Observation of oscillatory magnetoresistance periodic in $1/B$ and B in $Ca_3Ru_2O_7$

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We report magnetoresistive oscillations in high magnetic fields B up to 45 T and over a wide range of temperature in the Mott-like system $Ca_3Ru_2O_7$. For B rotating within the *ac* plane, slow and strong Shubnikov–de Haas (SdH) oscillations periodic in $1/B$ are observed for $T \leqslant 1.5$ K in the presence of metamagnetism. These oscillations are highly angular dependent and intimately correlated with the spin polarization of the ferromagnetic state. For $B \| [110]$, oscillations are also observed but periodic in B (rather than $1/B$) which persist up to 15 K. While the SdH oscillations are a manifestation of the presence of small Fermi surface (FS) pockets in the Mott-like system, the B-periodic oscillations, an exotic quantum phenomenon, may be a result of anomalous coupling of the magnetic field to the t_{2g} orbitals that makes the extremal cross section of the FS field dependent.

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I. INTRODUCTION

Landau levels arise from the quantization of electron orbits in a magnetic field B. As B is increased, the Landau levels break through the Fermi surface, giving rise to oscillations of the density of states at the Fermi surface with B. The oscillations of the density of states lead to oscillatory changes in many physical properties, e.g., electrical resistance. The oscillatory changes in the resistance is known as the Shubnikov–de Haas (SdH) effect and is an important tool to measure the cross-sectional areas of the Fermi surface. The SdH effect gives rise to oscillatory magnetoresistance periodic in $1/B$. The periods of these oscillations yield the maximal and minimal cross-sectional areas of the Fermi surface normal to B. This probe is particularly important for investigations of correlated electron systems when quantum oscillations are experimentally observable. There is another type of oscillatory magnetoresistivity that is characterized as a function of B rather than $1/B$. The oscillations periodic in B are usually a sign of size effects, such as the Aharanov-Bohm (AB) effect, the Sondheimer effect, etc., which can be expected only in a channel geometry and mesoscopic conductors at ultralow temperatures.[1,2] In this paper, we report observations of quantum oscillations periodic in both B and $1/B$ in the Mott-like system $Ca_3Ru_2O_7$ at elevated temperatures when B is applied along different crystallographic orientations. While observations of the SdH effect are rare in Mott systems such as $Ca_3Ru_2O_7$ because of the carrier mean-free path comparable with the lattice spacing, to the best of our knowledge, oscillatory behavior periodic in B has not been seen in any bulk materials before. The aim of this paper is to present this exotic new physics.

$Ca_3Ru_2O_7$ belongs to a class of new highly correlated electron materials rich in novel phenomena.[3–15] The central feature of 4*d*-electron-based materials is the extension of their orbitals that leads to competing energies including crystalline fields, Hund's rule interactions, spin-orbit coupling, *p*-*d* hybridization, and electron-lattice coupling. The interplay of the electron spin with the orbital and lattice degrees of freedom leads to exotic behavior, which is particularly susceptible to perturbations such as the application of magnetic fields. The long-range spin and orbital order (OO) of $Ca_3Ru_2O_7$ strongly depends on the orientation of B, hence, can be effectively manipulated and probed with B. Here, we present interplane or *c*-axis magnetoresistivity ρ_c, with B (i) rotating within the *ac* plane (actually by rotating the sample relative to B) and (ii) aligned with the [110] direction (diagonal direction in the *ab* plane) for temperatures ranging from 0.4 to 15 K and B up to 45 T. The results reveal slow yet strong SdH oscillations in the *ac* plane with frequencies ranging from 30 to 117 T in the presence of metamagnetism, which leads to a ferromagnetic (FM) state. These frequencies are highly angular dependent and intimately correlated with the FM state. For $B \| [110]$, the unusual oscillations in the resistance are observed with *periodicity in B* (rather than $1/B$) persisting up to 15 K with the amplitude of the oscillations slowly decreasing with increasing temperature.

The crystal structure of $Ca_3Ru_2O_7$ is severely distorted by a tilt of the RuO_6 octahedra, which projects primarily onto the *ac* plane $(153.22°)$, and only slightly affects the *bc* plane $(172.0°)$.[3] These crucial bond angles directly impact the band structure and are the origin of the anisotropic properties. For low fields, $Ca_3Ru_2O_7$ undergoes an antiferromagnetic (AFM) transition at $T_N = 56$ K while remaining metallic, and then a Mott-like transition at $T_{MI} = 48$ K.[3–15] This transition is accompanied by an abrupt shortening of the *c*-axis lattice parameter below T_{MI}.[6] Such magnetoelastic coupling results in Jahn-Teller distortions of the RuO_6 octahedra, lowering the d_{xy} orbitals relative to the d_{zx} and d_{yx} orbitals with an orbital distribution of $(n_{xy}, n_{zx}/n_{yz}) = (2,2)$. Consequently, a phase with AFM *and* OO can occur, explaining the nonmetallic behavior for $T < T_{MI}$ and $B < B_c$ (metamagnetic transition). This scenario is consistent with Raman-scattering studies of $Ca_3Ru_2O_7$, which probe magnon, phonon and thus orbitals.[11,12,14]

II. EXPERIMENT

Single crystals were grown using both flux and floating zone techniques[9] and characterized by single crystal x-ray diffraction, Scanning electron microscopy, and transmission electron microscopy. All results indicate that the single crystals are of high quality. The highly anisotropic magnetic properties of $Ca_3Ru_2O_7$ are used to determine the magnetic easy *a* axis and to identify twinned crystals that often show a small kink at 48 K in the *b*-axis susceptibility. There is *no difference* in the magnetic and transport properties and Raman spectra of crystals grown using flux and floating zone methods. Our studies on oxygen-rich $Ca_3Ru_2O_{7+\delta}$ show that the resistivity for the basal plane displays a down turn below 30 K, indicating brief metallic behavior. The metallic behavior can be readily induced by other impurity doping, such as oxygen and La.[3] The reported metallic behavior in Ref. 10 is therefore not intrinsic behavior of the stoichiometric $Ca_3Ru_2O_7$. The resistivity was obtained using the standard four-lead technique. The magnetization was measured using the Quantum Design MPMS XL 7T magnetometer. High magnetic field measurements were performed at National High Magnetic Field Laboratory.

III. RESULTS AND DISCUSSION

Shown in Fig. 1(a) is the B dependence of the resistivity for the current along the c axis ρ_c (right scale) for $T=0.4$ K and $0 \leqslant B \leqslant 45$ T with $B \| a$, b, and c axes. A central feature of this system is that the resistivity is extraordinarily sensitive to the orientation of B. For the $B \| a$ axis (magnetic easy axis) ρ_c shows an abrupt drop by an order of magnitude at 6 T corresponding to the first-order metamagnetic transition leading to the FM state with a saturated moment M_s, of $1.8\mu_B$/Ru or more than 85% polarized spins [see left scale in Fig. 1(a)]. The reduction of ρ_c is attributed to the coherent motion of electrons between Ru-O planes separated by insulating Ca-O planes, an effect similar to spin filters. As B is increased further from 6 to 45 T, ρ_c increases linearly with B by more than 30%. Since a quadratic dependence is expected for regular metals (quantization of orbits), a linear variation of ρ_c over such a wide range of B is likely to arise from orbital t_{2g} degrees of freedom, which couple to B directly and may modify the dynamics of the electrons.

For the $B \| b$ axis (magnetic hard-axis) there is no spin-flop transition and the system remains AFM. However, for the $B \| b$ axis, ρ_c rapidly decreases by as much as three orders of magnitude at $B_c=15$ T, i.e., two orders of magnitude more than the drop for $B \| a$, where the spins are nearly fully polarized.[15] Hence, in $Ca_3Ru_2O_7$ a colossal magnetoresistance is achieved only when a FM state with full spin polarization is *avoided*. The FM state stabilizes OO, suppressing the hopping of the electrons. This in turn makes the FM state the least favorable for conduction.[15] This behavior is fundamentally different from that of all other colossal magnetoresistive materials that are primarily driven by spin polarization.[16]

