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Synthesis, structure and properties of new chain cuprates, $Na_3Cu_2O_4$ and $Na_8Cu_5O_{10}$

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Abstract

$Na_3Cu_2O_4$ and $Na_8Cu_5O_{10}$ were prepared via the azide/nitrate route from stoichiometric mixtures of the precursors CuO, NaN_3 and $NaNO_3$. Single crystals have been grown by subsequent annealing of the as prepared powders at 500 °C for 2000 h in silver crucibles, which were sealed in glass ampoules under dried Ar. According to the X-ray analysis of the crystal structures ($Na_3Cu_2O_4$: $P2_1/n$, $Z = 4$, $a = 5.7046(2)$, $b = 11.0591(4)$, $c = 8.0261(3)$ Å, $\beta = 108.389(1)^\circ$, 2516 independent reflections, $R_1(\text{all}) = 0.0813$, wR_2 (all) $= 0.1223$; $Na_8Cu_5O_{10}$: Cm, $Z = 2$, $a = 8.228(1)$, $b = 13.929(2)$, $c = 5.707(1)$ Å, $\beta = 111.718(2)^\circ$, 2949 independent reflections, $R_1(\text{all}) = 0.0349$, wR_2 (all) $= 0.0850$), the main feature of both crystal structures are CuO_2 chains built up from planar, edge-sharing CuO_4 squares. From the analysis of the Cu–O bond lengths, the valence states of either +2 or +3 can be unambiguously assigned to each copper atom. In $Na_3Cu_2O_4$ these ions alternate in the chains, in $Na_8Cu_5O_{10}$ the periodically repeated part consists of five atoms according to Cu^{II}–Cu^{II}–Cu^{III}–Cu^{II}–Cu^{III}. The magnetic susceptibilities show the dominance of antiferromagnetic interactions. At high temperatures the compounds exhibit Curie–Weiss behaviour ($Na_3Cu_2O_4$: $\mu = 1.7\,\mu_B$, $\Theta = -160$ K, $Na_8Cu_5O_{10}$: $\mu = 1.8\,\mu_B$, $\Theta = -58$ K, magnetic moments per divalent copper ion). Antiferromagmetic ordering is observed to occur in these compounds below 13 K ($Na_3Cu_2O_4$) and 24 K ($Na_8Cu_5O_{10}$).

Keywords: Sodium copper oxide; Azide/nitrate route; Crystal structure; Magnetic properties

1. Introduction

Transition metal oxides exhibit a fascinating richness in physical properties. Among these, metal–insulator transitions, high-temperature superconductivity and colossal magnetoresistance provide a basis for manifold applications. Primarily, the underlying microscopic effects can be traced back to the strong electron interactions effective in such compounds, expressing themselves in order–disorder phenomena with respect to charges, spins and orbitals [1]. Efforts in developing a comprehensive microscopic description of the underlying interactions have suffered from the lack of simple model systems with undisturbed translational symmetry.

Recently, a novel, and versatile, route [2] to the synthesis of alkalioxometallates has become available which offers a number of advantages over the conventional approaches. As a source for the alkali metal component, mixtures of the respective alkali azides and nitrates (or nitrites) are used instead of the alkali oxides which are intricate to prepare and notoriously difficult to handle. As a most attractive feature, beside the metals' ratio also the oxygen content, and thus the degree and kind of doping, of the desired product can be effectively controlled by weighing out the starting materials in appropriate portions. Employing this procedure, the title compounds have been prepared as microcrystalline pure phases in gram-amounts. In this work, we present synthesis, crystal structures and properties of these sodium oxocuprates (II, III) with precisely adjusted Cu^{II}/Cu^{III} rations and fully expressed translational order. The unique phenomenon, the formation of one-dimensional Wigner lattices, was observed in the title compounds [3].

