Orbital degeneracy removed by charge order in triangular antiferromagnet AgNiO$_2$

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(Dated: February 1, 2008)

We report a high-resolution neutron diffraction study on the orbitally-degenerate spin-1/2 hexagonal metallic antiferromagnet AgNiO$_2$. A structural transition to a tripled unit cell with expanded and contracted NiO$_6$ octahedra indicates $\sqrt{3} \times \sqrt{3}$ charge order on the Ni triangular lattice. This suggests charge order as a possible mechanism of lifting the orbital degeneracy in the presence of charge fluctuations, as an alternative to the more usual Jahn-Teller distortions. A novel magnetic ground state is observed at low temperatures with the electron-rich $S = 1$ Ni sites arranged in alternating ferromagnetic rows on a triangular lattice, surrounded by a honeycomb network of non-magnetic and metallic Ni ions. We also report first-principles band-structure calculations that explain microscopically the origin of these phenomena.

PACS numbers: 75.25.+z, 71.45.Lr

Electronic systems on triangular lattices have attracted wide interest theoretically and experimentally due to the possible existence of unconventional ground states stabilized by the frustrated lattice geometry. The layered cobaltite NaCoO$_2$ with a triangular lattice of orbitally-nondegenerate Co$^{3+}$ ions [2] shows a number of unusual phases upon hole doping via deintercalation of Na, as well as superconductivity upon hydration at a particular doping [1]. The addition of orbital degeneracy creates more instabilities for cooperative order and the behavior in the presence of metallic conductivity is not well understood and largely experimentally unexplored. In more localized systems such as NaNiO$_2$ with spin-1/2 Ni$^{3+}$ ions in the $e_g^2 e_g^2$ configuration the two-fold $e_g$ orbital degeneracy is lifted by a Jahn-Teller (JT) structural distortion to a monoclinic structure [3], which splits the $e_g$ band and opens a gap. However it is unclear if such a mechanism applies in less localized systems where the local tendency for JT distortions competes with the charge transfer between sites, allowed by an efficient metallic screening [4]. The metallic layered silver nickelates AgNiO$_2$ [5] and Ag$_2$NiO$_2$ $[6]$ are ideal candidates to explore this physics.

Here we report high-resolution structural studies of AgNiO$_2$ and find that no JT distortions occur but the ideal structure is distorted to a hexagonal tripled unit cell with expanded and contracted NiO$_6$ octahedra. This implies that the orbital degeneracy of the formally Ni$^{3+}$ sites is lifted by a novel $\sqrt{3} \times \sqrt{3}$ charge ordering (CO) that occurs via the charge transfer $3e_g^1 \rightarrow e_g^2 + e_g^{0.5} + e_g^{0.5}$, which to the best of our knowledge is the first experimental example of such a CO pattern in a triangular system. Using band-structure calculations we show that this CO is a 2D analogue of the metal-insulator transition in the 3D NiO$_2$ $[8]$ attributed to the charge transfer $2e_f^2 \rightarrow e_g^2 + e_g^{0.5}$ $[2]$. However, in contrast to the 3D nickelates in AgNiO$_2$ the triangular lattice geometry allows the system to remain metallic in the CO phase, as itinerant electrons can hop on the inter-connected honeycombe network formed by the two electron-depleted sublattices ($e_g^{0.5}$); those sites remain magnetically unordered at base temperature. The remaining one third of Ni sites are strongly magnetic ($e_g^2$) and form an effectively tripled antiferromagnetic (AFM) triangular lattice, which orders in an unusual collinear $2 \times 1$ structure of alternating stripes.

Powder samples of 2H-AgNiO$_2$ (a polymorph of the better known rhombohedral 3R-polytype [3]) were prepared as described in Ref. $[5]$ and neutron diffraction indicates a nearly pure hexagonal phase with less than 1% admixture of the rhombohedral polytype. Neutron diffraction patterns at 300 K were collected using the high-resolution time-of-flight diffractometers OSIRIS and HRPD at the ISIS pulsed neutron source and representative results are shown in Fig. $[1a]$, yielding the hexagonal space group $P6_3/mmc$ as proposed earlier $[3]$, with triangular Ni, O, and Ag layers stacked as ABBBA (Ni-O-Ag-O-Ni). However the neutron data shows additional diffraction peaks [see Fig. $[1b]$-(d)] which can be consistently indexed by an ordering wavevector $k_0 = (1/3, 1/3, 0)$ in the original undistorted structure, indicating a tripled unit cell in the hexagonal plane. To test the accuracy of the indexing we have refined the lattice parameters using only the main peaks and only the supercell peaks (more than 20 observed) and obtained the same values to within the experimental accuracy of $10^{-4}$Å. Furthermore, upon cooling to 2 K the super-
cell peaks were displaced in $Q$ following the lattice contraction but maintained their commensurate index with respect to the main peaks. This further confirms that the supercell peaks are due to a modulation of the main structure rather than an extra impurity phase.

