Neutron scattering study of novel magnetic order in Na$_{0.5}$CoO$_2$

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We report polarized and unpolarized neutron scattering measurements of the magnetic order in single crystals of Na$_{0.5}$CoO$_2$. Our data indicate that below $T_N = 88$ K the spins form a novel antiferromagnetic pattern within the CoO$_2$ planes, consisting of alternating rows of ordered and non-ordered Co ions. The domains of magnetic order are closely coupled to the domains of Na ion order, consistent with such a two-fold symmetric spin arrangement. Magnetoresistance and anisotropic susceptibility measurements further support this model for the electronic ground state.

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The layered cobaltates Na$_x$CoO$_2$ have attracted much attention due to their unusual thermoelectric properties [1, 2] and because of the recent discovery of superconductivity in the hydrated composition [3]. The Co ions in these compounds form a hexagonal lattice, and the average valence can be changed by varying the Na concentration $x$. The Co$^{4+}$ ions can formally be regarded as magnetic ions with $S = \frac{1}{2}$ on a frustrated low-dimensional lattice. It is believed that strong electronic correlations play an important role in the physics, and, as a function of the Na concentration, a rich phase diagram has been reported [4]. For $x < \frac{1}{2}$, the material is a paramagnetic metal, while for $x > \frac{1}{2}$ an unusual “Curie-Weiss metallic” phase is observed. At $x = \frac{1}{2}$, a unique state is realized: the Na ions are chemically ordered to form zig-zag chains in an orthorhombic superstructure with two-fold symmetry [5, 6], and it has been speculated that this leads to Co$_{3.5+\delta}$/Co$_{3.5-\delta}$ charge order within each CoO$_2$ layer [5, 6, 7, 8, 9, 10]. The ground state is believed to be a magnetically ordered insulator: resistivity, Hall coefficient, thermal transport [4], and angular magnetoresistance oscillation measurements [11] are all consistent with such a two-fold symmetric ground state.

In order to further investigate the electronic ground state of the half-doped CoO$_2$ plane, we have performed neutron scattering, susceptibility, and transport studies on single crystal samples. The combination of polarized and unpolarized neutron scattering data allow us to determine the ordered spin direction and arrangement. We find that the ground state is well described by an ordered array of stripes of antiferromagnetic spins interleaved with stripes of non-ordered Co ions. Our transport and anisotropic susceptibility data further support such a model.

The samples used in this study were prepared by electrochemically deintercalating a floating-zone grown Na$_x$CoO$_2$ crystal to yield a final concentration of $x = 0.5$ [12, 13]. Figure 1 shows measurements of the bulk properties of the resulting Na$_{0.5}$CoO$_2$ crystals. In Fig. 1(a), we plot the in-plane resistivity $\rho_{ab}$.

FIG. 1: Bulk physical properties measured using Na$_{0.5}$CoO$_2$ single crystals. (a) In-plane resistivity $\rho_{ab}$. (b) Fractional change of $\rho_{ab}$ measured in a magnetic field of 14 T with $H \parallel c$ and $H \parallel ab$. (c) Anisotropic magnetic susceptibility in a field of 1 T. The vertical dashed lines denote the temperatures of $T = 51$ K and $T_N = 88$ K.
shift in the onset temperature of the resistivity upturn. A new observation is that, for \( H \parallel c \), the data exhibit a positive magnetoresistance below 88 K. As we discuss further below, this behavior coincides with the magnetic phase transition at \( T_N = 88 \) K and is consistent with our proposed ground state. The magnetic susceptibility (Fig. 1(c)) is anisotropic and exhibits kinks at \( T = 88 \) K and 51 K [14][15].

Our neutron scattering experiments were conducted at the NIST Center for Neutron Research using the BT9 and BT2 triple-axis spectrometers. The incident energy was fixed at 14.7 meV, and the collimations were 40′-40′-sample-60′-open. Pyrolytic graphite filters were placed in the beam before the sample to reduce higher order neutron contamination. For the polarized measurements, Heusler crystals were used for the monochromator and analyzer, and polarization guide fields were created at the sample position using Helmhotlz coils (a flipping ratio of \( \sim 21 \)) was achieved. The crystal studied was cylindrically shaped, with mass 2.41 g and a mosaic of 1 to \( 2^\circ \) (full-width half maximum), depending on the orientation. The temperature was controlled using a \( ^4 \)He closed cycle refrigerator. We label reciprocal space peaks using the hexagonal \( P63/mmc \) space group, with low temperature lattice parameters \( a = 2.816 \) Å, and \( c = 11.05 \) Å. As mentioned previously, in Na\(_{0.5}\)CoO\(_2\), Na ion ordering leads to an orthorhombic supercell (\( a_o = \sqrt{3}a \) and \( b_o = 2a \)) in real space, which produces nuclear superlattice reflections in reciprocal space [5].

Figure 2 shows unpolarized neutron diffraction evidence for magnetic order below \( T_N = 88 \) K. At low temperatures, new peaks arise which are distinct from the Na superlattice reflections. In the \((HHL)\)-zone, we observe such peaks at \( \vec{Q} = (\frac{1}{2}, \frac{1}{2}, odd) \). The temperature dependence of the peak intensities of the \((\frac{1}{2}, \frac{1}{2}, 1)\) and \((\frac{1}{2}, \frac{1}{2}, 3)\) peaks are shown in Figure 2(a). Also plotted are the integrated intensities of the \((\frac{1}{2}, \frac{1}{2}, 1)\) reflection which match the \( T\)-dependence of the peak intensity. Figures 2(b) and 2(c) show reciprocal-space scans through the \((\frac{1}{2}, \frac{1}{2}, 1)\) peak along the \((HH0)\) and \((00L)\) directions, respectively, at \( T = 8 \) K and \( T = 120 \) K. The low temperature peak widths are resolution-limited, indicating long-range order (\( > 50 \) Å).

In order to confirm that these peaks originate from magnetic order, we performed polarized neutron measurements. This is the clearest way to distinguish magnetic peaks from weak nuclear superlattice peaks. In general, the magnetic diffraction cross section is given by \( \frac{\Delta I}{I_0} \sim \sum_{i,f} |\langle f| \sum_{\ell} e^{i\vec{Q} \cdot \vec{r}_\ell} U_i^{S_i S_f} |i\rangle|^2 \), where \( i \) and \( f \) denote the initial and final states of the system, \( U_i^{S_i S_f} \sim F(Q)|S_f \rangle \hat{M}_{S_f} |S_i\rangle \) is the scattering amplitude for neutron spin state \( S_i \) to \( S_f \) at atomic site \( l \), where \( F(Q) \) is the magnetic form factor, \( \hat{M} \) is the component of the magnetic moment perpendicular to the scattering wavevector \( \vec{Q} \), and \( \hat{r} \) is the spin operator.

We have measured both the spin-flip and non-spin-flip cross-sections with neutron polarizations both parallel and perpendicular to the wavevector \( \vec{Q} \). Figure 2(d) shows the scattering measured at \( T = 8 \) K with \( \vec{P} \parallel \vec{Q} \) at the \((\frac{1}{2}, \frac{1}{2}, 1)\) peak in the \((HHL)\)-zone. In this geometry, all magnetic scattering will occur in the spin-flip channel, and nuclear scattering will be non-spin-flip. The data show that the scattering is entirely spin-flip. The small peak in the non-spin-flip channel is consistent with the background measured at high-temperature (not shown), taking into account the instrumental flipping ratio. The temperature dependence of this scattering (scaled to match the unpolarized data at low-\( T \)) is denoted by the filled circles in Figure 2(a). We see that the temperature dependence is identical. Hence, this proves that the scattering below 88 K at \((\frac{1}{2}, \frac{1}{2}, 1)\) is entirely magnetic.

Neutron polarization analysis is also an extremely use-
full method to deduce the direction of the ordered moment. In Figure 2(e), we plot the scattering data measured with $\vec{P} \perp \vec{Q}$; that is, the \((HHL)\)-zone of the sample is horizontal and the neutron polarization direction is vertical. In this geometry, magnetic scattering can occur in the non-spin-flip channel if the ordered moment has a component parallel to the polarization direction. A peak in the spin-flip channel would arise from ordered moments with a component in the \((HKL)\)-plane. Here, the signal predominately occurs in the non-spin-flip channel. Therefore, the direction of the ordered moments lies within the \(ab\) plane, and the ordered moment along the \(c\)-axis must be small (or zero). The error bars on our data allow us to conclude that the size of the \(c\)-axis component which contributes to the scattering at \((\frac{1}{2} \frac{1}{2} 1)\) is less than $\sim 0.04\mu_B$. To further specify the direction of the moments within the plane, the twin domain distribution must be taken into account, as we discuss below. The temperature dependence of the polarized data indicates that the \(c\)-axis component remains small at all measured temperatures below $T_N = 88$ K.

