Shubnikov de Haas effect in the metallic state of Na$_{0.3}$CoO$_2$

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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 (FBZ), were observed in single crystals of Na$_{0.3}$CoO$_2$. The existence of Na superstructures in Na$_{0.3}$CoO$_2$, coupled with this observation, suggests the possibility that the periods are due to the reconstruction of the large Fermi surface around the $\Gamma$ point. An alternative interpretation in terms of the long sought-after $\varepsilon'_g$ 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$_2$CoO$_2$ is unconventional and that it probably corresponds to a spin-triplet state. 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, a hypothesis supported by muon spin resonance ($\mu$SR) experiments, or simply in terms of inhomogeneity in the Na content. Measurements of the $^{59}$Co nuclear magnetic resonance Knight shift support either spin-triplet or singlet pairing. At the same time $\mu$SR experiments 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 depends 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 Na$_{0.3}$CoO$_2$ whose FS size and precise shape still is a central but unsettled issue. Local-density approximation (LDA) calculations for the unhydrated Na$_2$CoO$_2$ compound indicate that two bands, the $A_{1g}$ and one of the $\varepsilon'_g$ bands, cross the Fermi level creating respectively, a large hexagonal Fermi surface around the $\Gamma$ 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 superconducting theories [1, 12], where the existence of small nearly perfectly elliptical hole pockets resulting from the $\varepsilon'_g$ band is essential. However, angle-resolved photoemission (ARPES) on Na$_x$CoO$_2$ (for $0.3 \leq x \leq 0.72$) reveals only a single FS centered around the $\Gamma$ point whose area changes with $x$ according to the Luttinger theorem [12, 13], while the $\varepsilon'_g$ 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, 15, 16] or Na disorder [17].

For over half a century, quantum oscillatory (QO) 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 (CO) state of Na$_{0.3}$CoO$_2$ [18]. The area of these orbits $\lesssim 0.25\%$ of the hexagonal FBZ, are nearly one order of magnitude smaller than what is expected for the pocket areas resulting from the $\varepsilon'_g$ band, see Fig. 1 (a). In Fig. 1 (b) we follow Bobroff et al. [14] and plot the orthorhombic Brillouin zone resulting from the Na superstructure reported for $x = 0.5$ [20], superimposed to the $A_{1g}$ FS assuming the absence of the $\varepsilon'_g$ pockets as suggested by ARPES. Notice how the new BZ intersects the FS and leads to a series of smaller pockets.

The largest of these are the oblong-shaped pockets which are well nested by the wave vector $\mathbf{Q}$ show in Fig. 1(b). Bobroff et al. proposed a spin density wave instability associated with this nesting as the explanation of the magnetic ordering at 86 K. However, this ordering vector is inconsistent with that observed by neutron scattering [21]. Furthermore, the resistivity is largely insensitive to the magnetic transition at 86 K [21]. These observations, together with the local moment nature of the magnetic order, suggest to us that the explanation of the 86 K transition lies in strong correlation physics which produces a local moment in a metallic state with
FIG. 1: (a) The Fermi surface of Na$_{0.3}$CoO$_2$ within the first Brillouin zone as calculated by the Local Density Approximation. The corresponding Shubnikov de Haas frequencies associated with the FS cross-sectional areas are indicated. The gray rectangle depicts the reconstructed Brillouin zone due to the Na superstructure observed in Na$_{0.3}$CoO$_2$. (b) The Na ordering observed in Na$_{0.3}$CoO$_2$ (blue and red lines). Possible nesting vectors leading to a density-wave like instability are easily identifiable. (c) The Na ordering observed in Na$_{0.3}$CoO$_2$ would also lead to a similarly reconstructed FS.

only a small degree of charge disproportionation, as seen in NMR. Instead, we propose that a charge or spin density wave with wavelength $Q$ is responsible for the increase in resistivity at 51 K. A similar suggestion was made by Qian et al. Note that the resistivity rises sharply only below 20 K. We interpret this rise to be due to charge localization in the remaining two small pockets. We further suggest that there may be small regions in the sample where the Na ions are particularly well ordered and localization can be avoided. The quantum oscillation of one or both of these pockets may explain the SdH effect of small amplitude that we observed in an otherwise insulating sample. We believe that this scenario could explain the origin of the insulating state and the very small SdH frequencies seen by us. Interestingly, as shown in Fig. 1(c) the incommensurate Na superstructure reported for Na$_{0.3}$CoO$_2$ would also lead to a similarly reconstructed FS although in the absence of hydration no electronic ordering has been reported so far.