The prominent supercell peaks indicate a distortion of the high-symmetry P6$_3$/mmc structure where all Ni sites are equivalent. e)-g) Supercell peaks are not observed in x-ray data indicating that the distortion involves mainly the light oxygen ions. Solid lines in all panels are fits to the data indicating that the distortion mainly involves displacements of oxygen ions. X-ray data collected using a Phillips Cu K$\alpha$ powder diffractometer [Fig (b)-g)] do not show supercell peaks, indicating that the distortion involves mainly the light oxygen ions. Thus we refined the neutron data in a $\sqrt{3} \times \sqrt{3}$ hexagonal unit cell assuming only oxygen displacements. We eliminated the space groups that were not compatible with the observed low-temperature magnetic structure (to be described later) dictating at least two different Ni crystallographic sites. The highest symmetry space group in which both the structural and magnetic data could be described is P6$_3$22 (≠182). Good agreement with the data is obtained (solid line fits [9]) in Fig (b) and the extracted unit cell parameters are listed in Table I. As a further check of the space group identification we have performed full structural optimization calculations (as described later) starting from a lower symmetry structure (P6$_3$ space group) and those invariably converged to the higher P6$_3$22 symmetry, with the optimized positions agreeing well with the experimental ones (Table I [10]).

The resulting structure in one NiO$_2$ layer is shown in Fig 2. There are three inequivalent Ni sites. Oxygen breathe in towards Ni2 and Ni3 ions ($d_{Ni2-O} = d_{Ni3-O} = 1.934$ Å) and out from Ni1 ($d_{Ni1-O} = 2.022$ Å). No Jahn-Teller distortion is present. The different Ni-O distances indicate that Ni1 is electron rich (Ni$^{2+}$ in a CO scenario) and Ni2,3 are electron depleted (Ni$^{3.5+}$). In the adjacent NiO$_2$ layer Ni1 and Ni3 sites swap places, leading to a zigzag arrangement of the (expanded) electron-rich Ni1 sites along $c$ [11].

Earlier susceptibility data [3] showed dominant antiferromagnetic couplings with a Curie-Weiss constant $\theta = -107.6$ K and AFM order below $T_N=22$ K. Below this temperature additional peaks appear in the neutron

**TABLE I: Unit cell lattice parameters in the ideal (P6$_3$/mmc) and CO (P6$_3$22) structures at 300 K. Internal parameters $\delta$, $\zeta$, $\xi$, $\epsilon$, $\alpha$, $\beta$, and $\gamma$ are 0, 0.08050(5), 0 and 0.0133(2) (exp.) and 0, 0.0792, 0 and 0.0102 (calc.), respectively.**

| Structure | $a_0$ (Å) | $c$ (Å) |
|-----------|----------|---------|
| P6$_3$/mmc (no. 194) | 2.93919(5) | 12.2498(1) |
| P6$_3$22 (no. 182) | 5.0908(1) | 12.2498(1) |

| Atom Site (x, y, z) | Ni1 2a (0, 0, 0) | Ni1 2c $(\frac{1}{3}, \frac{1}{3}, 0)$ |
|---------------------|-----------------|---------------------------|
| Ni2 2b $(0, 0, \frac{1}{2})$ | Ni3 2d $(\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$ |
| Ag 6g $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ | O 12(1) $(\frac{1}{4}, -\frac{1}{4}, \zeta)$ |

**FIG. 1:** a) (color online) 300 K neutron powder diffraction pattern and b)-d) zoomed-in regions showing some of the prominent supercell peaks which indicate a distortion of the high-symmetry P6$_3$/mmc structure where all Ni sites are equivalent. e)-g) Supercell peaks are not observed in xray data indicating that the distortion mainly involves displacements of oxygen ions. Solid lines in all panels are fits to the model with periodic arrangement of expanded and contracted NiO$_6$ octahedra shown in Fig 2 and peak indexing is in the triple unit cell (space group P6$_3$22).

**FIG. 2:** (color online) Bottom NiO$_2$ layer showing the expanded NiO$_6$ octahedra (large circle) surrounded by a honeycomb network (thick lines) of contracted Ni2 and Ni3 sites (small circles). The small balls are oxygen ions and the small arrows indicate the displacements from the ideal structure.
diffraction pattern, see Fig. 3b). These peaks are indexed by the ordering wavevector $k = (1/2, 0, 0)$, as shown in Fig. 3b inset. The best fit was obtained when only one Ni sublattice was ordered, either Ni1 or Ni3, with a moment of 1.522(7) $\mu_B$ along the c-axis. As discussed above, this must be the strongly-magnetic Ni1 (Ni$^{2+}$) with a large available moment of $S=1 (2\mu_B)$, because Ni3 and Ni2 are Ni$^{3.5+}$ with only a small available moment.

The observed magnetic structure is shown in Fig. 3b): in each layer ordered spins are arranged in alternating FM stripes, in the adjacent layer stripes are parallel but have an in-plane offset that follows the c-axis zig-zag arrangement of the electron-rich Ni1 sites, see Fig. 3b). This magnetic structure implies that (a) the exchange between nearest in-plane magnetic neighbors is AFM, (b) there is an easy-axis anisotropy $-DS^2$, and (c) the net interplanar interaction with the 3 magnetic neighbors in the layer above (below) see Fig. 3b) is FM.

