Stripe correlations in Na$_{0.75}$CoO$_2$

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The many-body effects in correlated electron systems based on square lattices often result in the development of intrinsic charge inhomogeneities [1, 2, 3]. A particularly prominent example is the so-called stripe ordered state based on square lattices often result in the development of intrinsic charge inhomogeneities [1, 2, 3]. A particularly prominent example is the so-called stripe ordered state, having attracted considerable attention due to the discovery of superconductivity in water-intercalated compounds [4] as well as the anomalous metallic state of these materials.

Recently Na$_x$CoO$_2$, being a correlated electron system based on a triangular lattice, has attracted considerable attention, due to the discovery of superconductivity in water-intercalated compounds [14, 15]. The mosaicity spread of the sample was determined to be about 0.24°. The mosaicity spread of the sample was determined to be about 0.24°. Furthermore, the observed room temperature lattice parameters $a_H = 2.83$ Å and $c_H = 10.84$ Å of the Na$_{0.75}$CoO$_2$ sample under study agree well with the values reported in the literature [15].

Since the $c$-axis depends strongly on $x$, the resolution limited radial ($\Theta$/$\Theta$-) scan through the (004) reflection at T=8 K shown in Fig. 1 verifies a well-defined and homogeneous sodium concentration in the probed sample volume.

During a survey in reciprocal space at 8 K, a number of superstructure reflections were observed around the (100) reflection in the (H0K)-zone, which are summarized in Fig. 1. In this figure, the indicated reciprocal lattice vectors $b_{112}$ correspond to the direct lattice vectors $a_{112}$ that are parallel to the Na- and CoO$_2$-layers (cf. Fig. 4). Corresponding superstructures were also observed around the (110) position. Radial scans through the superstructure reflections at the commensurate (1.5,-0.25,0) and (2,0.5,0) positions taken at T=8 K are shown on the right hand side of Fig. 1. The observation of superstructure reflections at equivalent positions together with the fact that these reflections do not vanish upon a rotation around the scattering vector, excludes multiple scattering as a possible origin for the observed intensities. The intensity profile at the (1.5,-0.25,0) position was fitted by a single Lorentzian squared function. The FWHM determined by this fit together with the experimental resolution determined at the (100) position yield a correlation length of about 300 Å for the corresponding...
superlattice modulation below $T_{SO}$ vanishes upon heating at $T_{SO}$. The conclusion that the phase transition at 350 K, indicating that these two superlattice modulations are coupled. Nonetheless, the intensity at the (2,-0.5,0) reflection also varies across the investigated temperature range instead. The slope change of the (2,-0.5,0) intensity around 150 K roughly coincides with the temperature regime where the (1.5,-0.25,0) intensity starts to increase considerably. Furthermore, the intensity of this reflection measured after rapid cooling shown in Fig. 4 and the data given in Fig. 3 have been obtained during the same run, verifying a completely different temperature dependence of the two reflections. As can be observed in Fig. 3, the (2,-0.5,0) reflection does not disappear above 350 K, but is observed in the whole investigated temperature range instead. The slope change related to the Na-sites has been revealed, whereas rearrangement. However, in this study only a symmetry change related to the Na-sites has been revealed, whereas no enlargement of the unit cell has been reported.

Based on the experimental data for $T=8$ K we can un-
ous calculations in the literature \[19\], we used non-spin-polarized and all calculations were performed with the FPLO package version 5.20 \[18\]. The calculations were based on the identified supercell using the relaxed for each structure and resulted in the same oxygen Wyckoff position for all Na patterns considered. In order to assess our calculations we recalculated the total energies of a number of structures considered in Ref. \[19\] and obtained very good agreement in the structural energy differences. The LDA calculations yield the lowest total energy for the structure given in Fig. 4(a), which amounts to \(E_a = 1662.091\) mhartree per \(\text{Na}_{0.75}\text{CoO}_2\) formula unit. The two structures shown in Fig. 4(b) and (c) correspond to higher total energies. We obtain \(E_b - E_a = 1.3\) mhartree and \(E_c - E_a = 1.7\) mhartree, respectively. With respect to the stacking in the third direction, two possibilities were considered with an inversion center at the Co site and midway between two nearest neighbor Co sites, respectively. However, the corresponding energy differences are negligible. The differences between the structures \((a)\), \((b)\) and \((c)\) can essentially be understood by Coulomb energy arguments: \((a)\) and \((c)\) comprise a charge density wave of comparable amplitude, but with wave vector \(2\mathbf{a}_1 + 4\mathbf{a}_2\) in the case \((a)\), while \((c)\) has the shorter wave vector \(2\mathbf{a}_1\). The structure \((b)\) has also a charge density wave with wave vector \(2\mathbf{a}_1 + 4\mathbf{a}_2\), however with a considerably larger amplitude.