For the $B \| c$ axis, on the other hand, ρ_c displays slow SdH oscillations in the absence of the metamagentism, signaling the existence of very small Fermi surface cross sections. Local density approximation calculations[17] for $Sr_3Ru_2O_7$, which shares common aspects with $Ca_3Ru_2O_7$, find the Fermi surface very sensitive to small structural changes. In particular, the d_{xy} orbitals give rise to small lens shaped Fermi surface pockets. The observed oscillations must then be associated with the motion of the electrons in the *ab* plane, i.e., with the d_{xy} orbitals. The oscillations in ρ_c correspond to extremely low frequencies $f_1=28$ T and $f_2=10$ T, which, based on crystallographic data[3] and the Onsager relation $F_0=A(h/4\pi^2 e)$ (e is the electron charge, h Planck constant), correspond to a cross-sectional area of only 0.2% of the first Brillouin zone. From the T dependence of the amplitude, the cyclotron effective mass is estimated to be $\mu_c=(0.85\pm0.05)m_e$. This is markedly smaller than the enhanced thermodynamic effective mass (~ 3) estimated from the electronic contribution γ to the specific heat.[4,7] There are two

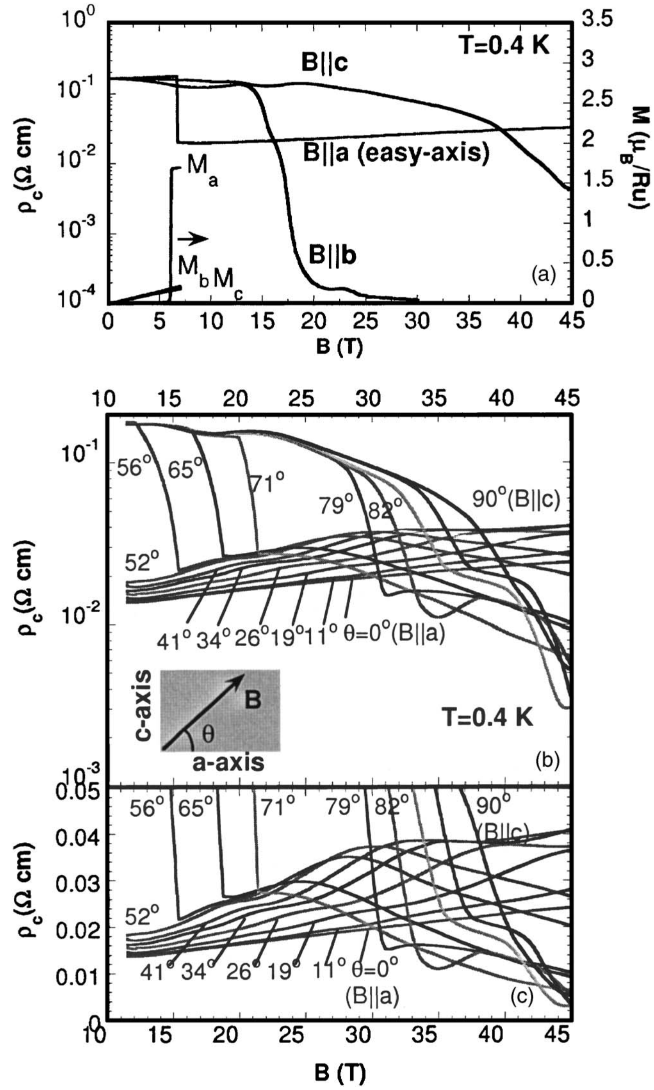

FIG. 1. (a) The c-axis resistivity ρ_c at $T=0.4$ K (right scale) and magnetization M (left scale) at 2 K as a function of B ranging from 0 to 45 T for $B \| a$, b, and c axes. (b) ρ_c for B rotating in the *ac* plane with $\theta=0$ and 90° corresponding to $B \| a$ and $B \| c$, respectively. (c) Enlarged ρ_c on a linear scale for clarity. Note that the range of B is from 11 to 45 T in (b) and (c).

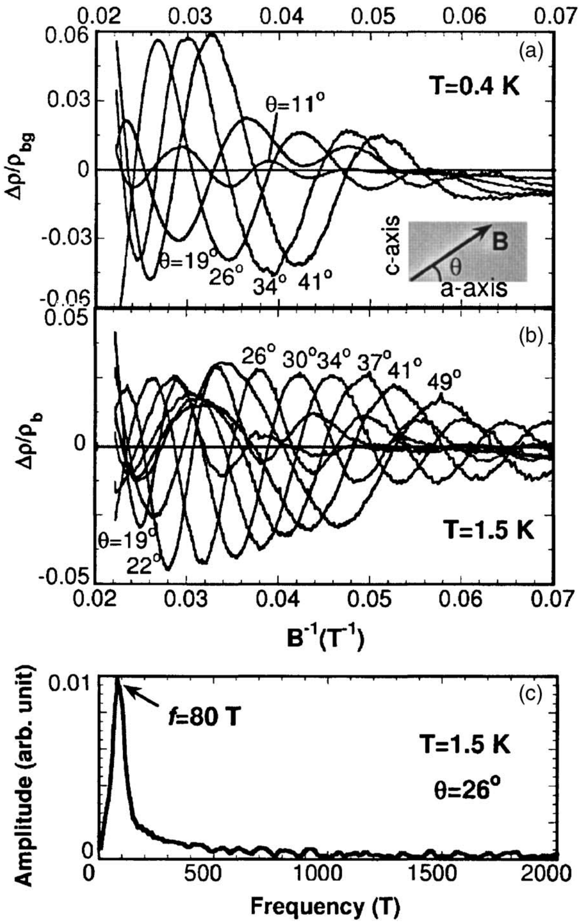

FIG. 2. The amplitude of the SdH oscillations defined as $\Delta\rho/\rho_{bg}$ as a function of inverse field B^{-1} for various θ and for (a) $T=0.4$ K and (b) 1.5 K; (c) the SdH amplitude as a function of frequency obtained from the fast fourier transformation for a representative ρ_c at $T=1.5$ K and $\theta=26°$.

possible sources for this discrepancy: (1) The cyclotron effective mass is measured in a large magnetic field that quenches correlations, while the specific heat is a zero-field measurement and (2) μ_c only refers to one closed orbit, while the thermodynamic effective mass measures an average over the entire Fermi surface. In addition, the Dingle temperature $T_D=h/4\pi^2 k_B \tau$, a measure of scattering, is estimated to be 3 K, comparable to those of good organic metals.

The field dependence of ρ_c (on a logarithmic scale) for B rotating in the ac plane ($B\|a$ axis $\theta=0°$ and $B\|c$ axis $\theta=90°$) at $T=0.4$ K is shown in Fig. 1(b) for B ranging from 11 to 45 T. B_c occurs at 6 T for the $B\|a$ axis, and increases with increasing θ, i.e., as B rotates towards to the c axis. The striking finding is that strong SdH oscillations are qualitatively different for $11° \leqslant \theta < 56°$ and $56° < \theta \leqslant 90°$. It is then likely that the vicinity of $\theta=56°$ marks the onset of the melting of the OO state as B rotates further away from the easy axis of magnetization (a axis). This destabilizes the FM state, and thus the OO state via direct coupling to the field or the spin-orbit interaction. (This is only possible perturbatively, because the spin-orbit interaction is quenched by crystalline fields.) Consequently, the electron mobility increases drastically, explaining the largely enhanced conductivity for $56° < \theta \leqslant 90°$.

For $\theta < 56°$ the strong oscillations occur only for $B > B_c$ and with frequencies significantly larger than the ones previously observed for the $B\|c$ axis. For clarity, Fig. 1(c) exhibits ρ_c on a linear and enlarged scale for $B > B_c$. For $0° < \theta < 56°$ and $B > B_c$, ρ_c increases with both B and θ, and displays oscillatory behavior only for $11° \leqslant \theta < 56°$. While the extremal orbits responsible for the oscillations are facilitated by the FM state, it is remarkable that no oscillations are seen when $\theta=0$ ($B\|a$ axis), where the FM state is fully established at $B_c=6$ T. In contrast, no oscillations were discerned for B rotating within the bc plane at B up to 45 T.[18] The bumps seen in ρ for $B\|b$ [Fig. 1(a)] are not oscillatory at higher B. The bc plane is perpendicular to the easy axis of magnetization and has no FM component,[5,6,18] suggesting a critical link of the SdH oscillations to the fully polarized FM state. The FM and the different projections of the tilt angles of the RuO_6 octahedra onto the ac and bc planes[3] are expected to affect the Fermi surface.

On the other hand, for $56° < \theta = 90°$, the oscillations disappear for $B > B_c$ but are present for $B < B_c$, accompanying the much more conducting phase at high fields, as shown in Figs. 1(b) and 1(c). The frequency of the oscillations seen for $B < B_c$ remains essentially unchanged with θ for $65° < \theta < 90°$. Since the d_{xy} orbitals are believed to be responsible for the oscillations $B\|c$ axis, the nearly constant frequency upon tilting of B suggests that the oscillations in the absence of the metamagnetism originate from a nearly spherical pocket of the same d_{xy} orbitals. Conversely, the oscillations for $11° \leqslant \theta < 56°$ and $B > B_c$ could be associated with a configuration of the FM state and ordered d_{zx} and/or d_{yz} orbitals. These orbitals offer only limited electron hopping (as confirmed by a larger ρ_c), and thus lower density of charge carriers and longer mean free path which in turn facilitates electrons to execute circular orbits.

Figure 2 shows the amplitude of the SdH oscillations as a function of $1/B$ for several representative θ at (a) $T=0.4$ K and (b) 1.5 K. The SdH signal is defined as $\Delta\rho/\rho_{bg}$, where

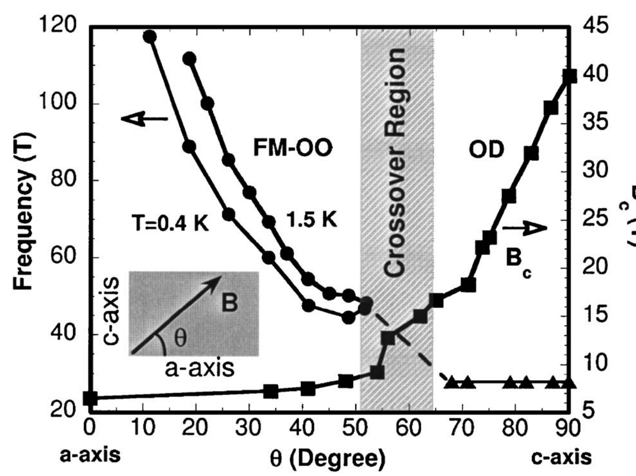

FIG. 3. The angular dependence of the frequency (solid circles for $B > B_c$, and empty circle for $B < B_c$) for $T=0.4$ and 1.5 K (left scale) and B_c (solid squares) (right scale). Note that the shaded area in the vicinity of 56° marks the melting of OO as θ increases.

$\Delta\rho=(\rho_c-\rho_{bg})$ and ρ_{bg} is the background resistivity. ρ_{bg} is obtained by fitting the actual ρ_c to a polynomial. The Fast Fourier Transformation (FFT) yields the same frequencies as those determined from Figs. 2(a) and 2(b). The result from the FFT is shown as Fig. 3(c) for a representative ρ_c at $T=1.5$ K and $\theta=26°$. Clearly, the oscillations are strong and slow, and their phase and frequency shift systematically with changing θ. The oscillations vanish for $\theta>56°$, suggesting that the extremal cross section responsible for the oscillations is highly susceptible to the orientation of B. SdH oscillations are usually rather weak in metals;[1] the remarkably strong oscillatory behavior for $11° \leqslant \theta < 56°$ may arise from an extremal orbit with a flat dispersion perpendicular to the cross section, so that a large constructive interference can occur. It is also noted that the $1/\cos\theta$-like behavior seen in Figs. 2(a) and 2(b) may imply the cylindrical Fermi surface elongated along the c axis, which favors the two-dimensional conductivity. With further increasing θ (=56°), the impact of B on the Fermi surface becomes even more dramatic and the closed orbit is no longer observed. The closed orbit is possibly replaced by open ones that do not contribute to oscillations.

Figure 3 illustrates the angular dependence of the SdH frequency for $T=0.4$ and 1.5 K (left scale) and B_c (right scale). The unusual feature is that the frequency is temperature dependent, increasing about 15% when T is raised from 0.4 to 1.5 K. The frequency for $B>B_c$ rapidly decreases with increasing θ and reaches about 45 T in the vicinity of $\theta=56°$, whereas the frequency for $B<B_c$ stays essentially constant for $\theta>56°$. The oscillations become difficult to measure in the vicinity of B_c. This is expected if B_c is associated with the melting of OO. The frequencies for $B>B_c$ are significantly larger than those for $B<B_c$, suggesting the former oscillations either originate from different electron orbits or a restructured Fermi surface. The angular dependence of B_c, on the other hand, is rather weak for $\theta<56°$ but