To gain more insight into the physical origin for the observed charge and magnetic orderings, we have performed density functional (DFT) calculations. Since Ag$_x$NiO$_2$ is metallic and only weakly correlated, introducing a Hubbard $U$ in the calculation is not necessary. Optimizing the oxygen positions in the $\sqrt{3} \times \sqrt{3}$ unit cell precipitates the CO and reproduces the observed structure in Fig. 2 indicating that the driving force for charge disproportionation is entirely accounted for in the LDA. The calculated total magnetization for the three Ni ions varies between 1.3 and 1.5 $\mu_B$, depending on the exact O position, and is nearly entirely located at the expanded Ni1 site in good quantitative accord with the neutron data. The computed ferromagnetic band structure (Fig. 2) shows fully exchange-split Ni1 derived bands with the magnetic moment diminished from its formal count of 2 $\mu_B$ by hybridization. One can also see that Ni2 and Ni3 states are not visibly exchange split. The Ag sp band is entirely above the Fermi level. This electronic structure can be visualized as a magnetic insulator formed by Ni$^{2+}$ (cf. NiO) with a strong tendency to magnetic order, superimposed on a Ni$^{3.5+}$ metal. The latter has larger bandwidths, due to the smaller Ni-O distance, and by itself does not satisfy the Stoner criterion for metallic magnetism, $I(N(E_F)) > 1$, where $I$ is the atomic Stoner parameter.

The natural tendency for charge order in a NiO$_2$ layer can be explained by energetic arguments. The Hund’s rule energy gain in a metal in DFT is $M^2(I - N^{-1})/4$, where $N$ is the average density of states per spin. Without charge ordering, $M_1 = M_2 = M_3 = 1\mu_B$ and $N_1 = N_2 = N_3 = N_0$. After charge ordering, $M_1 \approx 2\mu_B$, $M_2 = M_3 \approx 0$ and $N_1 > N_2 = N_3$. The CO state is energetically favored since $4(I - N^{-1})/4 > 3(I - N^{-1})/4$. In insulators such as NaNiO$_2$ the Hubbard repulsion would forbid this mechanism, but in this metallic system it is well screened and cannot prevent CO. Our band-structure calculations reproduce fully the observed 3D CO pattern, both the in-plane $\sqrt{3} \times \sqrt{3}$ arrangement as well as the zig-zag arrangement of the electron rich sites along c. We also found a metastable solution where the CO layers form straight columns along c, i.e. the electron rich and strongly magnetic Ni$^{2+}$ occupy the Ni2 site; this indicates that the in-plane CO is very robust and independent of the inter-layer magnetic interactions.

To study the stability of the observed magnetic structure we have calculated ground state energies for a number of potential structures using DFT for the full magnetic unit cell (12 formula units and lower symmetry, C2). In addition to the observed stripe-order with the zig-zag ferromagnetic pattern along c shown in Figs. 3b-c) (called stripe-F), we also found stable solutions for hypothetical ferromagnetic (FM), A-type AFM (alternating FM layers), as well as in-plane stripe-order but with a zig-zag AFM pattern along c (stripe-A, every other plane flipped compared to stripe-F). The results are listed in Table II, the state found experimentally has the lowest energy.

The magnetic structure indicates that the in-plane exchange between magnetic neighbors is AFM. This arises naturally because Ni$^{2+}$ sites are insulating and lack...
both metallic Stoner ferromagnetism and 90° FM superexchange, but do have a classical AFM superexchange via the Ni1-O-Ni1 path, with effective hopping $t_{eff} \sim t_{p3d}^2 t_{p3p} / (E_d - E_p)^2$. The appearance of collinear order instead of the conventional 120° order for a triangular AFM implies a significant easy-axis anisotropy. This is normally provided by spin-orbit induced coupling to the crystal field, but the Ni1 ion is close to a tetragonal distortion. Our results indicate the complex cooperative charge and magnetic order patterns that can occur in orbitally-degenerate metallic systems on frustrated lattices.

We acknowledge support from EPSRC UK.

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10. Experimentally, Ni-O bond is 4.5% longer than the other two Ni-O bonds; the calculations find 3.5%. The optimized position of O is mainly insensitive to the position of Ag ions. The Ag ions (located between two O’s in the high symmetry structure) do not follow the O ions upon the breathing distortion, remaining instead in a practically ideal triangular lattice. These facts indicate that CO is the favored mechanism to lift the orbital degeneracy as opposed to the conventional Jahn-Teller distortions that occurs in more insulating systems. An unusual magnetic order is observed at low temperatures with only one third of sites carrying a magnetic moment with an unexpected collinear stripe order pattern on an antiferromagnetic triangular lattice. Our results indicate the complex cooperative charge and magnetic order patterns that can occur in orbitally-degenerate metallic systems on frustrated lattices.