Quantum Critical Behavior and Possible Triplet Superconductivity in Electron Doped CoO$_2$ Sheets

D.J. Singh
Center for Computational Materials Science, Naval Research Laboratory, Washington, DC 20375
(March 22, 2002)

Density functional calculations are used to investigate the doping dependence of the electronic structure and magnetic properties in hexagonal Na$_x$CoO$_2$. The electronic structure is found to be highly two dimensional, even without accounting for the structural changes associated with hydration. At the local spin density approximation level, a weak itinerant ferromagnetic state is predicted for all doping levels in the range $x = 0.3$ to $x = 0.7$, with competing but weaker itinerant antiferromagnetic solutions. The Fermi surface, as expected, consists of simple rounded hexagonal cylinders, with additional small pockets depending on the $c$ lattice parameter. Comparison with experiment implies substantial magnetic quantum fluctuations. Based on the Fermi surface size and the ferromagnetic tendency of this material, it is speculated that a triplet superconducting state analogous to that in Sr$_2$RuO$_4$ may exist here.

The last few years have seen the discovery of a number of novel unconventional superconductors associated with magnetic phases. Focusing on triplet (or likely triplet) superconductors these include UGe$_2$ ($T_c \sim 1$ K),$^1$ URhGe ($T_c \sim 0.25$ K),$^2$ and ZrZn$_2$ ($T_c \sim 0.3$ K),$^3,4$ where ferromagnetism coexists with superconductivity, and Sr$_2$RuO$_4$ ($T_c \sim 1.5$ K),$^5,6$ which has a paramagnetic Fermi liquid normal state, but is “near” magnetic phases. Although the exact pairing mechanism has not been established in these materials, it is presumed that spin fluctuations are involved, most probably the quantum critical fluctuations in the materials with co-existing ferromagnetism and superconductivity.$^8-$14 In Sr$_2$RuO$_4$, strong nesting related antiferromagnetic spin fluctuations are found in local density approximation (LDA) calculations and experiment.$^{15,16}$ In addition ferromagnetic fluctuations may also be present, and if so these would favor a triplet superconducting state.$^{17}$

Recently, Takada and co-workers reported the discovery of superconductivity with $T_c \sim 5$ K, in the CoO$_2$ layer material, Na$_x$CoO$_2 \cdot y$H$_2$O.$^{18}$ Based on the two dimensional 3d transition metal oxide structural motif, they speculate that the superconductivity may be related to that of the cuprate high-$T_c$ superconductors. Here an alternate possibility is discussed, that is the connection with the triplet superconductors mentioned above. The parent compound of Na$_x$CoO$_2 \cdot y$H$_2$O is Na$_{0.5}$CoO$_2$, which was synthesized and studied in single crystal form by Terasaki and co-workers.$^{19,20}$ The compound consists of CoO$_2$ layers (Co is in at the center of distorted O octahedra formed by layers of O above and below the Co planes) separated by layers of Na ions.$^{21}$ The result is a highly anisotropic metal with a large thermopower at room temperature and a substantial renormalization of the Fermi liquid properties at low temperature.$^{19,20,22}$ Modifications of this compound consisting of substitutions for the Na layer have been made to obtain technologically useful thermoelectric materials,$^{23} - 26$ and, in fact, Na$_{0.5}$CoO$_2$ itself is a good thermoelectric at high temperature.$^{27}$ Significantly, the Seebeck coefficient of Na$_{0.5}$CoO$_2$ as calculated from the LDA band structure using standard kinetic transport theory is in quantitative agreement with experiment, indicating that the Fermi liquid description at higher temperature is robust.$^{28}$ Band structure calculations for the higher performance so-called misfit compounds formed by replacement of the Na layer also reasonably account for room temperature experimental data.$^{29}$

Turning to the low temperature properties, as mentioned, there are substantial renormalizations in Na$_{0.5}$CoO$_2$, for example in specific heat and susceptibility. LDA calculations indicate a ferromagnetic ground state for this parent compound, while experimentally ferromagnetism is not observed, one possible explanation being that quantum fluctuations suppress the ordered ferromagnetic state.$^{28}$ Interestingly, the related misfit compound, Ca$_3$Co$_4$O$_9$ shows a large negative magnetoresistance at low temperature reaching 35% at 7 T, which could be interpreted as a sign of proximity to a ferromagnetic quantum critical point. Other evidence for a proximity to magnetism is the formation of a spin density wave when Cu doped,$^{30}$ and the production of a weak magnetic ground state with strong magnetoresistance upon increasing the Na concentration to $x = 0.75$.$^{30}$

The reported crystal structure of superconducting Na$_x$CoO$_2 \cdot y$H$_2$O differs from that of the parent compound by a reduction in the Na content to $x \sim 0.35$ and the intercalation of water molecules around the Na sites. The structure of the CoO$_2$ sheets is very similar to that of the parent compound Na$_{0.5}$CoO$_2$ – the in-plane $a$ lattice parameter is slightly lower (2.823 Å vs. 2.84 Å) as is the height of the O (0.885 Å vs. an LDA value of 0.908 Å in the parent). It should be noted that a slight contraction of the CoO$_6$ octahedra, as implied by these structural differences, is consistent with the lower Na content, in particular a lower electron count on the CoO$_2$ sheets would be expected to lead to a small contraction.