In order to explore this possibility, here we report a high magnetic-field electrical transport study in Na$_{0.3}$CoO$_2$ single crystals at low temperatures.

FIG. 2: (a) The inter-plane resistivity $\rho_{zz}$ for a Na$_{0.3}$CoO$_2$ single crystal as a function of magnetic field $B$ at $T \simeq 0.5$ K and for a few angles $\theta$ between $B$ and the inter-plane c-axis. Notice the presence of Shubnikov de Haas oscillations of very small amplitude which quickly disappears as $\theta$ increases. (b) Normalized inter-plane resistivity, $(\rho_{zz} - \rho_0)/\rho_0$, where $\rho_0 = \rho(\theta = 0)$ as a function of $\theta$ at $H = 45$ T and $T \simeq 0.5$ K.

Single crystals of Na$_{0.75}$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 $^3$He cryostat. Shubnikov-de-Haas oscillations were observed in only 3 crystals which showed basically the same two SdH frequencies. High magnetic fields up to $H = 45$ T were provided by the hybrid magnet at the NHMFL.

Figure 2 shows the inter-plane resistivity $\rho_{zz}$ of a Na$_{0.3}$CoO$_2$ single crystal as a function of the external field $H$ at a temperature $T \simeq 0.5$ K and for several angles $\theta$ between $H$ and the inter-plane c-axis. Notice the appearance of small oscillations in the resistivity, i.e., Shubnikov-de-Haas oscillations, that disappear very quickly as $\theta$ increases. Fig. 3 (a) displays the SdH signal defined as $(\sigma - \sigma_b)/\sigma_b$, where $\sigma = 1/\rho_{zz}$ and $\sigma_b = 1/\rho_b$ with $\rho_b$ being the background resistivity as 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 $\rho_{zz}$. The FFT spectrum of this SdH signal is presented in Fig. 3 (b). Two pronounced peaks are observed at $F_a = 475 \pm 50$ T and $F_\beta = 800 \pm 50$ T which according to the Onsager relation $F = A(h/2\pi e)$, where $A$ is the FS cross-sectional area perpendicular to $H$, correspond respectively to 0.8 and
Gray lines correspond to fits to the Lifshitz-Kosevich expression as a function of inverse field $H^{-1}$ and for several temperatures. (b) The FFT spectrum of the Shubnikov-de Haas signal shown in the upper panel for $T = 0.45$ K. Two pronounced peaks at $F_\alpha \simeq 475$ and $F_\beta \simeq 812$ T are clearly seen. Additional smaller peaks close to values of harmonics of $F_\alpha$ and $F_\beta$ are also observed.

1.35% of the area of the undistorted hexagonal FBZ. Unfortunately the very limited angular range where the oscillations were observed did not allow us to clearly define the dimensionality of these orbits though 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 $F_\alpha$ and $F_\beta$, we only consider here the peaks associated with $F_\alpha$ and $F_\beta$.

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 $x = 14.69\mu T/B$ where $\mu$ 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 $F_\alpha$ and $F_\beta$, respectively. These values for the effective masses are considerably larger than what was obtained for $x = 0.5$ $\text{K}$. 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. 3(c) we include the Shubnikov-de Haas signal for $T = 0.45$ K and a fit of this signal to two Lifshitz-Kosevich oscillatory components, from which we can extract the so-called Dingle temperature $T_D = \hbar/2\pi k_B \tau$, where $\tau^{-1}$ is the quasiparticle scattering rate. The Shubnikov-de Haas signal is clearly well reproduced by just two components, justifying our previous decision of neglecting the other peaks seen in the FFT spectrum. It yields values between 2 and 3 K for $T_D$, lower than those obtained for $x = 0.5$ $\text{K}$.