The refinement of the magnetic structure is complicated by the presence of multiple twin domains (structural and magnetic). These domains, in principle, can have different populations. To characterize the structural domains, diffraction measurements were taken with the sample aligned in the \((HK0)\)-zone. Since the Na ion order reduces the six-fold hexagonal symmetry to two-fold, there are three possible Na-order domains whose relative orientations differ by a rotation of $60^\circ$ about the \(c\)-axis. In Fig. 3(a), we show $\theta$-scans through peaks at $\vec{Q} = (\frac{1}{2} \frac{1}{2} 0)$, \((1 \frac{1}{2} 0)\), and \((\frac{1}{2} 1 0)\). Each peak is comprised of scattering from the Na superlattice of two different structural twin domains. The measured intensities of the peaks are proportional to the populations of the twin domains which contribute to that peak. (We note that the long axis of our cylindrically shaped sample lies in the scattering plane in this geometry. Hence, part of the intensity variation is related to neutron absorption.) The Na order peaks are resolution limited in all three crystallographic directions, indicating that they are macroscopic in size. Also, the relative intensities of these superlattice peaks compared to the fundamental reflections, shown in Table I, indicate that the Na ordering occurs in essentially 100% of our sample.

In conjunction with characterizing the structural twins, we have also performed scans through the magnetic positions: \((\frac{1}{2} \frac{1}{2} 2)\), \((1 \frac{1}{2} 1)\), and \((\frac{1}{2} 1 1)\). These scans, shown in Fig. 3(b), were performed by first aligning a \((\frac{1}{2} \frac{1}{2} 0)\) peak, then tilting the sample by $14.3^\circ$ to bring the \((\frac{1}{2} \frac{1}{2} 1)\) position into the horizontal scattering plane. We find that the intensities of these magnetic peaks are proportional to the intensities of the corresponding Na order peaks. This suggests that each structural twin domain corresponds to a magnetic twin domain. That is, the arrangement of ordered magnetic moments is closely coupled to the arrangement of the Na ions. This is a natural expectation due to the symmetry of both arrangements and now has experimental support.

The above information on the domain distribution and the moment direction can be combined with measurements of intensities of several nuclear and magnetic Bragg peaks to determine the magnetic structure. Our data are well described by the model shown in Figure 4. Within each CoO$_2$ layer, for a single magnetic twin domain, the Co ions are arranged in alternating rows (or stripes) of magnetically ordered and “non-ordered” ions. For the magnetic ions, the nearest neighbor spins are coupled antiferromagnetically, both along the row and between rows. Between CoO$_2$ planes, the rows of magnetic Co ions are stacked directly on top of each other, and the nearest neighbor interplane coupling is also antiferromagnetic. The directions of the ordered moments are parallel to the rows. The error bars on our data allow us to put restrictions on the deviations of the ordered

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**TABLE I: Observed and calculated integrated intensities of selected nuclear and magnetic Bragg peaks at $T = 8$ K.**

| $Q$ | $I_{\text{nucl}}^{\text{exp}}$ | $I_{\text{nucl}}^{\text{calc}}$ | $I_{\text{magn}}^{\text{exp}}$ | $I_{\text{magn}}^{\text{calc}}$ |
|-----|------------------|------------------|-----------------|-----------------|
| \((\frac{1}{2} \frac{1}{2} 1)\) | 3.9(0.3) | 3.4 |
| \((\frac{1}{2} \frac{1}{2} 2)\) | 2.2(0.1) | 2.3 |
| \((\frac{1}{2} 1 1)\) | 0.6(0.3) | 1.2 |
| \((0 1)\) | 8.1(4.4) | 4.4 |
| \((0 3)\) | 3.9(1.6) | 3.8 |