Here, well converged LDA calculations are reported for Na$_x$CoO$_2$ for $x=0.3,0.5,0.7$. In addition, calculations
are reported for a strained lattice corresponding to the structure reported for superconducting Na$_x$CoO$_2$·yH$_2$O, but neglecting the intercalating water. The calculations were done using the general potential linearized augmented planewave method with local orbitals $^{31,32}$ as described in Ref. 28, except that better Brillouin zone samples, corresponding to a minimum special k-points mesh of $16 \times 16 \times 2$ in the hexagonal zone is used here to obtain convergence of the magnetic energies. As discussed in Ref. 28, a virtual crystal method is used to account for the partially occupied Na site.

Although there is some hybridization, the valence band structure of Na$_{0.35}$CoO$_2$ consists of three manifolds of bands separated by gaps – a lower lying occupied O 2$p$ derived manifold, followed by Co $t_{2g}$ and $e_g$ manifolds. $^{28}$ As expected from ionic considerations the Fermi energy, $E_F$ lies near the top of the $t_{2g}$ manifold, which contains 0.5 holes per Co ion. Because of the actual axial site symmetry, the $t_{2g}$ manifold can be regarded as consisting of two-fold (also labeled $e_g$) and one-fold (labeled $a_g$) crystal field states. These overlap, but the top of the $t_{2g}$ manifold is primarily of $a_g$ character in Na$_{0.5}$CoO$_2$, with the result that the band structure near $E_F$ can be roughly viewed as consisting of one band per Co ion with an filling of $3/4$ (1/2 hole per Co). The present LDA calculations for the electronic structure of Na$_{0.35}$CoO$_2$ and Na$_{0.3}$CoO$_2$ follow this picture. These were done holding the crystal structure fixed at that of Na$_{0.5}$CoO$_2$ and varying the Na occupancy in the virtual crystal. The dominant $a_g$ character at the top of the $t_{2g}$ manifold is, however, lost for the strained lattice, discussed below.

The magnetic properties are similar for the various Na contents in the range $x = 0.3$ to $x = 0.7$. Results of fixed spin moment constrained LDA calculations are shown in Fig. 1. In particular, itinerant ferromagnetism is found. In each case, the energy decreases with magnetization until a magnetization at which the band edge is reached in the majority spin. Then the energy increases rapidly reflecting the crystal field induced gap between the $t_{2g}$ and $e_g$ manifolds.

Thus, independent of $x$ in this range, the LDA predicts a ferromagnetic ground state, with a spin moment per Co equal to the number of holes $(p = 1 - x)$ and a half metallic band structure (here we refer to the hole concentration as the concentration of holes in the $t_{2g}$ manifold; without any Na $p = 1$; Na electron dopes the sheets, which leads to a reduction in $p$). The fixed spin moment curves show a shape crossing over from parabolic at low moment to more linear as the band edge is approached. As may be seen, the shapes and initial curvatures for the different doping levels are roughly similar. The trend towards slightly weaker initial curvatures at higher Na concentration is possibly an artifact due to the fixed crystal structure used in the present calculations. It reflects increasing hybridization (increasing band width and decreasing density of states) as charge is added to the CoO$_2$ planes. In reality, the lattice would be expected to expand, perhaps compensating this trend. In any case, for this range of $x$, ferromagnetism with a magnetic energy of approximately, $E(FM) \approx 50p$ in meV/Co and spin moment $M(FM) = p$ in $\mu_B$/Co is found. As mentioned, calculations were also done for a strained cell with the structure of the superconducting sample, but without H$_2$O. These calculations were done for $x = 0.5$ and $x = 0.35$, the latter corresponding to the experimentally determined doping level. In both cases, the LDA predicted a ferromagnetic state. The magnetic energies were $E(FM) = 20$ and 27 meV/Co for $x = 0.5$ and $x = 0.35$, respectively. Thus the behavior is similar, but the magnetic energies are somewhat larger.

LDA calculations were also done for an antiferromagnetic configuration with the unit cell doubled along one of the in-plane lattice vectors. Thus, within a Co plane, each Co ion has four opposite spin nearest neighbors and two like spin nearest neighbors. At all three doping levels investigated an antiferromagnetic instability was found, but this instability is weaker than the ferromagnetic one. Details of the LDA moments and energies are given in Table I. Essentially, the energy of the antiferromagnetic configuration examined tracks the ferromagnetic energy at a value $\sim 1/4$ as large.