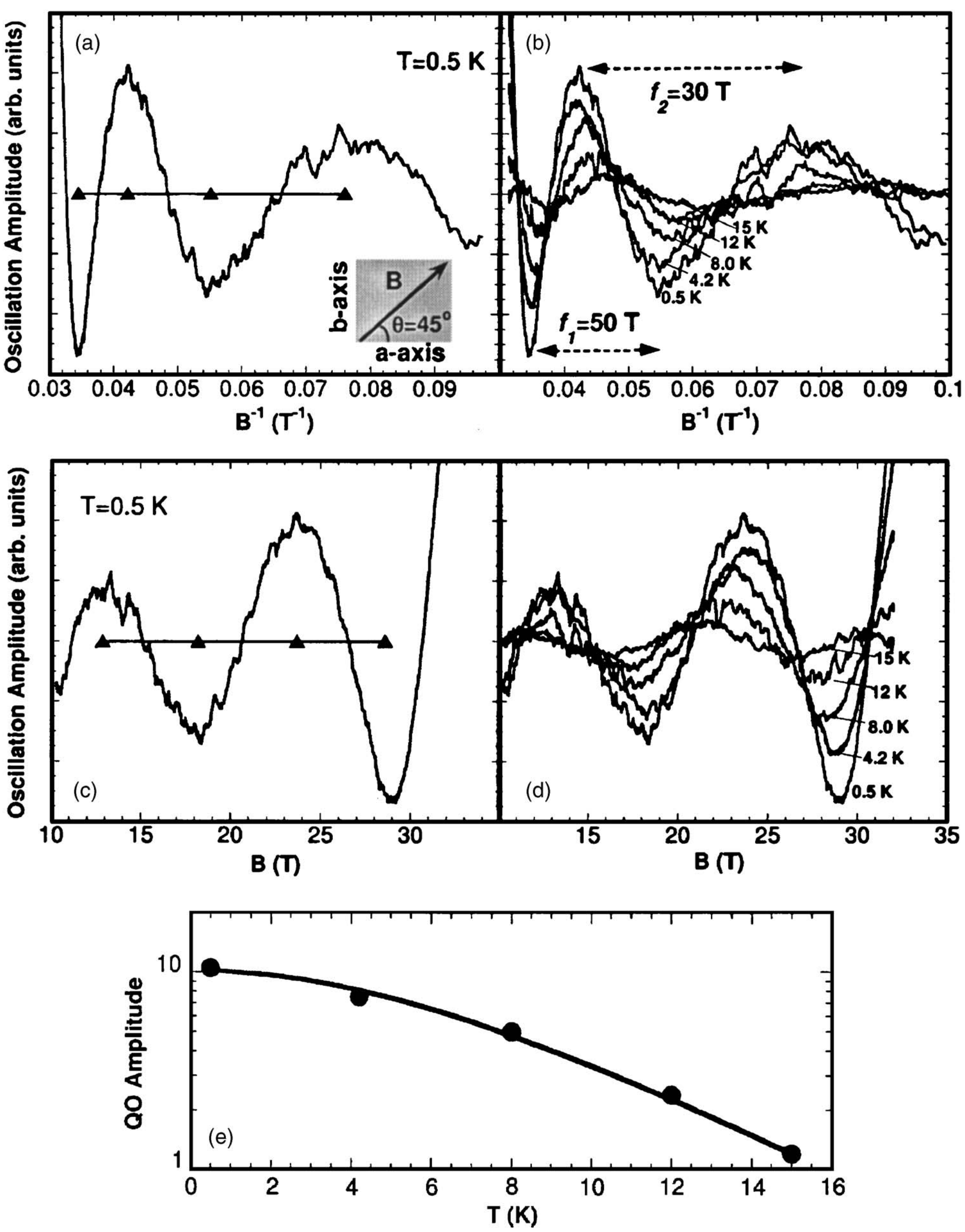

FIG. 4. (a) The amplitude of the quantum oscillations as a function of B^{-1} for $B\|[110]$ and $T=0.5$ K and (b) for various temperatures up to 15 K. (c) The amplitude of the oscillations as a function of B for $B\|[110]$ and $T=0.5$ K and (d) for various temperatures up to 15 K. (e) The amplitude of the oscillations (QO) as a function of temperature.

becomes much stronger for $\theta > 56°$. Note that ρ_c displays a weak plateau at high magnetic fields and θ approaching 90°, which disappears for the $B \| c$ axis because the FM state is no longer energetically favorable. Such an inverse correlation between the frequency and B_c reinforces the point that the FM state reconstructs the Fermi surface and facilitates the oscillatory effect. It is evident that the vicinity of $\theta = 56°$ or $52 < \theta < 65°$ marks a crossover region between the FM-OO state and the orbital degenerate (OD) state as shown in Fig. 3.

