3\mathrm{D}}(\ll g_{1\mathrm{D}})$ now being the field-averaged density of states of the 3D pocket created by the imperfect nesting of one pair of these sheets, while $R_{\mathrm{res}}\approx g_{3\mathrm{D}}/g_{\mathrm{res}}$ is an additional factor that accounts for the damping of $\tilde{\mu}$ caused by the existence of a background reservoir of states g_{res}.[17] The pocket responsible for the very weak F_2 frequency together with the possible existence of unnested 1D sheets can both constitute this reservoir.

It therefore follows that the experimentally observed second harmonic is a linear superposition of the FD effect and conventional $p=2$ term from Eq. (1); hence

$$\frac{\tilde{\sigma}_{2F}+\tilde{\sigma}_2}{\sigma_0}\approx\frac{cB^{1/2}}{A''^{(1/2)}}\left[k\left(\frac{F_0}{F}\right)^2R_{T,1}^2R_{\mathrm{D},1}^2R_{\mathrm{s},1}^2-\frac{1}{\sqrt{2}}R_{T,2}R_{\mathrm{D},2}R_{\mathrm{s},2}\right]. \tag{3}$$

Since g, γ and c have already been determined above, a fit to Eq. (3) involves the adjustment of only one parameter; $k=4ng_{3\mathrm{D}}g_{1\mathrm{D}}/g_{\mathrm{res}}^2\times(r^2B/8F_0)^{1/2}$. In Fig. 3 (dashed line), it now appears that the behavior of the experimentally observed second harmonic can be satisfactorily reproduced by setting $k=2.5\pm0.1$.[18]

We have shown that not only does the FD model fit the experimentally observed quantum oscillations in $NbSe_3$ reasonably well, but also yields potentially useful parameters regarding the reconstruction of the Fermi surface within the low temperature CDW phase.[18] The question nevertheless remains as to why the thermodynamic behavior of $NbSe_3$ appears to be indistinguishable from that of a commensurate CDW system;[5] i.e., in a similar way to a commensurate CDW, the incommensurate CDW ground state in $NbSe_3$ yields more easily to quasiparticle excitations than it does to soliton excitations as the magnetic field is varied. This type of rigidity could conceivably be a consequence of bulk, collective impurity pinning interactions,[19] or, alternatively, could result from pinning interactions with the underlying lattice following near-commensurability effects.[4] The fact that the degree of splitting is gradually alleviated by the application of large electric fields[13] could be considered conducive to the involvement of some form of pinning mechanism. It should be noted, however, that we can only assert the

existence of this rigidity of the CDW to bulk concertina-like motions in the low temperature ($T \lesssim 4$ K) regime within which the FD effects are observed. While conventional studies of the CDW dynamics, albeit at somewhat elevated temperatures ($T \gg 4$ K), have shown that the CDW appears to behave more elastically,[4,20] these experiments usually involve local phase deformations of the CDW's around individual impurities as the CDW's undergo translational motion. Unfortunately, x-ray diffraction and nuclear magnetic resonance measurements, which often provide information on the structural properties of CDW's, have not been extended into the very low T regime.

A greater paradox, perhaps, is why the FD effect should occur in incommensurate $NbSe_3$, which has, perhaps, one of the highest carrier mobilities among metals,[21] and not in certain other metallic, incommensurate CDW compounds such as η-Mo_4O_{11}.[3] The dimensionality of the FS could be one contributory factor, with the free energy to be gained by shifting **Q** to minimize the density of states at μ being approximately $\Gamma_{3D} = (4A''F/\pi B)^{1/2}$ times smaller in $NbSe_3$ than in density wave systems in which the residual pockets are 2D.

In summary, we show, by means of a study of the field orientation dependence of the split wave form in $NbSe_3$, that it cannot be attributed to the Zeeman splitting of the Landau levels in a magnetic field. The behavior of the second harmonic is, however, consistent with the ''frequency doubling'' mechanism that occurs when the oscillations of μ interfere with the CDW ground state.[5] These results show that CDW's in $NbSe_3$ at very low temperatures exhibit bulk rigidity, although it is clear that some further theoretical developments will be necessary to fully understand this phenomenon.

The work was supported by the Department of Energy, the National Science Foundation (NSF) and the State of Florida. One of us (J.S.B.) would like to acknowledge the provision of a NSF grant (Grant No. DMR-9510427). We would like to thank Robert Thorne for useful comments.

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[10] The proportionality $F \propto m^*$ always holds for a single closed section of the Fermi surface, since the ratio of these two quantities gives the Fermi energy ($\epsilon_F = e\hbar F/m^*$) which is invariant under changes in the size and direction of B. See Ref. 8 for actual values of m^*.

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[15] The ability of the LK theory to fit the behavior of the fundamental is somewhat conditional upon the other conventional $p>1$ harmonics being of significantly lower amplitude compared to the fundamental. In cases where the conventional LK signal exhibits other strong harmonics, rather than just resulting in FD, the CDW would cause a substantial amount of mixing betwen all of the harmonics. The small size of the $p>1$ LK harmonics in $NbSe_3$ implies that this is not a significant effect in this material.

[16] This is obtained using the relations $\chi_{2F} = -\partial^2 g_{1D}\tilde{\mu}^2/\partial B^2$ (Ref. 5) and $\tilde{\mu} = -B\tilde{M}/Fg_{3D}$ (Ref. 9).

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[18] If g_{res} consists primarily of 1 remaining unnested pair of 1D sheets, as conjectured in Ref. 7, then $n=3$, $g_{res} \approx g_{1D}$ and we obtain $g_{3D} \sim 0.3 \times g_{1D}$. If, on the other hand, all 4 of the 1D sheets are nested, as suggested on the basis of a scanning-tunneling-microscopy analysis [J. Ren and M.-H. Whangbo, Phys. Rev. B **46**, 4917 (1992)], then, if $g_{res} < g_{1D}$, we obtain $g_{3D} \lesssim 0.2 \times g_{res}$. The latter possibility would imply the existence of several large pockets within the CDW phase in addition to those giving rise to F_1 and F_2.

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