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2. Experimental

Starting materials for the preparation of the sodium cuprates were sodium nitrate (Merck, 99.99%), sodium azide (Sigma-Aldrich, 99.99%) and copper oxide CuO prepared by heating $Cu(C_2O_4)\,\frac{1}{2}H_2O$ in a flow of oxygen at 320 °C, for 20 h. The starting materials (NaN_3, $NaNO_3$ and CuO) were mixed in the ratio required according to the general Eq. (1) with respect to the desired x ($x = 0.5$ for $Na_3Cu_2O_4$ and $x = 0.6$ for $Na_8Cu_5O_{10}$):

$$\left(\tfrac{2}{3} + x\right)NaN_3 + \tfrac{1}{3}NaNO_3 + CuO = Na_{1+x}CuO_2 + \left(2\tfrac{1}{3} + 3x\right)/2N_2 \quad (1)$$

milled in a planet ball mill, pressed in pellets under 10^5 N, dried under vacuum (10^{-3} mbar) at 150 °C for 12 h, and placed under argon in a tightly closed steel container [4], provided with a silver inlay. In a flow of dry argon the following temperature profile was applied: 25→260 °C (100 °C/h); 260→400 °C (5 °C/h); 400→650 °C (600 °C/h); 650→670 °C (200 °C/h) and subsequent annealing for 20 h at 670 °C. Caution: If heated too rapidly the containers may blow up!

The obtained black powders, being very sensitive to humid air, were sealed in glass ampoules under argon atmosphere and all following manipulations with these substances were performed in inert atmospheres of purified argon.

Single crystals have been grown by subsequent annealing of the pressed in pellets powders at 500 °C for 2000 h in silver crucibles, which were sealed in glass ampoules under dried Ar.

The X-ray investigation on powder samples was performed using a STOE Stadi P diffractometer with Cu-$K_{\alpha 1}$ radiation ($\lambda = 1.54178$ Å) at room temperature using a position-sensitive detector and a curved germanium monochromator. The collected powder data for $Na_3Cu_2O_4$ and $Na_8Cu_5O_{10}$ are given in Figs. 1 and 2, respectively. The single crystal diffraction data were collected on a four-cycle diffractometer (Bruker AXS) equipped with a SMART-CCD (APEX), at 293 K.

Thermal analyses were carried out using a DTA/TG device (STA 409, Netzsch) coupled with a quadrupole mass spectrometer (QMG 421, Balzers). The samples were heated at a rate of 10 K/min in a corundum crucible, under dry argon.

The magnetic susceptibility χ(T) was measured in the temperature range from 2 to 350 K ($Na_8Cu_5O_{10}$), and from 5 to 330 K ($Na_3Cu_2O_4$), in magnetic fields up to 5 T using a SQUID-Magnetometer (MPMS 5.5, Quantum Design). The diamagnetic correction has been applied using tabulated values [5].

3. Results and discussion

The title compounds $Na_3Cu_2O_4$ and $Na_8Cu_5O_{10}$ have been prepared as microcrystalline, pure phases in gram-amounts. They begin to decompose at about 700 °C ($Na_3Cu_2O_4$) and 750 °C ($Na_8Cu_5O_{10}$), leaving mixtures of NaCuO [6–8] and $NaCu_2O_2$ [8–10] as the only solid residues. The crystal structures of the title compounds were determined from single crystal data collected at 293 K. According to the systematic extinction only one space group ($P2_1/n$) was possible for $Na_3Cu_2O_4$, while for Na_8Cu_5O10 there were three potential candidates: *C*2, *Cm* and *C*2/*m*. All these three possibilities were proven by solving the structure by direct methods. Only in the space group *Cm* a reasonable solution could be found. For X-ray and crystallographic data, see Tables 1 and 2. Atom coordinates and temperature parameters are given in Tables 3–6.

The new oxocuprates(II/III) belong to the compositional series $Na_{1+x}CuO_2$, with the end members $NaCuO_2$ [11–13]