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FIG. 3: (a) Neutron diffraction peaks measured in the \((HK0)\)-zone at $T = 8$ K. The three sets of data correspond to peaks from three different twin domains due to Na ion ordering: \((\frac{1}{2} \frac{1}{2} 0)\) (●), \((1 \frac{1}{2} 0)\) (○), and \((\frac{1}{2} 1 0)\) (□) (the angle $\theta$ was offset by $60^\circ$ for two of the peaks). The weak peak at $\sim 56^\circ$ is due to a small crystallite. (b) Magnetic Bragg peaks measured in scattering zones tilted from the \((HK0)\)-zone by $14.3^\circ$ in order to reach the positions \((\frac{1}{2} \frac{1}{2} 1)\) (●), \((1 \frac{1}{2} 1)\) (○), and \((\frac{1}{2} 1 1)\) (□). The solid lines correspond to Gaussian fits.
moments away from this direction to be less than 10° out of the ab plane. However, within the ab plane, our data are less restrictive, and the moments may be oriented up to 30° away from the stripe direction. The low temperature (T = 8 K) static magnetic moment is 0.25(2) μB per magnetic Co ion. The size of the observed moment is smaller than that expected for S = 1/2, which may suggest the presence of quantum fluctuations or deviations from a local moment picture. The order that we observe differs somewhat from the models proposed by Yokoi et al., though we agree on the fundamental periodicity. The structure proposed in Figure 4 is the simplest model which is consistent with our data, assuming a local moment description of the magnetic order. It is consistent with having rows of Co⁴⁺ ions which are magnetic (in the S = 1/2 low spin state) alternating with rows of Co³⁺ ions (in the S = 0 spin state) which are nonmagnetic, as suggested previously. However, we emphasize that our neutron data do not directly probe the valence of the Co ions, only their magnetic moments. For example, the rows of non-ordered ions may correspond to Co ions with fluctuating moments which do not contribute to the long-range antiferromagnetism. The valence difference between the two distinct Co sites may, in fact, be small. Recent NQR studies suggest that unit-valence charge disproportionation does not occur at T_N. It is possible that some degree of valence disproportionation exists already at temperatures above T_N = 88 K, and it is primarily the spin components which order at T_N. A delocalized moment model may also describe the data, so long as the periodicity and spin orientation are the same as discussed.

The anisotropic magnetic susceptibility measurements shown in Figure 1(c) are consistent with our model. A clear drop is seen at T_N = 88 K for H ∥ ab, whereas no kink is visible for H ∥ c, consistent with the observation that there is essentially no c-axis component to the ordered moment below T_N. The susceptibility data also show an almost isotropic drop below T = 51 K, coincident with the upturn in ρ_{ab}(T). A previous μSR study suggested that a spin-reorientation transition occurs near this temperature. We find that there is no indication of this transition in the magnetic neutron diffraction. Specifically, the ratio of intensities of the (1 1 1) and (1 1 3) Bragg peaks should change if there were a significant spin-reorientation below T = 51 K, but the inset of Fig. 2(a) shows that the ratio is constant. This is consistent with the polarized neutron results and implies any spin reorientation must be small (<10° out of the ab plane). Further, this suggests that the drop in susceptibility near T = 51 K is not caused by the spins which participate in the magnetic order below T_N = 88 K. Hence, this feature may be related to a gap developing in the excitation spectrum of the “non-ordered” Co ions. Finally, the positive magnetoresistance observed below T_N = 88 K in Figure 1(b) can be understood in terms of the orbital motion of charge carriers within this stripe-like ground state. The increased resistivity for H ∥ c may be caused by enhanced scattering for charge motion along one-dimensional chains due to the Lorentz force. Understanding the interplay between spin order and charge motion in this correlated electron system remains an important issue for further study.

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[1] I. Terasaki, et al., Phys. Rev. B 56, R12685 (1997).
[2] Y. Wang, et al., Nature (London) 423, 425 (2003).
[3] K. Takada, et al., Nature (London) 422, 53 (2003).
[4] M. L. Foo, et al., Phys. Rev. Lett. 92, 247001 (2004).
[5] H. W. Zandbergen, et al., Phys. Rev. B 70, 024101 (2004).
[6] Q. Huang, et al., J. Phys.: Cond. Mat. 16, 5803 (2004).
[7] N. L. Wang, et al., Phys. Rev. Lett. 93, 147403 (2004).
[8] J. Hwang, et al., cond-mat/0405200.
[9] K.-W. Lee, et al., Phys. Rev. Lett. 94, 026403 (2005).
[10] T. P. Choy, et al., cond-mat/0502164.
[11] L. Balicas, et al., Phys. Rev. Lett. 94, 236402 (2005).
[12] F. C. Chou, et al., J. Phys. Chem. Solids 66, 155 (2005).
[13] F. C. Chou, et al., Phys. Rev. Lett. 92, 157004 (2004).
[14] F. C. Chou, et al., Phys. Rev. B 70, 144526 (2004).
[15] M. Yokoi, et al., cond-mat/0506220.
[16] J. Bobroff, et al., cond-mat/0507514.
[17] P. Mendels, et al., Phys. Rev. Lett. 94, 136403 (2005).