The LDA generally provides a good description of itinerant ferromagnetic materials. It is known to fail for strongly correlated oxides where on-site Coulomb (Hubbard) repulsions play an important role in the physics. In such cases, the LDA underestimates the tendency of the material towards local moment formation and magnetism. Here, the LDA is found to predict ferromagnetic ground states for materials that are paramagnetic metals in experiment. While materials in which the LDA substantially overestimates the tendency towards magnetism are rare, a number of such cases have been recently found. These are generically materials that are close to quantum critical points, and include Sc$_2$In, $^{33}$ ZrZn$_2$, $^5$ and Sr$_3$Ru$_2$O$_7$ (Ref. 34). Sr$_3$Ru$_2$O$_7$ displays a novel metamagnetic quantum critical point, $^{35}$ while, as mentioned, ZrZn$_2$ shows coexistence of ferromagnetism and superconductivity.

Density functional theory is in principle an exact ground state theory. It should, therefore, correctly describe the spin density of magnetic systems. However, common approximations to the exact density functional theory, such as the LDA, neglect Hubbard correlations beyond the mean field level, yielding the underestimated magnetic tendency of strongly Hubbard correlated systems. Overestimates of magnetic tendencies, especially in the LDA are very much less common. Another type of correlations that is missed in these approximations are quantum spin fluctuations. This is because the LDA is parameterized based on electron gases with densities typical for atoms and solids. However, the uniform electron gas is very far from magnetism in this density range. In solids near quantum critical points, the result is an overestimate of the magnetic moments and tendency toward magnetism (i.e. misplacement of the position of the critical point) due to neglect of the quantum critical
fluctuations.36,37

The present results for Na$_x$CoO$_2$ show a weak ferromagnetic instability that is robust with respect to doping and structure (note the instability for the strained lattice). Based on this, and the experimentally observed renormalized paramagnetic state, it seems likely that Na$_x$CoO$_2$ is subject to strong ferromagnetic quantum fluctuations of this type, and that these are the reason for the disagreement between the LDA and experimental ground states.

The effects of such quantum fluctuations can be described on a phenomenological level using a Ginzburg-Landau theory in which the magnetic properties defined by the LDA fixed spin moment curve are renormalized by averaging with an assumed (usually Gaussian) function describing the beyond LDA critical fluctuations.38 Although a quantitative theory allowing extraction of this function from first principles calculation has yet to be established, one can make an estimate based on the LDA fixed spin moment curves as compared with experiment. In particular, Na$_x$CoO$_2$ shows a disagreement between the LDA moment and experiment equal to $1 - x$, and has a very steeply rising LDA energy for moments larger than $p$. Thus one may estimate an r.m.s. amplitude of the quantum fluctuations of $\xi \approx \alpha p$ in $\mu_B$, with $1/2 < \alpha < 1$, and most likely closer to 1. These are large values c.f. ZrZn$_2$. It is therefore tempting to associate the superconductivity of Na$_x$CoO$_2$·$y$H$_2$O with ferromagnetic quantum critical fluctuations. Considering the simple 2D Fermi surface, which consists of rounded hexagonal cylinders plus small sections,38 and the ferromagnetic fluctuations a triplet state like that originally discussed for Sr$_2$RuO$_4$ (Ref. 7) seems plausible. I now speculate about the ingredients in a spin fluctuation mediated triplet superconducting state.

Within a spin fluctuation induced pairing approach analogous to that employed for Sr$_2$RuO$_4$ the key ingredient is the integral over the Fermi surface of the $k$-dependent susceptibility with a function of the assumed triplet symmetry,3,6-9,17 i.e., in the simplest case, $\langle k | k' \rangle / k' k$. For a Fermi surface in the shape of a circular cylinder, radius $k_F$, the needed integral is proportional to $\int_0^{2\pi} d\theta \cos(\theta) V(2k_F \sin(\theta/2))$, where $V(k)$ is the assumed pairing interaction. In any case, for a smooth variation of the spin fluctuations with $k$ and a maximum at $k=0$ (ferromagnetic), the integral is roughly proportional to $k_F$ times the variation of $V$ from $k = 0$ to $k = 2k_F$. This latter variation depends on the detailed shape of $V(k)$, but may be expected to cross over from being proportional to $k_F^2$ for small $k_F$ to proportional to $k_F$ for larger $k_F$. Neglecting small Fermi surface sections, $k_F$ varies as $p^{1/2}$. One possibility for $V(k)$ is a function smoothly going from a finite value at $k = 0$ to near zero at the zone boundary (reflecting the rather weak antiferromagnetic instability relative to the ferromagnetic), with a size at $k = 0$ given by the LDA ferromagnetic energy ($\propto p^2$) or alternately a Hund’s coupling ($p$ independent) times $\xi$ ($\propto p$).