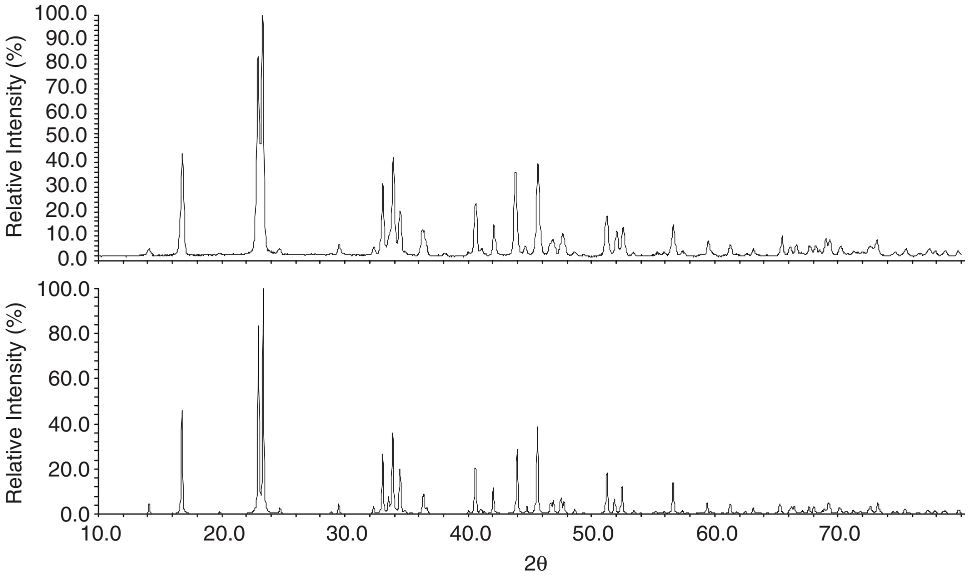

Fig. 1. Measured XRD pattern of $Na_3Cu_2O_4$ (above) and calculated from single-crystal data (below).

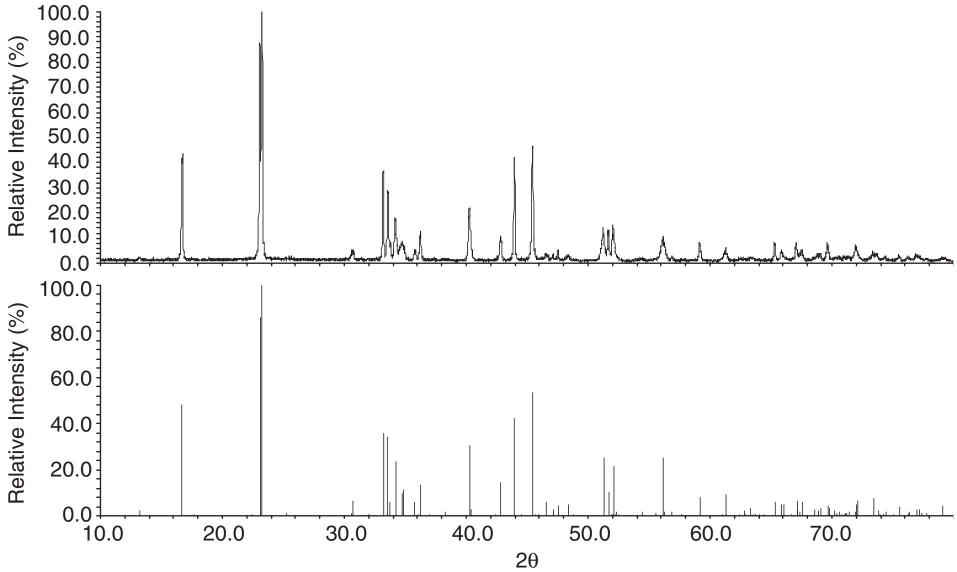

Fig. 2. Measured XRD pattern of $Na_8Cu_5O_{10}$ (above) and calculated from single-crystal data (below).

Table 1
X-ray and crystallographic data for $Na_3Cu_2O_4$

Crystal data	
Crystal system	Monoclinic
Space group, Z	$P2_1/n$ (No. 14), 4
Lattice constants (powder data) (Å and deg.)	$a = 5.7046(2)$ $b = 11.0591(4)$ $c = 8.0261(3)$ $\beta = 108.389(1)$
Molar volume (cm^3/mol)	120.4
Molar mass (g/mol)	260.05
Calculated density (g/cm^3)	3.59
Crystal shape, colour	Sticks, black
Crystal size, (mm^3)	$0.3 \times 0.2 \times 0.1$
Structure determination	
Structure solution, refinement	Direct methods, full-matrix least-squares on F^2
Parameters refined	82
R_1 ($Fo > 4\,\mathrm{sig}\,Fo^2$/all)	0.0525/0.0813
wR_2	0.1223
Weighting factor w	$w = 1/(\sigma^2(Fo^2) + (0.0621P)^2)$, $P = (\max(Fo^2,0) + 2Fc^2)/3$
$\Delta\rho_{\min}/\rho_{\max}$ (e$^-$/Å^3)	$-1.47/3.58$
Data collection	
Diffractometer	Bruker AXS, APEX SMART-CCD
Monochromator	Graphite
Wavelength λ (Å)	Mo-K_α, 0.71073
2Θ range for data collection	$2\Theta < 75.10$
$h\,k\,l$-range	$-9 < h < 9$, $-18 < k < 18$, $-13 < l < 13$
Absorption correction	SADABS [17]
Total no. reflections	9556
Unique reflections	2516
Absorption coefficient μ (mm^{-1})	9.00
$F(000)$	492

Table 2
X-ray and crystallographic data for $Na_8Cu_5O_{10}$

Crystal data	
Crystal system	Monoclinic
Space group, Z	Cm (No. 8), 2
Lattice constants (Å and deg.)	$a = 8.228(1)$ $b = 13.929(2)$ $c = 5.707(1)$ $\beta = 111.718(2)$
Molar mass (g/mol)	330.81
Molar volume (cm^3/mol)	365.96
Calculated density (g/cm^3)	3.62
Crystal shape, colour	Sticks, black
Crystal size (mm^3)	$0.4 \times 0.2 \times 0.2$
Structure determination	
Structure solution, -refinement	Direct methods, full-matrix least-squares on F^2
Parameters refined	112
R_1 ($F_0 > 4\,\mathrm{sig}(Fo)$/all)	0.0299/0.0349
wR_2	0.0850
Weighting factor w	$w = 1/(\sigma^2(Fo^2) + (0.0467P)^2)$, $P = (\max(Fo^2,0) + 2Fc^2)/3$
$\Delta\rho_{\min}/\rho_{\max}$ (e$^-$/Å^3)	$-1.31/0.79$
Data collection	
Diffractometer	Bruker AXS, APEX SMART-CCD
Monochromator	Graphite
Wavelength λ (Å)	Mo-K_α, 0.71073
2Θ range for data collection	$2\Theta < 72.94$ $-13 < h < 13$, $-23 < k < 23$, $-9 < l < 9$
Absorption correction	SADABS [17]
Total no. reflections	5747
Unique reflections	2949
Absorption coefficient μ (mm^{-1})	8.94
$F(000)$	626

and still elusive Na_2CuO_2. The most prominent structural feature, common to all representatives known thus far, is a one-dimensional polyanion $^{1}_{\infty}CuO_2^{n-}$ constituted of CuO_4-square units sharing edges in trans-position, see Fig. 3. The chains, running along b (Fig. 4), are slightly wave-like, as can be seen in Fig. 5. The sodium ions, which achieve coordination numbers (CN) of 4–5 with plausible Na–O bond lengths ranging from 2.270 to 2.788 Å (c.f. Tables 7 and 8), are embedded between these anionic entities in the structure. The projections of the crystal structures on (0 1 0) are given in Fig. 4. The geometric data as determined by single-crystal structural analyses give clear evidence for a charge ordering at the copper sites. Based on the copper oxygen bond lengths, one can distinguish Cu^{II} and Cu^{III} sites, unambiguously. In $Na_3Cu_2O_4$ these ions alternate in the chains, while in $Na_8Cu_5O_{10}$ the periodically repeated part consists of five copper atoms in the sequence Cu^{II}–Cu^{II}–Cu^{III}–Cu^{II}–Cu^{III} (see Fig. 3). The way of linking the primary structural units (squares), together with the variations of the copper to oxygen distances, inevitably lead to deviations of the O–Cu–O angles from the ideal 90°. Interatomic distances, CN, effective coordination numbers (ECoN) and mean fictive ionic radii (MEFIR) [14] for $Na_3Cu_2O_4$ and $Na_8Cu_5O_{10}$ are given in Tables 7 and 8, respectively.

Table 3
Atomic coordinates and isotropic thermal parameters (in Å^2) for $Na_3Cu_2O_4$

Atom	Site	x	y	z	U_{eq}
Cu1	4e	0.24258(8)	0.42473(4)	0.77268(6)	0.0104(1)
Cu2	4e	0.25876(8)	0.17312(4)	0.75895(6)	0.0089(1)
Na1	4e	0.2230(3)	0.5793(2)	0.1237(2)	0.0155(3)
Na2	4e	0.2255(3)	0.2975(2)	0.1192(2)	0.0160(3)
Na3	4e	0.3173(4)	0.3895(2)	0.4461(3)	0.0292(5)
O1	4e	0.0643(5)	0.2869(2)	0.8223(4)	0.0123(5)
O2	4e	0.4495(5)	0.2985(2)	0.7285(4)	0.0161(5)
O3	4e	0.4398(6)	0.5491(3)	0.7154(4)	0.0182(6)
O4	4e	0.0459(5)	0.5603(2)	0.8069(4)	0.0132(5)

