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Shubnikov–de Haas oscillations for two well-defined frequencies, corresponding, respectively, to areas of 0.8 and 1.36% of the first Brillouin zone, were observed in single crystals of $\text{Na}_{0.3}\text{CoO}_2$. The existence of Na superstructures in $\text{Na}_{0.3}\text{CoO}_2$, coupled with this observation, suggests the possibility that the periods are due to the reconstruction of the large Fermi surface around the Γ point. An alternative interpretation in terms of the long sought-after ε'_g pockets is also considered but found to be incompatible with existing specific heat data.

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A number of theoretical treatments have suggested that the nature of the superconducting pairing mechanism in hydrated Na_xCoO_2 is unconventional and that it probably corresponds to a spin-triplet state [1–4]. Nevertheless, the experimental situation remains unclear with heat capacity experiments in the superconducting state suggesting that the electronic contribution can either be described in terms of an order parameter having nodal lines [5], a hypothesis supported by muon spin resonance (μSR) experiments [6], or simply in terms of inhomogeneity in the Na content [7]. Measurements of the ^{59}Co nuclear magnetic resonance Knight shift supports either spin-triplet [8] or singlet pairing [9]. At the same time μSR experiments [10] find no indication of static moments in the superconducting state, implying that time reversal symmetry is not broken.

For conventional superconductivity, as well as for most unconventional superconductivity scenarios, the pairing mechanism and consequently the superconducting transition temperature critically depend on the electronic structure near the Fermi level. An accurate description of the Fermi surface (FS) is therefore critical for the superconductivity of the hydrated $\text{Na}_{0.3}\text{CoO}_2$ whose FS size and precise shape still is a central but unsettled issue. Local-density approximation (LDA) calculations [11] for the unhydrated NaCo_2O_4 compound indicate that two-bands, the A_{1g} and one of the ε'_g bands, cross the Fermi level creating, respectively, a large hexagonal Fermi surface around the Γ point of the Brillouin zone (BZ) and six small elliptical pockets of holes near the K point.

This Fermi surface geometry is the starting point for several of the proposed theories of unconventionally mediated superconductivity [1], where the existence of small nearly perfectly elliptical hole pockets resulting from the ε'_g band is essential. [3,4] However, angle-resolved photoemission (ARPES) on Na_xCoO_2 (for $0.3 \leq x \leq 0.72$) reveals only a single FS centered around the Γ point whose

area changes with x according to the Luttinger theorem [12,13], while the ε'_g band and the associated FS pockets were found to sink below the Fermi energy independently of the doping level or temperature [13]. This discrepancy between ARPES and LDA calculations were claimed to result either from strong electronic correlations [14–16] or Na disorder [17].

For over half a century, quantum oscillatory phenomena, such as the Shubnikov–de Haas (SdH) bulk effect, have provided detailed information about the geometry of the Fermi surface of high purity metals. Recently, we were able to observe SdH oscillations of very small frequencies even *within* the charge ordered state of $\text{Na}_{0.5}\text{CoO}_2$ [18]. The area of these orbits $\approx 0.25\%$ of the hexagonal first Brillouin zone (FBZ), are nearly 1 order of magnitude smaller than what is expected for the pocket areas resulting from the ε'_g band; see Fig. 1(a). Here we give an interpretation of these pockets as being due to magnetic ordering and possibly Na ordering as well. In Fig. 1(b) we draw the BZ of the 2×2 antiferromagnetic structure [19], a hexagon with half the linear dimension of the FBZ. The intersection of the FS with the reduced BZ produces small pockets. Note that the structure factor is such that there is no Bragg scattering connecting the top and bottom zone boundaries and no gaps are produced there [20], consistent with the orthorhombic symmetry of the magnetic structure. We propose that the small pockets shown in Fig. 1(b) account for the observed SdH oscillations. If the FS were perfectly hexagonal and the gap small, the area of these pockets is $\frac{1}{36}$ of that of the reduced BZ. Rounding of the FS and a finite gap can easily reduce this area to the 1% seen experimentally [18]. The remainder of the FS forms a bow-tie shaped FS shown at the bottom of Fig. 1(b). Now consider the superstructure due to Na ordering [21]. It produces an orthorhombic BZ with the same height as shown in Fig. 1(b) and the same area. However, the Na

FIG. 1 (color). (a) The Fermi surface of $\text{Na}_{0.3}\text{CoO}_2$ within the first Brillouin zone as calculated by the local density approximation. The Shubnikov–de Haas frequencies associated with the respective FS cross-sectional areas are indicated. The dotted rectangle depicts the reconstructed Brillouin zone due to the Na ordering observed in $\text{Na}_{0.3}\text{CoO}_2$. (b) Assuming the absence of the small ϵ'_g pockets, the magnetic structure reported for $x = 0.5$ redefines the Brillouin zone and leads to a reconstructed Fermi surface. (c) The Na ordering would also reconstruct the FS of $\text{Na}_{0.3}\text{CoO}_2$.

atoms are located symmetrically on either side of the cobalt layers, so that the potential seen by the cobalt atoms has half the real space periodicity and the corresponding BZ is twice the area of that shown in Fig. 1(b). The result is that the vertical zone boundaries do not intersect the FS [20]. However, the horizontal zone boundaries do and the Na superstructure will break up the bow-tie FS into two electronlike pockets and one holelike pocket. These may correspond to the weaker signals mention in Ref. [18]. At low temperatures the electrons in these pockets may be localized by Na disorder, but there may be small regions in the sample where the Na ions are particularly well ordered and localization is avoided. We propose that one or more of the pockets formed by magnetic and Na ordering in these regions explains the small amplitude SdH effect seen in these otherwise insulating samples.

Interestingly, as shown in Fig. 1(c) the incommensurate Na superstructure reported for $\text{Na}_{0.3}\text{CoO}_2$ [21] would also lead to a reconstructed FS. Here, we report a high magnetic-field electrical transport study in $\text{Na}_{0.3}\text{CoO}_2$ single crystals at low temperatures.

Single crystals of $\text{Na}_{0.75}\text{CoO}_2$ were grown using the floating-zone technique. By using an electrochemical de-intercalation procedure, samples were produced with a nominal Na concentration $x = 0.3 \pm 0.03$, as confirmed by electron microprobe analysis. Details of the crystal growth process are discussed in detail in Ref. [22]. Resistivity measurements were performed in 12 single

crystals using standard four-terminal technique in a rotating sample holder inserted in a ^3He cryostat. Shubnikov–de Haas oscillations were observed in only three crystals which showed basically the same two SdH frequencies. High magnetic fields up to $H = 45 \text{ T}$ were provided by the hybrid magnet at the NHMFL.

Figure 2(a) shows the interplane resistivity ρ_{zz} of a $\text{Na}_{0.5}\text{CoO}_2$ single crystal, studied in Ref. [18], and of a $\text{Na}_{0.3}\text{CoO}_2$ crystal studied here and as a function of temperature T . Figure 2(b) shows the interplane resistivity ρ_{zz} of a $\text{Na}_{0.3}\text{CoO}_2$ single crystal as a function of the external field H at a temperature $T \approx 0.5 \text{ K}$ and for several angles θ between H and the interplane c axis. Notice the appearance of small oscillations in the resistivity, i.e., Shubnikov–de Haas oscillations, that disappear very quickly as θ increases. Figure 3(a) displays the SdH signal defined as $(\sigma_{zz} - \sigma_b)/\sigma_b$, where $\sigma_{zz} = 1/\rho_{zz}$ and $\sigma_b = 1/\rho_b$ with ρ_b being the background resistivity (from a polynomial fit) as a function of H^{-1} for two temperatures $T = 0.5$ and 1.5 K , respectively. The maximum amplitude of the oscillatory signal corresponds to only $\sim 0.3\%$ of ρ_{zz} . The fast Fourier transform (FFT) spectrum of this SdH signal is presented in Fig. 3(b). Two pronounced peaks are observed at $F_\alpha = 475 \pm 50 \text{ T}$ and $F_\beta = 800 \pm 50 \text{ T}$ which according to the Onsager relation $F = A(\hbar/2\pi e)$, where A is the FS cross-sectional area perpendicular to H , correspond, respectively, to 0.8 and 1.35% of the area of the undistorted hexagonal FBZ. Unfortunately the very limited angular

FIG. 2. (a) The interplane resistivity ρ_{zz} as a function of temperature T for a $\text{Na}_{0.3}\text{CoO}_2$ and a $\text{Na}_{0.5}\text{CoO}_2$ single crystal used in our studies. (b) The interplane resistivity ρ_{zz} for a $\text{Na}_{0.3}\text{CoO}_2$ single crystal as a function of magnetic field H at $T \approx 0.5 \text{ K}$ and for a few angles θ between H and the interplane c axis. Notice the presence of Shubnikov–de Haas oscillations of very small amplitude which quickly disappear as θ increases.

FIG. 3. (a) The Shubnikov-de Haas signal $(\sigma_{zz} - \sigma_b)/\sigma_b$, where $\sigma_{zz} = 1/\rho_{zz}$ and σ_b is the inverse of the background resistivity, as a function of inverse field H^{-1} and for several temperatures. (b) The FFT spectrum of the SdH signal shown in the upper panel for $T = 0.45$ K. Two pronounced peaks at $F_\alpha \approx 475$ and $F_\beta \approx 812$ T are clearly seen. Additional smaller peaks close to values of harmonics of F_α and F_β are also observed.

range where the oscillations were observed did not allow us to clearly define the dimensionality of these orbits although one would expect them to follow a $1/\cos(\theta)$ dependence associated with two-dimensional Fermi surfaces. We also observe a series of other much smaller peaks. Given their quite small amplitudes however, and the fact that their frequencies are close to harmonic values of F_α and F_β , we only consider here the peaks associated with F_α and F_β .

Figure 4(a) displays the temperature dependence of both FFT amplitudes normalized with respect to T . Gray lines correspond to fits to the Lifshitz-Kosevich (LK) formula $x/\sinh x$ with $x = 14.69\mu T/H$ where μ corresponds to the effective mass in relative units of the free electron mass. We obtain $\mu_\alpha = 5 \pm 1$ and $\mu_\beta = 6 \pm 1$ for F_α and F_β , respectively. These values for the effective masses are considerably larger than what was obtained for $x = 0.5$ [18]. Notice that if one considers the error bars both masses have basically the same value, suggesting that they originate from the same Fermi surface sheet. Finally, in Fig. 4(b) we include the SdH signal for $T = 0.45$ K and a fit of this signal to two LK oscillatory components, from which we can extract the so-called Dingle temperature $T_D = \hbar/2\pi k_B \tau$, where τ^{-1} is the quasiparticle scattering rate. The SdH signal is clearly well reproduced by just two components. It yields values between 2 and 3 K for T_D , lower than those obtained for $x = 0.5$ [18].

In order to explore the possible existence of Na superstructure(s) for $x = 0.3$, electron diffraction measurements (EDMs) were performed in the single crystal whose data is

FIG. 4. (a) The amplitude of the FFT spectrum for both frequencies F_α and F_β normalized with respect to the temperature T . Gray lines are fits to the Lifshitz-Kosevich expression $x/\sinh x$. (b) A fit of the SdH signal to two Lifshitz-Kosevich oscillatory components (gray line). From the fit we extracted the Dingle temperatures $T_D^{\alpha,\beta}$.

shown in Figs. 3 and 4, (equipment and procedure described in Ref. [21]). The measurements reveal the existence of several Na superstructures having periods of 0.25[110], 0.33[110], and 0.5[110] with an occurrence ratio of 30, 10, and 20%, respectively, with 40% of the sample showing no Na pattern. This clearly indicates that Na is inhomogeneously distributed and thus the quantum oscillatory phenomena might emerge from regions of the sample where Na is particularly well ordered. Although EDM studies in all 3 single crystals could not reveal a common superstructure among them, we cannot discard this hypothesis without further work.

We now discuss a second possible interpretation of our data. We note that cross-sectional areas we observed are quite close to those predicted by the LDA calculations for the cylindrical Fermi surfaces having elliptical cross-sections resulting from the ε'_g band for $\text{Na}_{0.5}\text{CoO}_2$, i.e., 0.6 and 1.4% of the hexagonal FBZ, respectively [11]. We have not been able to detect the much higher frequency associated with the A_{1g} band-derived FS observed by ARPES [12,13]. According to LDA, one expects *two* frequencies as a result of the corrugation of the cylindrical Fermi surfaces from ε'_g band due to a finite interplane coupling. This leads to a maximal cross-sectional area within the Γ -K plane and to a minimal one in the A-H plane of the FBZ [11]. We should also point out that according to LDA the pocket area increases with decreasing x . For example, for $\text{Na}_{0.3}\text{CoO}_2$ the pocket shown in Ref. [16] is a factor of 2 larger in area than what we quoted earlier for $\text{Na}_{0.5}\text{CoO}_2$. This discrepancy may well be within the accuracy of LDA, especially given the possibility of

strong correlation corrections [14–16]. Indeed, Zhou *et al.* [14] argued that strong correlation pushes the ε'_g band below the Fermi energy. However, this effect weakens for smaller x , and may conceivably leave a small pocket by the time one reaches $x = 0.3$.

One difficulty with this interpretation lies in the disagreement with ARPES data, which clearly show that the top of the ε'_g band lies at 0.2 eV below the Fermi energy at $x = 0.3$ [13]. While the reconstruction of the large Fermi surface by Na superstructure may be beyond the resolution of ARPES, the sinking of the ε'_g band is not. A possible way out is to argue that the delicate placement of the ε'_g band may be surface sensitive and ARPES is probing only the top few layers. However, a more serious difficulty arises when we try to reconcile this interpretation with specific heat data. In two dimensions the linear coefficient γ of the specific heat depends only on the mass and not on the area of the pocket, with each pocket contributing $\gamma_1 = 3.4$ mJ/Co-mole-K² for $m/m_e \approx 5$. For six pockets, this gives $\gamma \approx 20$ mJ/Co-mole-K². While this estimate is only a factor of 2 larger than the observed γ of 12 mJ/Co-mole-K² [23,24], the discrepancy becomes much worse when we include the contribution of the large A_{1g} pocket. ARPES measurements found that the Fermi velocity is reduced from the LDA value by about a factor of 3 and from the data on Na_{0.3}CoO₂ we extract $\hbar v_F \approx 0.5$ eV-Å [25]. Hence the A_{1g} pocket alone should contribute about 10 mJ/Co-mole-K², sufficient to account for most, if not all, of the measured γ . This puts a severe upper limit on the mass of the ε'_g pockets, if they exist. Even allowing for a factor of 2 uncertainty in our measured mass, our data cannot be reconciled with existing ARPES and specific heat data if interpreted as bulk properties due to the ε'_g pockets. Given these difficulties, we favor the first interpretation that the SdH oscillations are due to reconstruction of the A_{1g} Fermi surface in part of the sample due to a Na superlattice. The observation of *reproducible* quantum oscillations in three crystals is a clear indication of their high degree of quality and ordering, or long mean free path, and indicates that the observed frequencies are intrinsic to $x = 0.3$. We speculate that the SdH signal comes from patches where Na is particularly well ordered. While our effort to correlate the SdH signal with Na ordering was inconclusive, we note that earlier EDM work on samples grown by a different method [21] also found sample to sample and patch to patch variation in Na ordering. This kind of variation is likely intrinsic and beyond our control at this point.

In summary, we have presented an electrical transport study on Na_{0.3}CoO₂ revealing the existence of small Fermi surfaces, which can be ascribed to a reconstruction of the Brillouin zone by Na superstructure. The observations of SdH in Na_{0.3}CoO₂ and Na_{0.5}CoO₂ are important steps toward a description of the superconducting state in Na_{0.3}CoO₂ · 1.4H₂O and the charge ordered state seen in Na_{0.5}CoO₂.

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