

Prediction of new structure candidates for quasi one-dimensional Wigner crystals $\text{Na}_{1+x}\text{CuO}_2$ ($0 \leq x \leq 1$) by enumeration

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The still young family of quasi one-dimensional mixed valent sodium cuprates(II/III), $\text{Na}_{1+x}\text{CuO}_2$ [1], represents intrinsically doped Mott insulators, i.e. they show unperturbed periodicities, and thus are well suited for experimentally and theoretically studying phenomena related to charge, spin and orbital ordering in mixed valent oxocuprates. Most interestingly, $\text{Na}_3\text{Cu}_2\text{O}_4$ and $\text{Na}_8\text{Cu}_5\text{O}_{10}$ have been shown to represent first unambiguous manifestations of Wigner crystallization and to display one-dimensional collinear magnetic structures [2]. These compounds appear to belong, together with the parent compound NaCuO_2 , to a homologous series $\text{Na}_{1+x}\text{CuO}_2$, with $x = 0, 0.5, 0.6$, and to feature characteristic sodium and CuO_2 partial structures. These partial structures extend quasi one-dimensionally along the same crystallographic direction. Since the number of sodium atoms varies with the number of Cu^{2+} present, these constitutive structural elements can be regarded as couples of vernier scales with independent periodicities along the direction of their extension.

Combining the structural elements in all sodium cuprates known up to now, has enabled us to derive a general structural building principle that provides predictive potential [3]. The crystal structures of NaCuO_2 , $\text{Na}_3\text{Cu}_2\text{O}_4$, and $\text{Na}_8\text{Cu}_5\text{O}_{10}$ differ in their Na/CuO_2 , and thus also in the $\text{Cu}^{2+}/\text{Cu}^{3+}$ ratios. The widely variable Na/CuO_2 ratio determines the periodicity D along b (direction of the chains of the edge sharing CuO_4 units), which corresponds to the smallest common multiple $D = n \times d_1 = m \times d_2$ between the average $\text{Na}-\text{Na}$ and $\text{Cu}-\text{Cu}$ distances d_1 and d_2 , respectively, along this direction. d_1 and d_2 can be regarded as the scales of the counterparts of a vernier slide gauge. The propagation vector $q = d_1/d_2$, which can also be expressed as $q = (1+x)/2$, maps both sides of the vernier scale onto each other.

The different periodicities in each representative thus far known can be expressed as $3 \times d_1 = 4 \times d_2$ for $\text{Na}_6\text{Cu}_4\text{O}_8$ ($\text{Na}_3\text{Cu}_2\text{O}_4$), and $4 \times d_1 = 5 \times d_2$ for $\text{Na}_8\text{Cu}_5\text{O}_{10}$. This series can easily be expanded by $5 \times d_1 = 6 \times d_2$ for 'Na₁₀Cu₆O₁₂' ($\text{Na}_5\text{Cu}_3\text{O}_6$), $6 \times d_1 = 7 \times d_2$ for 'Na₁₂Cu₇O₁₄', $7 \times d_1 = 8 \times d_2$ for 'Na₁₄Cu₈O₁₆' ($\text{Na}_7\text{Cu}_4\text{O}_8$), $8 \times d_1 = 9 \times d_2$ for 'Na₁₆Cu₉O₁₈', and so on. The respective general term is $n \times d_1 = (n+1) \times d_2$ based on the chemical formula $\text{Na}_{2n}\text{Cu}_{n+1}\text{O}_{2n+2}$, and $n \geq 3$. For $n < 3$, the big differences between d_1 and d_2 result in unreasonable $\text{Na}-\text{Na}$ and $\text{Cu}-\text{Cu}$ separations. The general algorithm given also includes the still elusive 'Na₂CuO₂' with $d_1 = d_2$ and $n \rightarrow \infty$. Here, we analyse the systematics of these super structures [3].

The structure of NaCuO_2 may be regarded as the basic structure of the $\text{Na}_{1+x}\text{CuO}_2$ family, showing the shortest translational vector along the CuO_2 chain direction. Its characteristic features are chains of edge-sharing CuO_4 squares along b , and layers of slightly distorted edge-sharing NaO_6 octahedra (o), c.f. Fig. 1a. The structure can be regarded as a slice of the NaCl structure, providing tetrahedral voids oriented up and down within the layers (t_+ , t_-).

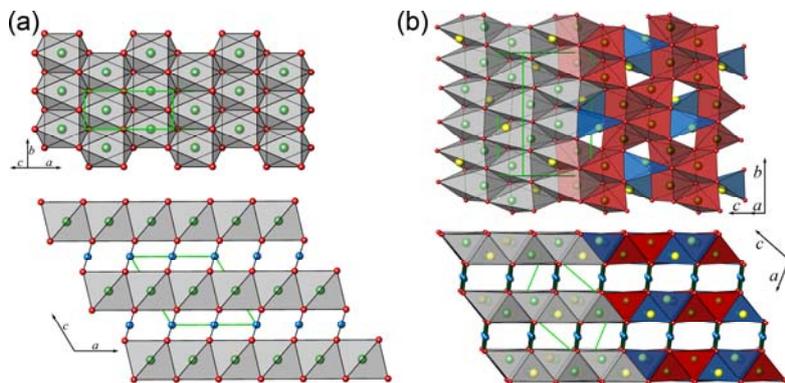


Figure 1: Crystal structure of NaCuO_2 (a) and $\text{Na}_3\text{Cu}_2\text{O}_4$ (b). Top: view along $[2\ 0\ 1]$, bottom: view along $[0\ 1\ 0]$. Colour code: O = red, Cu = blue, green spheres represent the sodium atoms in octahedral (grey polyhedra, a), and square pyramidal environment (red polyhedra, b), yellow spheres represent the sodium atoms with tetrahedral coordination (blue polyhedra, b).

Increasing the Na/Cu ratio generates the principal topological challenge of how to stuff NaCuO_2 with additional sodium atoms without changing its main structural building principle. The tetrahedral voids (t) between the occupied, virtually regular neighbouring octahedra (o) can not be filled additionally, because the resulting $\text{Na}_o\text{—Na}_t$ distances are too short. The space needed can be generated, however, by a distinct elongation of the octahedra, which then are better described as two face-sharing square pyramids (p_+ , p_-). Such a slight displacive structural change indeed provides additional sites for sodium atoms. When filling the pyramidal voids of two neighbouring octahedra (p_+ , p_+) the opposite tetrahedral void (t_-) becomes accessible, and a sequence ' p_+ , t_- , p_+ ' results, accommodating 1.5 times more sodium per copper atom than in NaCuO_2 . Only edge-sharing of polyhedra is required, and the $\text{Na}_p\text{—Na}_t$ distances (~ 300 pm) are even longer than the original $\text{Na}_o\text{—Na}_o$ distances in NaCuO_2 (~ 275 pm). This is exactly the situation realized in $\text{Na}_3\text{Cu}_2\text{O}_4$. Fig. 1b shows its structure in polyhedral representation. The sodium repetition unit can be coded as ' p_+ , t_- , p_+ , p_- , t_+ , p_- ' (short form ' $2p_+, 2p_-$ '), at $x = 1/2$. For the composition $\text{Na}_5\text{Cu}_3\text{O}_6$, the repetition unit is ' p_+ , t_- , p_+ , t_+ , p_+ , p_- , t_+ , p_- , t_+ , p_- ' ($3p_+, 3p_-$), at $x = 2/3$, and $\text{Na}_8\text{Cu}_5\text{O}_{10}$ can be addressed as a combination of $\text{Na}_3\text{Cu}_2\text{O}_4$ and $\text{Na}_5\text{Cu}_3\text{O}_6$ with the sequence ' $3p_+, 2p_-$ ' at $x = 3/5$, c.f. Fig. 2.