Table 4
Atomic coordinates and isotropic thermal parameters (in Å^2) for $Na_8Cu_5O_{10}$

Atom	Site	X	y	z	U_{eq}
Cu1	4b	0.2722(1)	0.9011(1)	0.2215(1)	0.0115(1)
Cu2	4b	0.2833(1)	0.6989(1)	0.2501(1)	0.0093(1)
Cu3	2a	0.3014(1)	$\frac{1}{2}$	0.2756(1)	0.0102(2)
Na1	4b	0.1550(3)	0.8898(1)	0.6399(5)	0.0153(4)
Na2	2a	0.9095(4)	0	0.8487(6)	0.0150(5)
Na3	4b	0.9261(3)	0.7790(1)	0.8569(4)	0.0221(4)
Na4	4b	0.5984(3)	0.8606(2)	0.6049(5)	0.0508(7)
Na5	2a	0.4759(3)	0	0.9013(5)	0.0257(4)
O1	2a	0.2175(8)	0	0.970(1)	0.0131(9)
O2	2a	0.3367(8)	0	0.472(2)	0.019(1)
O3	4b	0.2406(8)	0.5994(2)	0.019(1)	0.0179(9)
O4	4b	0.3210(6)	0.8009(2)	0.4698(9)	0.0172(8)
O5	4b	0.2241(7)	0.7924(2)	0.9953(8)	0.0188(9)
O6	4b	0.3467(6)	0.6071(2)	0.5059(8)	0.0113(7)

The crystal structures of both new cuprates are very similar, in spite of the fact, that the symmetry descriptions are most different. The two compounds differ in the Na/CuO_2 ratios, determining the Cu^{II}/Cu^{III} ratios, as well as the periodicity along b (chain direction). Both compounds belong to the general family $Na_{1+x}CuO_2$, out of which three members' $NaCuO_2$ [11–13] ($x = 0$), $Na_3Cu_2O_4$ ($x = 0.5$) and $Na_8Cu_5O_{10}$ ($x = 0.6$), are known, thus far. The title cuprates show a virtually identical chain arrangement, leading to nearly the same distribution of cation sites, which are filled by sodium ions in different ways (depending on the respective composition). The CuO_2 chains are stacked into layers separated by slabs of sodium atoms (Fig. 4). The chains' orientation in $Na_3Cu_2O_4$ and $Na_8Cu_5O_{10}$ differs from that one in $NaCuO_2$. In the latter the chains are canted against the layers mentioned, while they are oriented perpendicular to the planes in the mixed-valent cuprates (see Fig. 4). This leads to a significant divergence in the distances between the chains which is reflected by variations in the lattice constants. For a direct comparison of cell parameters, one can choose for $Na_3Cu_2O_4$ other basic vectors, which would correspond to those of $NaCuO_2$ and $Na_8Cu_5O_{10}$. The reduced b lattice

Table 5
Anisotropic thermal displacement parameters (in Å^2) for $Na_3Cu_2O_4$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu1	0.0108(2)	0.0089(2)	0.0139(2)	−0.0002(2)	0.0072(2)	0.0002(2)
Cu2	0.0082(2)	0.0090(2)	0.011(2)	−0.0010(1)	0.0578(2)	−0.0003(1)
Na1	0.0135(7)	0.0126(7)	0.0205(8)	−0.0005(6)	0.0056(6)	0.0006(6)
Na2	0.0144(8)	0.0165(8)	0.0175(7)	0.0024(6)	0.0055(6)	0.0017(6)
Na3	0.0233(9)	0.047(2)	0.0194(9)	0.0087(8)	0.0094(7)	0.0034(9)
O1	0.011(2)	0.011(2)	0.016(2)	−0.0013(9)	0.0060(9)	0.0023(9)
O2	0.013(2)	0.012(2)	0.028(2)	−0.004(2)	0.012(2)	−0.0025(9)
O3	0.018(2)	0.011(2)	0.031(2)	0.002(1)	0.016(2)	0.002(1)
O4	0.013(2)	0.010(2)	0.020(2)	0.0002(9)	0.010(1)	−0.0013(9)

Table 6
Anisotropic thermal displacement parameters (in Å^2) for $Na_8Cu_5O_{10}$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu1	0.0140(3)	0.0116(2)	0.0092(3)	0.0022(1)	0.0045(2)	0.0018(1)
Cu2	0.0108(1)	0.0099(1)	0.0072(1)	0.0014(1)	0.0031(1)	0.0013(1)
Cu3	0.0110(4)	0.0118(2)	0.0069(4)	0	0.0021(3)	0
Na1	0.0130(8)	0.0169(7)	0.016(2)	0.0008(5)	0.0060(7)	−0.0005(5)
Na2	0.019(2)	0.0159(9)	0.011(2)	0	0.0066(9)	0
Na3	0.0264(8)	0.0266(7)	0.0137(7)	−0.0099(6)	0.0080(6)	−0.0014(6)
Na4	0.0310(9)	0.102(2)	0.0231(8)	−0.040(2)	0.0144(8)	−0.026(2)
Na5	0.0129(8)	0.044(2)	0.0182(9)	0	0.0031(6)	0
O1	0.018(2)	0.018(2)	0.011(2)	0	0.006(2)	0
O2	0.031(2)	0.015(2)	0.010(2)	0	0.005(2)	0
O3	0.031(2)	0.011(2)	0.011(2)	−0.0028(9)	0.006(2)	−0.0010(9)
O4	0.021(2)	0.021(2)	0.009(2)	0.0078(9)	0.005(2)	0.0026(9)
O5	0.024(2)	0.022(2)	0.011(2)	0.008(1)	0.007(2)	0.006(2)
O6	0.014(2)	0.010(2)	0.009(2)	−0.0006(8)	0.003(2)	−0.0001(8)

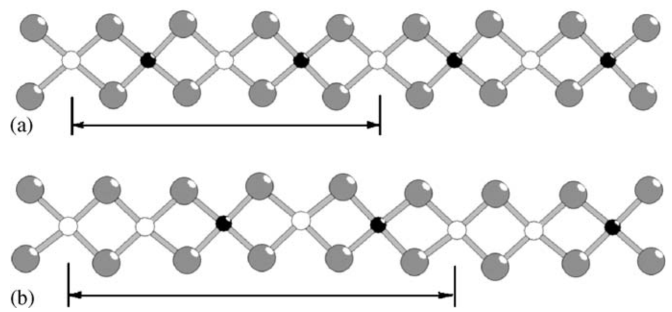

Fig. 3. CuO_2 chains in $Na_3Cu_2O_4$ (a) and $Na_8Cu_5O_{10}$ (b): Cu^{II}—white, Cu^{III}—black, O—gray. The perioically repeated units are marked for each chain.

constant was defined as $\frac{1}{4}$ for $Na_3Cu_2O_4$, and $\frac{1}{5}$ for $Na_8Cu_5O_{10}$, of the original b parameters. A comparison of the uniformed cells is given in Table 9.

Two neighbouring CuO_2 chains in $Na_{1+x}CuO_2$ cuprates are shifted against each other by $b/2$. This constitutes a principle difference with respect to the $MCuO_2$ cuprates formed by the bigger alkali metals ($M = K$ [12], Rb, Cs [15]), where the chains are not shifted in the b direction, with respect to each other. Thus, in these latter compounds there is only one cation site per copper atom, a prism with a distorted rhombic basis. In the $Na_{1+x}CuO_2$ family, however, one has one octahedral and two tetrahedral sites per copper atom.

The structures of title cuprates can be interrelated by introducing the fourth dimension into the symmetry description and considering the structures as composite modulated ones. In such a description the title compounds have a common small basic unit cell (containing only one CuO_2 unit) and the same superspace group, but different propagation vectors along the chain direction, which are in