Within this $p$-wave scenario it would be quite interesting to measure the variation of the superconducting properties of Na$_x$CoO$_2$·$y$H$_2$O as a function of doping level. The above arguments imply a substantial model dependent variation up to the level where proximity to the critical point suppresses $T_c$, with the implication that still higher values of $T_c$ may be obtained. However, it should be emphasized that the mechanism and superconducting symmetry of Na$_x$CoO$_2$·$y$H$_2$O have yet to be established, and in fact, even conventional electron-phonon superconductivity competing with spin fluctuations has not been excluded.

I am grateful for helpful discussions with R. Asahi, I.I. Mazin, A.J. Millis, W.E. Pickett, S.S. Saxena and I. Terasaki. Some computations were performed using facilities of the DoD HPCMO ASC and ARL centers. The DoD-AE code was used for some of this work.

1. S.S. Saxena, P. Agarwal, K. Ahilan, F.M. Grosche, R.K.W. Haselwimmer, M.J. Steiner, E. Pugh, I.R. Walker, S.R. Julian, P. Monthoux, G.G. Lonzarich, A. Huxley, I. Sheikin, D. Braithwaite, and J. Floquet, Nature 406, 587 (2000).
2. D. Aoki, A. Huxley, E. Ressouche, D. Braithwaite, J. Floquet, J.P. Brison, E. Lhotel and C. Paulsen, Nature 413, 613 (2001).
3. C. Pfleiderer, M. Ulhrarz, S.M. Hayden, R. Vollmer, H. von Lohneysen, N.R. Bernhoeft, and G.G. Lonzarich, Nature 412, 58 (2001).
4. An alternate, Fulde-Ferrell-Larkin-Ovchenikov, non-triplet state is not excluded in ZrZn$_2$.5
5. D.J. Singh and I.I. Mazin, Phys. Rev. Lett. 88, 187004 (2002).
6. Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J.G. Bednorz, and F. Lichtenberg, Nature 372, 532 (1994).
7. T.M. Rice and H. Sigrist, J. Phys. Condens. Matter 7, L643 (1995).
8. D. Fay and J. Appel, Phys. Rev. B 22, 3173 (1980).
9. P.B. Allen and B. Mitrovic, Solid State Phys. 37, 1 (1982).
10. K. Machida, and T. Ohmi, Phys. Rev. Lett. 86, 850 (2001).
11. D. Belitz and T.R. Kirkpatrick, Phys. Rev. Lett. 89, 247202 (2002).
12. T.R. Kirkpatrick and D. Belitz, Phys. Rev. B 67, 024515 (2003).
13. R. Rousseve and A.J. Millis, Phys. Rev. B 63, 140504 (2001).
14. G. Santi, S.B. Dugdale and T. Jarlborg, Phys. Rev. Lett. 87, 247004 (2001).
15. I.I. Mazin and D.J. Singh, Phys. Rev. Lett. 82, 4324 (1999).
16. Y. Sidis, H. Braden, P. Bourges, B. Hennion, S. Nishizaki, Y. Maeno, and Y. Mori: Phys. Rev. Lett. 83, 3320 (1999)
17. I.I. Mazin and D.J. Singh, Phys. Rev. Lett. 79, 733 (1997).
18. K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi,
TABLE I. LSDA spin magnetizations and energies for Na$_x$CoO$_2$. All quantities are on a per Co basis. Energies are in meV, spin moments are in $\mu_B$, FM denotes ferromagnetic and AF denotes the partially frustrated nearest neighbor AF configuration discussed in the text. M is the total spin magnetization, m is the magnetization inside the Co LAPW sphere, radius 1.95 Bohr.

| x   | E(FM) | M(FM) | m(FM) | E(AF) | m(AF) |
|-----|-------|-------|-------|-------|-------|
| 0.3 | 25    | 0.70  | 0.56  | 9     | 0.36  |
| 0.5 | 13    | 0.50  | 0.41  | 3     | 0.21  |
| 0.7 | 4     | 0.30  | 0.25  | $\leq$1 | 0.04 |

FIG. 1. LDA fixed spin moment energy as a function of constrained spin magnetization of Na$_x$CoO$_2$ on a per Co atom basis for $x=0.7$ ($\times$), $x=0.5$ (*) and $x=0.3$ (+). The curves are spline interpolations as a guide to the eye. Note the breaks at 0.3, 0.5 and 0.7 $\mu_B$ for $x=0.7$, 0.5 and 0.3, respectively. These correspond to the band gap between crystal field split Co $d$ manifolds. The calculations were done keeping the structure fixed and varying the Na site occupation via the virtual crystal method (see text).