Note, that the model reproduced in Fig. 4(c) corresponds to the lowest energy state reported by Zhang et al. based on electron diffraction (ED) data \[19\] \[20\]. Obviously, the supercell determined by ED disagrees with the ambigiously identify the unit cell of \(\text{Na}_{0.75}\text{CoO}_2\) at low temperatures: We start from the hexagonal layered lattice structure belonging to the \(\text{P}6_3/\text{mmc}\) space group \[17\]. In this setting, the \(\text{CoO}_2\)-layers and the Na-planes are parallel to the \((\mathbf{a}_1, \mathbf{a}_2)\)-planes and alternate along the perpendicular stacking direction \(\mathbf{c}\). The lattice symmetry allows for two in-equivalent lattice sites within the Na-planes, referred to as Na(1) and Na(2) in the following, which together form a honeycomb lattice (cf. Fig. 4). However, not all the sites of this lattice can be occupied, because the Na(1)-Na(2) nearest neighbor distance is far too short to allow a simultaneous occupation. If \(\mathbf{b}_1\), \(\mathbf{b}_2\) are the reciprocal lattice vectors of the \(\text{P}6_3/\text{mmc}\) lattice, then the additionally found superstructure peaks at low temperatures correspond to an orthogonal basis \(\mathbf{b}_1/2 - \mathbf{b}_2/4\), \(\mathbf{b}_2/4\) (cf. Fig. 4). Since we did not observe any additional structural modulation along \(\mathbf{c}\), the HXS data implies an orthorhombic unit cell of the direct lattice, spanned by \(2\mathbf{a}_1\), \(2\mathbf{a}_1 + 4\mathbf{a}_2\), and \(\mathbf{c}\) (cf. Fig. 4(a) and (b)).

In the second step of this study, we performed LDA calculations \[17\] based on the identified supercell using the FPLO package version 5.20 \[18\]. The calculations were performed non-spin-polarized and all calculations were done for a fixed unit cell volume. To compare to previous calculations in the literature \[18\], we used \(a_H = 2.82\) and \(c_H = 10.89\), which slightly differ from the observed values by about 0.5\%. The aim of these calculations was twofold: (i) To determine the lowest energy state in agreement with the HXS data, since several sodium ordering patterns are possible within the observed supercell as demonstrated by Fig. 4(a) and (b). (ii) To determine the effect of the sodium order on the electronic states of the \(\text{CoO}_2\)-planes.

The free parameter of the oxygen Wyckoff position was relaxed for each structure and resulted in the same oxygen position for all Na patterns considered. In order to assess our calculations we recalculated the total energies of a number of structures considered in Ref. \[19\] and obtained very good agreement in the structural energy differences. The LDA calculations yield the lowest total energy for the structure given in Fig. 4(a), which amounts to \(E_a = 1662.091\) mhartree per \(\text{Na}_{0.75}\text{CoO}_2\) formula unit. The two structures shown in Fig. 4(b) and (c) correspond to higher total energies. We obtain \(E_b - E_a = 1.3\) mhartree and \(E_c - E_a = 1.7\) mhartree, respectively. With respect to the stacking in the third direction, two possibilities were considered with an inversion center at the Co site and midway between two nearest neighbor Co sites, respectively. However, the corresponding energy differences are negligible. The differences between the structures \((a)\), \((b)\) and \((c)\) can essentially be understood by Coulomb energy arguments: \((a)\) and \((c)\) comprise a charge density wave of comparable amplitude, but with wave vector \(2\mathbf{a}_1 + 4\mathbf{a}_2\) in the case \((a)\), while \((c)\) has the shorter wave vector \(2\mathbf{a}_1\). The structure \((b)\) has also a charge density wave with wave vector \(2\mathbf{a}_1 + 4\mathbf{a}_2\), however with a considerably larger amplitude.

Note, that the model reproduced in Fig. 4(c) corresponds to the lowest energy state reported by Zhang et al. based on electron diffraction (ED) data \[19\] \[20\]. Obviously, the supercell determined by ED disagrees with the
presented HXS results. This discrepancy is most likely related to the different sample volumes, which are probed by the two techniques. HXS, being a bulk probe, is not sensitive to the sample surface, while ED is surface sensitive. This implies that the sodium ordering is strongly affected by surface effects, which should be taken into account for the interpretation of surface sensitive probes like angular resolved photoemission.

The obtained ground state corresponds to the formation of sodium-density stripes within the Na-planes, as indicated by the gray shading in Fig. 1(a). The LDA calculations prove, that this ordering produces a sizeable dip in the density of the Co-states at the Fermi level, pointing to band structure effects as a driving force for the stripe formation. This is a very strong indication that the ordering within the Na-planes is coupled to intrinsic stripe-like charge correlations within the CoO$_2$-planes.

Taking into account that the hydrated Na$_x$CoO$_2$ samples have been shown to be of the composition Na$_{0.337}$(H$_2$O)$_2$CoO$_2$·yH$_2$O, where the additionally intercalated H$^+$-ions of the H$_3$O$^+$ also occupy Na-sites [21], it follows that the effective doping of the superconducting materials corresponds to Na$_x$CoO$_2$ with $x \approx 0.7$. This leads to an astonishing analogy to the high-temperature superconducting cuprates: In the case of the doped cuprates, the cooperative octahedral tilts in the so-called stripe-like angular resolved photoemission.

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