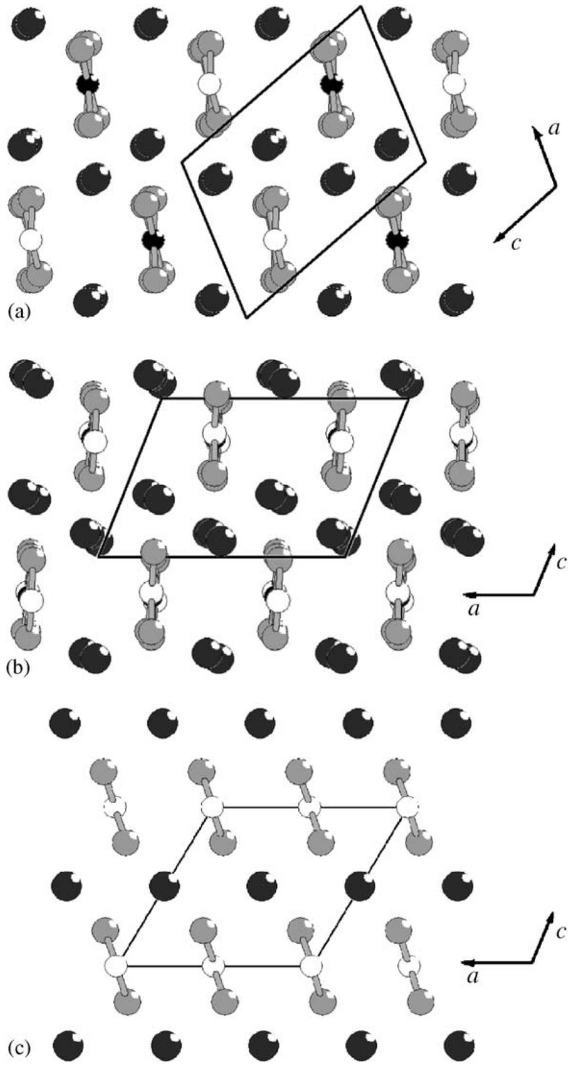

Fig. 4. Crystal structures of $Na_3Cu_2O_4$ (a), $Na_8Cu_5O_{10}$ (b) and $NaCuO_2$ (c). Views along [010].

case of commensurate modulations $3/4b^*$ and $4/5b^*$, for $Na_3Cu_2O_4$ and $Na_8Cu_5O_{10}$, respectively. The detailed structure descriptions in 4D space for both cuprates as well as observed formation of nonstoichiometric $Na_{8\pm y}Cu_5O_{10}$ compositions with incommensurate modulations are out of the coverage of this work and will be published elsewhere [16].

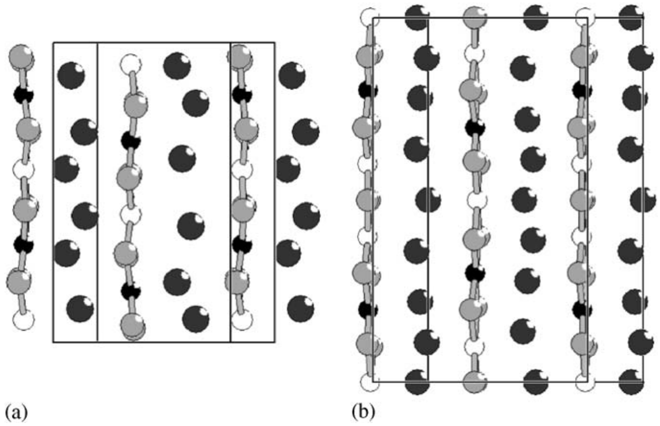

Fig. 5. Crystal structures of $Na_3Cu_2O_4$ (a) and $Na_8Cu_5O_{10}$ (b) showing the periodicities of Na atoms and CuO_2 units.

The magnetic susceptibilities of $Na_3Cu_2O_4$ and $Na_8Cu_5O_{10}$ have been measured for magnetic fields ranging from 0.001 to 5 T. The susceptibilities, which were independent on the magnetic field strength, are displayed in Fig. 6 for $H = 1\,T$. For a better comparability, the susceptibility data are given per one magnetic centre ($S^{+2}_{Cu} = \frac{1}{2}$, $S^{+3}_{Cu} = 0$), that is $\chi = \chi_{mole}$ for $Na_3Cu_2O_4$ and $\chi = 1/3\chi_{mole}$ for $Na_8Cu_5O_{10}$. Qualitatively, both compounds show a similar behaviour reflecting an antiferromagnetic character of one-dimensional spin interactions. The most obvious difference in the magnetic properties as displayed in Fig. 6 is the significantly higher χ-values of $Na_8Cu_5O_{10}$ (given per one Cu^{+2} ion) as compared to $Na_3Cu_2O_4$. The difference amounts to about 15% at 300 K and grows rapidly on lowering the temperature. This is indicative of a stronger antiferromagnetic spin exchange in $Na_3Cu_2O_4$, which is also reflected by the maximum of $\chi(T)$ occurring already at 110 K while it takes place at 28 K for

Table 7
Interatomic distances (in Å), CN, ECoN and MEFIR [14] (in Å) for $Na_3Cu_2O_4$