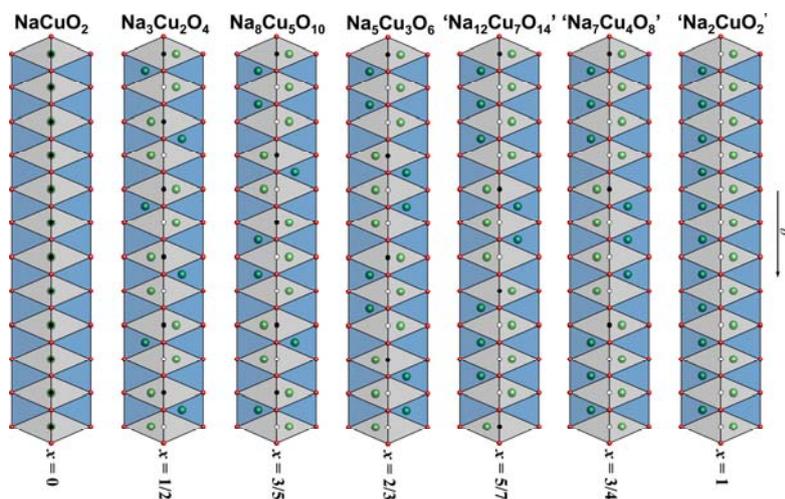


Figure 2: Schematic representation of a step wise replenishment of sodium in NaCuO_2 . O_6 oxygen octahedra (o) built up by two face-sharing pyramids (p_+ , p_-) in grey, O_4 tetrahedra (t_+ , t_-) in blue. White and black dots represent Cu^{2+} and Cu^{3+} , located above the corresponding octahedral edges.

All members of the $\text{Na}_{1+x}\text{CuO}_2$ family known so far can be described in this way, and obviously, following such a structural principle exclusively generates discrete compositions. Applying the recipe to derive new possible compositions (given in quotation marks in Fig. 2) leads for example to ' $\text{Na}_7\text{Cu}_4\text{O}_8$ ' ($4p_+, 4p_-$), c.f. Fig. 2 and 3.

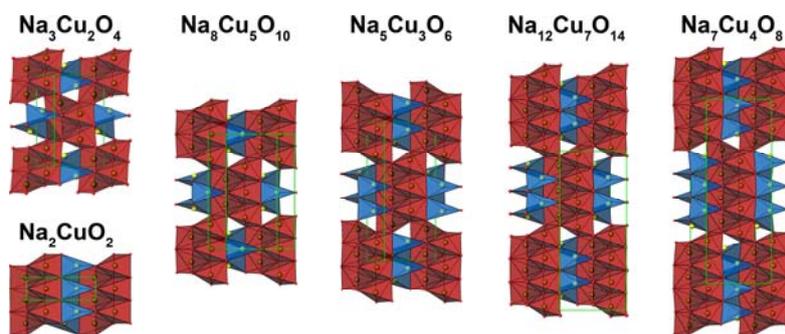


Figure 3: Distribution of sodium in the octahedral layers of oxygen, showing the possible variants by filling square pyramidal and tetrahedral voids, resulting in a layer of edge sharing pyramids (red) and tetrahedra (blue), exclusively. The fragments of $\text{Na}_3\text{Cu}_2\text{O}_4$, $\text{Na}_8\text{Cu}_5\text{O}_{10}$, and $\text{Na}_5\text{Cu}_3\text{O}_6$ show the experimental structures [1, 4], while $\text{Na}_{12}\text{Cu}_7\text{O}_{14}$, $\text{Na}_7\text{Cu}_4\text{O}_8$, and Na_2CuO_2 are locally optimized structures derived from the predicted ones [3].

It is obvious that even elusive ' Na_2CuO_2 ' can exist in the topology of a stuffed NaCuO_2 structure, $x = 1$. In this case all square pyramidal voids (p_+) and all tetrahedral voids (t_-) are occupied (see Fig. 3). Interestingly, such a structure candidate for ' Na_2CuO_2 ' represents a completely new type of structure.