As shown in Fig. 1 (c), the observation of two frequencies $F_\alpha$ and $F_\beta$ normalized with respect to the temperature $T$. Gray lines are fits to the Lifshitz-Kosevich expression $x/\sinh x$. (b) A fit of the Shubnikov-de Haas signal to two Lifshitz-Kosevich oscillatory components (gray line). From the fit we extracted the Dingle temperatures $T_D^{\alpha,\beta}$.

As shown in Fig. 1 (c), the observation of two frequencies suggests the possible existence of Na superstructure(s) that redefines the Brillouin zone and thus the geometry of the Fermi surface for $x = 0.3$. In order to explore this hypothesis electron diffraction measurements (EDM) were performed in this single crystal, (equipment and procedure described in Ref. 20). 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 $\epsilon'_q$ band for Na$_{0.3}$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 \( \varepsilon'_{g} \) band due to a finite inter-plane coupling. This leads to a maximal cross-sectional area within the \( \Gamma-K \) plane and to a minimal one in the A-H plane of the FBZ [11]. In fact, neutron scattering experiments [24] have pointed to the relevant role of the inter-plane exchange interaction in stabilizing the three-dimensional magnetic structures seen in \( \text{Na}_2\text{CoO}_2 \). This has been explained in terms of superexchange interactions via, for example, O-O hopping which would couple each Co to its nearest inter-planar neighbors [22]. However, we should point out that according to LDA the pocket area increases with decreasing \( x \). For example, for \( \text{Na}_0.9\text{CoO}_2 \) 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, 15, 16]. Indeed, Zhou et al. [14] argued that strong correlation pushes the \( \varepsilon'_{g} \) 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 \( \varepsilon'_{g} \) band lies at 0.2 eV below the Fermi energy at \( x = 0.3 \) [12]. While the reconstruction of the large Fermi surface by Na superstructure may be beyond the resolution of ARPES, the sinking of the \( \varepsilon'_{g} \) band is not. A possible way out is to argue that the delicate placement of the \( \varepsilon'_{g} \) 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 \( \gamma \) of the specific heat depends only on the mass and not the area of the pocket, with each pocket contributing \( \gamma = 3.4 \text{ mJ/Co-mole-K}^2 \) for \( m/m_e \geq 5 \). For 6 pockets, this gives \( \gamma \approx 20 \text{ mJ/Co-mole-K}^2 \). Whilst this estimate is only a factor of 2 larger than the observed \( \gamma \) of 12 mJ/Co-mole-K\(^2\) [26, 27], the discrepancy becomes much worse when we include the contribution of the small \( A_{1g} \) 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 \( \text{Na}_{0.3}\text{CoO}_2 \) we extract \( hv_F \approx 0.5 \text{ eV-A} \) [22]. Hence the \( A_{1g} \) pocket alone should contribute about 10 mJ/Co-mole-K\(^2\), sufficient to account for most, if not all of the measured \( \gamma \). This puts a severe upper limit on the mass of the \( \varepsilon'_{g} \) pockets, if they exist. Even allowing for a factor of two 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 \( \varepsilon'_{g} \) pockets. Given these difficulties, we favor the first interpretation that the SdH oscillations are due to reconstruction of the \( A_{1g} \) Fermi surface in a small part of the sample with a particular Na superlattice.

In summary, we have presented a detailed electrical transport study on \( \text{Na}_{0.3}\text{CoO}_2 \) revealing the existence of small Fermi surfaces, which can be ascribed to a reconstruction of the Brillouin zone by a particular Na superstructure. The observations of SdH in \( \text{Na}_{0.5}\text{CuO}_2 \) and \( \text{Na}_{0.5}\text{CoO}_2 \) are important steps towards a description of the superconducting state in \( \text{Na}_{0.3}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O} \) and the charge ordered state seen in \( \text{Na}_{0.5}\text{CoO}_2 \).

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