Atom	O1	O2	O3	O4	CN	ECoN	MEFIR
Cu1	1.942	1.931	1.923	1.943	4	4.0	0.53
Cu2	1.852	1.826	1.831	1.857	4	4.0	0.43
Na1	2.348	2.307	2.412	2.364 2.431	5	4.9	0.93
Na2	2.270 2.297	2.292	2.585	2.409	5	4.6	0.90
Na3	2.768	2.375	2.279 2.707	2.464	5	4.2	0.94
CN	6	5	6	6			
ECoN	5.3	5.0	5.1	5.9			
MEFIR	1.42	1.41	1.44	1.45			

Table 8
Interatomic distances (in Å), CN, ECoN and MEFIR [14] (in Å) for $Na_8Cu_5O_{10}$

Atom	O1	O2	O3	O4	O5	O6	CN	ECoN	MEFIR
Cu1	1.921	1.915		1.923	1.933		4	4.0	0.52
Cu2			1.8543	1.843	1.878	1.864	4	4.0	0.45
Cu3			1.940 1.940			1.931 1.931	4	4.0	0.53
Na1	2.333	2.563		2.308	2.328	2.363	5	4.8	0.93
Na2	2.368		2.408 2.408			2.360 2.360	5	5.0	0.97
Na3			2.665	2.335	2.289 2.312	2.447	5	4.5	0.92
Na4		2.788	2.286	2.279		2.356	4	3.4	0.90
Na5	2.299	2.287	2.455 2.455				4	3.8	0.91
CN	6	7	6	5	5	6			
ECoN	6.0	5.4	5.5	5.0	5.1	5.9			
MEFIR	1.41	1.46	1.44	1.41	1.42	1.43			

Table 9
Cell constants of uniformed cells for $NaCuO_2$, $Na_3Cu_2O_4$ and $Na_8Cu_5O_{10}$

Cell constants	$NaCuO_2$	$Na_3Cu_2O_4$	$Na_8Cu_5O_{10}$
a (Å)	6.35	8.24	8.23
b (Å)	2.75	(2*)2.76	(5*)2.79
c (Å)	6.10	5.72	5.71
β (deg.)	120.77	112.49	111.72
V (Å^3)	91.50	(2*)120.40	(5*)121.52

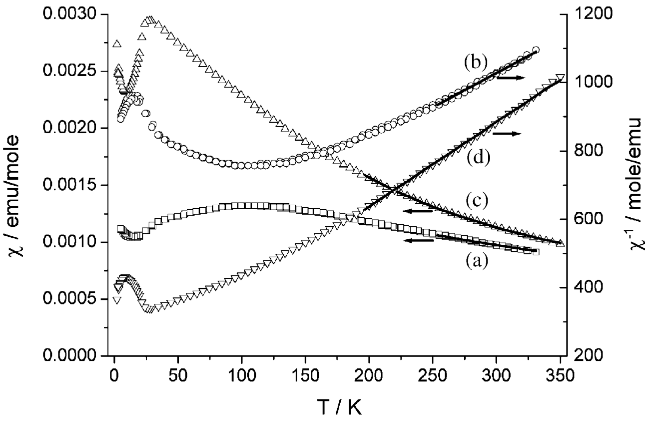

Fig. 6. Magnetic properties of $Na_3Cu_2O_4$ (a, b) and $Na_8Cu_5O_{10}$ (c, d) represented as χ vs. T (a, c) and χ^{-1} vs. T (b, d). The full line corresponds to the fit by the Curie–Weiss law.

$Na_8Cu_5O_{10}$. In the high temperature range (250–330 K for $Na_3Cu_2O_4$ and 200–350 K for $Na_8Cu_5O_{10}$) the magnetic behaviour can be evaluated applying the Curie–Weiss law, resulting in $\mu = 1.7\,\mu_B$, $\Theta = -160\,K$ and $\mu = 1.8\,\mu_B$, $\Theta = -58\,K$, for $Na_3Cu_2O_4$ and $Na_8Cu_5O_{10}$, respectively. At low temperatures, the interchain exchange becomes significant. Thus, below 13 K ($Na_3Cu_2O_4$), and 24 K ($Na_8Cu_5O_{10}$), three-dimensional antiferromagnetic ordering occurs.

In this article, the synthesis via the azide/nitrate route, structure determination from single-crystal data, as well as thermal and magnetic properties of two new sodium mixed-valent sodium cuprate (II,III) are present. The structural and magnetic properties are discussed.

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