Moreover, a rule for the charge ordering of Cu^{2+} and Cu^{3+} can be derived. Cu^{3+} is most favourably placed when p_- follows p_+ , and vice versa. This sounds arbitrary, on first view, but it appears reasonable, when comparing the various stuffed Na-O layers. Pronounced spatial gaps result, when p_-

switches to p_+ , and freedom is given to the oxygen atoms to approach the copper sites, providing shorter Cu—O distances, thus satisfying the requirement for Cu^{3+} (Fig. 3). This simple building principle reproduces the correct charge ordering for all known $\text{Na}_{1+x}\text{CuO}_2$ compounds, and allows predicting new possible constitutions (Fig. 4).

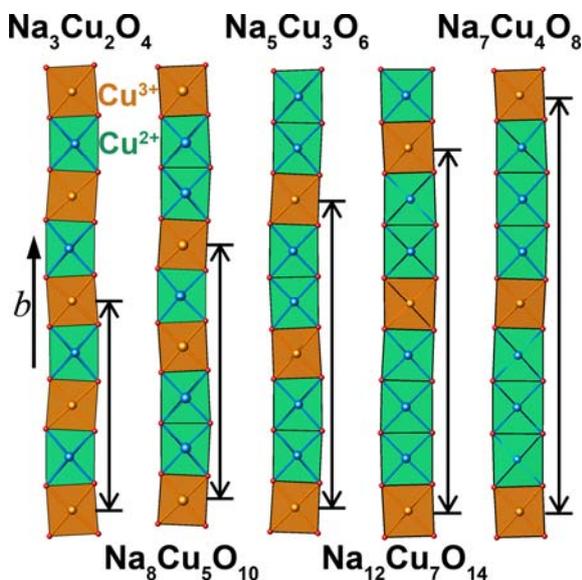


Figure 4: Charge ordering patterns in the CuO_2 chains of known and predicted $\text{Na}_{1+x}\text{CuO}_2$ compounds. The repetition units, with respect to the unit cells, are marked for each chain.

The hypothetical $\text{Na}_{1+x}\text{CuO}_2$ structures derived by the given recipe reflect the topology of the assumed charge ordering; however, they do not display any structural details such as the different Cu—O distances for Cu^{3+} and Cu^{2+} sites. Thus, the structure candidates derived qualitatively need to be subjected to a geometry optimisation using quantum chemical tools [3]. Such an investigation would reveal at the same time whether the configurations identified are at least kinetically stable. For this purpose, local structure optimizations at the DFT level were performed on $\text{Na}_{12}\text{Cu}_7\text{O}_{14}$ and $\text{Na}_7\text{Cu}_4\text{O}_8$. In addition, the structures of NaCuO_2 and Na_2CuO_2 were investigated, in order to derive signatures for the different copper states, and, in the case of NaCuO_2 , to judge the suitability of the applied computational approach to describe the structures of these cuprates. Indeed, the computed and the experimental structural data of NaCuO_2 are in fair agreement. As expected, the Cu—O distances in Na_2CuO_2 are significantly larger than in NaCuO_2 . The computed spin density provides a clear signature of the valence state of copper. The spin charge is zero for Cu^{3+} in NaCuO_2 , but 0.47 for Cu^{2+} in Na_2CuO_2 . In the mixed-valent compounds the predicted Cu^{2+} sites have a spin charge of 0.39 to 0.46, whereas at the Cu^{3+} sites it is less than 0.1. Notably, the spin density converges to the predicted patterns, although the calculations were started without a bias. This is also true for the Cu—O distances at the various sites, which show the same ratio as in the experimentally known mixed-valent structures. The calculations on $\text{Na}_{12}\text{Cu}_7\text{O}_{14}$ and $\text{Na}_7\text{Cu}_4\text{O}_8$ not only converge to the predicted charge order (Fig. 4), but also result in local minima on the energy landscape, showing them to be structure candidates capable of existence.

The recently synthesized $\text{Na}_5\text{Cu}_3\text{O}_6$, with a hole filling factor of $1/3$ (Cu^{3+}) complies with the concept presented. All structural characteristics that have been predicted are confirmed by single crystal X-ray diffraction. Interestingly, in this case the experimental magnetic susceptibility data can be modelled only, when excitations across the Wigner gap are assumed [4].

References:

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