For $B \| [110]$, ρ_c also shows oscillations in the magnetoresistance as displayed in Fig. 4. The striking behavior is that these oscillations are periodic in B, instead of $1/B$, with a period of $\Delta B = 11$ T and persistent up 15 K. This highly unusual observation is corroborated by plotting the data both as a function of $1/B$ [Figs. 4(a) and 4(b)] and B [Figs. 4(c) and 4(d)]. The oscillations die off rapidly if B slightly departs from the [110] direction (within ±5°).

IV. CONCLUSIONS

Oscillations in the magnetoresistivity periodic in $1/B$ (SdH effect) are a manifestation of the constructive interference of quantized extremal orbits of Fermi surface cross sections perpendicular to the field. Due to the Pauli principle the electrons are bound to follow the Fermi surface. The projection of the real space trajectory of a free electron onto a plane perpendicular to **B** reproduces the k-space trajectory rotated by $\pi/2$ and scaled by a factor $c\hbar/|e|B$. Hence, trajectories with constructive interference in real space are expected to be periodic in B rather than $1/B$ (the frequency is proportional to the cross-sectional area in reciprocal space, so that the relation to the real space is B^2). Oscillations in the magnetoresistivity periodic in B are realized in some mesoscopic systems and always related to finite size effects. Examples are (i) the Aharanov-Bohm (AB) effect,[1,2,19] (ii) the Sondheimer effect,[1,20] and (iii) the edge states in quantum dot.[21] Each of the cases involves a geometrical confinement. The AB interference occurs when a magnetic flux threading a metallic loop changes the phase of the electrons generating oscillations in the magnetoresistance and is observed only in mesoscopic conductors, but not in bulk materials. The Sondheimer effect requires a thin metallic film with the wave function vanishing at the two surfaces. The thickness of the film has to be comparable with the mean free path. This gives rise to boundary scattering of the carriers that alters the free electron trajectories and the possibility of interference. Finally, the edge states require a quantum Hall environment with real space confinement.[21]

Since the bulk material has no real space confinement for the orbits of the carriers, the most likely explanation for the periodicity as a function of B is a Fermi surface cross section that changes with field. The t_{2g} orbitals have off-diagonal matrix elements with the orbital Zeeman effect, and hence couple directly to the magnetic field. Consequently, the magnetic field could lead to a dramatic change of the Fermi surface if it points into a certain direction. Note that the pockets involved are very small (low frequencies as a function of $1/B$) and susceptible to external influences. If there is more than one conducting portion of the Fermi surface, occupied states can be transferred from one pocket to another with relatively small changes in the external parameters. This is also consistent with the 15% of change in the frequency when T is raised from 0.4 to 1.5 K shown in Fig. 3. Indeed, the amplitude of the oscillations follows the Lifshitz-Kosevich behavior expected for SdH oscillations [see Fig. 4(e)]. It is noted that the AB effect at finite T would show the same amplitude dependence.[22] What is still perplexing is that the cross section of the observed pocket is only 0.2% of the Brillouin zone, so the position of the Fermi energy is fixed at the nonquantized level of other Fermi surface branches. In such a situation, the density of states oscillates only against $1/B$. In addition, if the origin of the oscillations periodic in B is ascribed to the Landau quantization, it is then perplexing as to why there is no SdH oscillations in the [110] direction, together with the oscillations periodic in B.

The observations of the magnetoresistance oscillations in $Ca_3Ru_2O_7$ periodic both in B and $1/B$ reflect the crucial dependence of the quantized orbits on the orientation of B. The novel phenomena highlight the critical role of the orbital degrees of freedom embodied via the coupling of the t_{2g} orbitals to the magnetic field and certainly merit more experimental and theoretical efforts.

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