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


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 \( \text{NaCuO}_2 \), to a homologous series \( \text{Na}_{1+x}\text{CuO}_2 \), with \( x = 0, 0.5, 0.6 \), and to feature characteristic sodium and \( \text{CuO}_2 \) 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 \( \text{Cu}^{2+} \) 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 \( \text{NaCuO}_2 \), \( \text{Na}_3\text{Cu}_2\text{O}_4 \), and \( \text{Na}_8\text{Cu}_5\text{O}_{10} \) differ in their \( \text{NaCuO}_2 \) units, and thus also in the \( \text{Cu}^{2+}/\text{Cu}^{3+} \) ratios. The widely variable \( \text{Na/CuO}_2 \) ratio determines the periodicity \( D \) along \( b \) (direction of the chains of the edge sharing \( \text{CuO}_4 \) units), which corresponds to the smallest common multiple \( D = n \times d_1 = m \times d_2 \) between the average \( \text{Na—Na} \) and \( \text{Cu—Cu} \) 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 '\( \text{Na}_{10}\text{Cu}_4\text{O}_{12} \)‘ (\( \text{Na}_5\text{Cu}_2\text{O}_6 \)), \( 6 \times d_1 = 7 \times d_2 \) for '\( \text{Na}_{12}\text{Cu}_7\text{O}_{14} \)‘, \( 7 \times d_1 = 8 \times d_2 \) for '\( \text{Na}_{14}\text{Cu}_9\text{O}_{16} \)‘ (\( \text{Na}_7\text{Cu}_4\text{O}_8 \)), \( 8 \times d_1 = 9 \times d_2 \) for '\( \text{Na}_{16}\text{Cu}_9\text{O}_{18} \)‘, 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 \( \text{Na—Na} \) and \( \text{Cu—Cu} \) separations. The general algorithm given also includes the still elusive '\( \text{Na}_2\text{CuO}_2 \)‘ with \( d_1 = d_2 \) and \( n \rightarrow \infty \). Here, we analyse the systematics of these superstructures [3].

The structure of \( \text{NaCuO}_2 \) may be regarded as the basic structure of the \( \text{Na}_{1+x}\text{CuO}_2 \) family, showing the shortest translational vector along the \( \text{CuO}_2 \) chain direction. Its characteristic features are chains of edge-sharing \( \text{CuO}_4 \) squares along \( b \), and layers of slightly distorted edge-sharing \( \text{NaO}_6 \) octahedra (o), c.f. Fig. 1a. The structure can be regarded as a slice of the \( \text{NaCl} \) structure, providing tetrahedral voids oriented up and down within the layers (t, t).
Increasing the Na/Cu ratio generates the principal topological challenge of how to stuff NaCuO₂ 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 Naₜ—Naₜ 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 NaCuO₂. Only edge-sharing of polyhedra is required, and the Naₜ—Naₜ distances (~300 pm) are even longer than the original Naₜ—Naₜ distances in NaCuO₂ (~275 pm). This is exactly the situation realized in Na₃Cu₂O₄. 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 Na₅Cu₃O₆, the repetition unit is 'p⁺, t⁻, p⁺, t⁻, p⁺, p⁺, p⁺, p⁺, t⁻, p⁻, p⁻, p⁺, p⁺, p⁺, p⁻' (3p⁺,3p⁻), at x = 2/3, and Na₈Cu₂O₁₀ can be addressed as a combination of Na₃Cu₂O₄ and Na₅Cu₃O₆ with the sequence '3p⁺,2p⁻' at x = 3/5, c.f. Fig. 2.

All members of the Na₁₊ₓCuO₂ 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 'Na₇Cu₄O₈' (4p⁺,4p⁻), c.f. Fig. 2 and 3.

It is obvious that even elusive 'Na₂CuO₂' can exist in the topology of a stuffed NaCuO₂ 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 'Na₂CuO₂' represents a completely new type of structure.

Moreover, a rule for the charge ordering of Cu²⁺ and Cu³⁺ can be derived. Cu³⁺ 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 Na$_{1+x}$CuO$_2$ compounds, and allows predicting new possible constitutions (Fig. 4).

The hypothetical Na$_{1+x}$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 Na$_{12}$Cu$_7$O$_{14}$ and Na$_7$Cu$_4$O$_8$. In addition, the structures of NaCuO$_2$ and Na$_2$CuO$_2$ 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$_7$Cu$_4$O$_8$ 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$_2$CuO$_2$. 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 Na$_{12}$Cu$_7$O$_{14}$ and Na$_7$Cu$_4$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 Na$_5$Cu$_3$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: