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Crystal Structures of $NaCuO_2$ and $KCuO_2$ by Neutron Diffraction

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The structures of $NaCuO_2$ and $KCuO_2$ have been refined from time-of-flight neutron data. $NaCuO_2$ is monoclinic: space group $C2/m$, a = 6.3512(2) Å, b = 2.7474(1) Å, c = 6.1027(2) Å, β = 120.767(2)° with Cu–O = 1.839(1) Å (4×). $KCuO_2$ is orthorhombic: space group $Cmcm$, a = 4.3742(1) Å, b = 11.6859(4) Å, c = 5.4124(2) Å with Cu–O = 1.826(3) Å (2×) and 1.832(2) Å (2×). Both structures contain strings of edge-sharing CuO_4 rectangles. The sodium atoms center octahedra and the potassium atoms center trigonal prisms. Aspects of the crystal chemistry of both compounds are discussed.

Introduction

Pervading the extensive literature on oxide superconductors is a general interest in trivalent copper materials. Although band (*1–3*) and Madelung potential (*4*) calculations suggest that O^{2-} is more readily oxidized than Cu^{2+} in these compounds, it is instructive to analyze them in terms of bond valences (*5*). To this end, we wanted to determine accurate bond valence parameters for Cu^{3+} to oxygen.

Much of the work on trivalent copper oxides was done by Hoppe and his co-workers. $KCuO_2$ was first prepared by Wahl and Klemm (*6, 7*), and the structure was solved by Hestermann and Hoppe using data from single crystal X-ray photographs (*8*). $RbCuO_2$ and $CsCuO_2$ are isostructural. The structure of $NaCuO_2$ was solved in $P\bar{1}$ by trial and error from a Guinier powder pattern (*9*).

Since these structure determinations were not very precise and since standard cell reduction programs suggested $NaCuO_2$ was actually monoclinic (indeed very close to orthorhombic metrically), we undertook neutron diffraction studies of these materials. The bond lengths determined from these studies are expected to be more accurate.

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Experimental

Synthesis

$KCuO_2$ can be formed at temperatures ranging from 300 to 450°C. The neutron powder sample was prepared by pressing equimolar amounts of KO_2 (96.5%, Alfa) and CuO (A. C. S. reagent, Aldrich) into pellets and heating for 6 days under flowing O_2 at 400°C. The pellets increase in size and become more porous during the course of reaction. The blue-black product was quickly transferred to an Ar-filled dry box, since it reacts with water vapor very rapidly.

The neutron sample of $NaCuO_2$ was prepared by heating Na_2O_2 (98%, Alfa) and CuO for 2 weeks at 400°C. A 10% M excess of Na_2O_2 was used. The ternary compound formed from both pellets and intimately mixed free-flowing powders and was also blue-black in color. Again samples were handled in a dry box.

Structural Study

Neutron diffraction data were collected at room temperature on the high intensity powder diffractometer (HIPD) of the LANSCE facility at Los Alamos National Laboratory. The powder data were refined with use of the generalized crystal structure analysis system (GSAS), a Rietveld profile analysis code (*10*). Data were collected from the $2\theta = 153°, 90°, 39°$, and 20° detector banks.

$NaCuO_2$. Hoppe originally solved this structure from X-ray powder data in the triclinic space group $P\bar{1}$. A standard cell reduction program produced a *C*-centered monoclinic cell of twice the original volume. In order to maintain the center of symmetry, we chose the space group $C2/m$ (confirmed by the subsequent analysis). The final refinement included 993 reflections in the range $0.4\ \text{Å} < d < 3.0\ \text{Å}$ (4180 profile points). The 36 variables refined included a scale factor, nine background parameters, four peak profile parameters (*11*) (α_1, β_0, β_1, σ_1), a diffractometer zero constant, lattice parameters, atomic positional parameters and occupancies (the refined values did not differ significantly from unity and therefore were not included in the final refinement), and anisotropic thermal parameters. In addition, the scale factor for a trace of CuO impurity was included. The final agreement indices are $R_p = 0.019$ and $R_{wp} = 0.029$ with a reduced $\chi^2 = 2.32$. Figure 1 shows the final Rietveld profile fit for $NaCuO_2$. Atomic parameters and anisotropic thermal parameters are given in Tables I and II, respectively. Structure amplitudes are given in Table III.[2]

TABLE I

POSITIONAL PARAMETERS[a] FOR $NaCuO_2$

Atom	Site	x	y	z	$100U_{iso}$
Na	2*d*	0	$\frac{1}{2}$	$\frac{1}{2}$	0.90
Cu	2*a*	0	0	0	0.41
O	4*i*	0.3334(1)	0	0.7773(1)	0.60

[a] Space group $C2/m$, $a = 6.3512(2)$ Å, $b = 2.7474(1)$ Å, $c = 6.1027(2)$ Å, $\beta = 120.767(2)°$.

$KCuO_2$. Hoppe's model in the space group *Cmcm* was used as a starting model. Since $KCuO_2$ has higher symmetry than $NaCuO_2$, fewer peaks were found. Therefore we used the data from both the 153° and 90° detector banks. The final refinement included 921 independent reflections in the range $0.48\ \text{Å} < d < 3.0\ \text{Å}$ for the backscattering data, and 735 reflections in

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[2] See NAPS Document No. 4712 for 20 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 up to 20 pages plus \$.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling, for the first 20 pages, and \$1.00 for additional 10 pages of material, \$1.50 for postage of any microfiche orders.

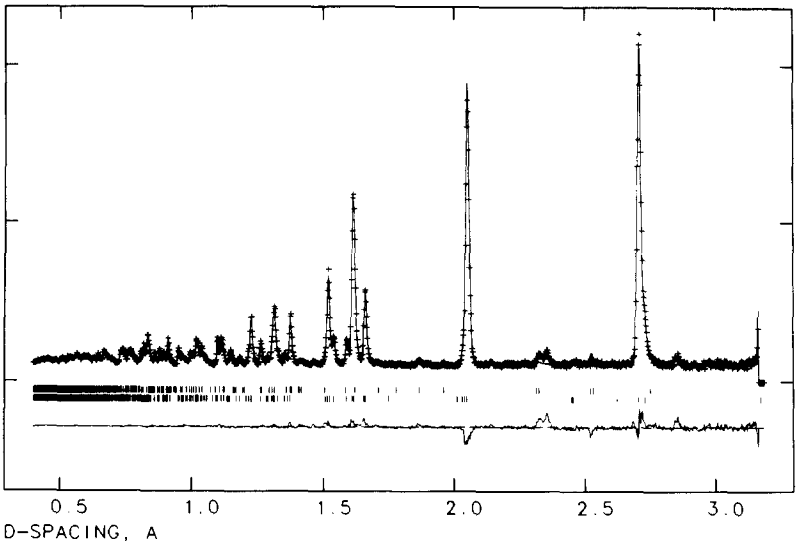

FIG. 1. Neutron diffraction profile fit for $\mathrm{NaCuO_2}$. The data points are shown as "+" and the calculated profile is the solid line. The difference curve at the bottom is on the same scale as the data. The lower tick marks indicate peak positions for $\mathrm{NaCuO_2}$ and the upper marks show the positions of peaks due to CuO. The unmatched peaks at 2.85 and 2.35 Å arise from the moderator.

the range 0.5 Å $< d <$ 4.2 Å for the 90° bank. The 44 variables refined included two scale factors, 18 background parameters (9 for each bank), two peak profile parameters (σ_1), diffractometer zero constants, lattice parameters, atomic positional parameters and occupancies (the refined values did not differ significantly from unity and therefore were not included in the final refinement), and anisotropic thermal parameters. In addition two scale factors for CuO were included. The final agreement indices are $R_p = 0.022$ and $R_{wp} = 0.030$ with a reduced $\chi^2 = 2.69$. Figure 2 shows the final Rietveld profile fit for $\mathrm{KCuO_2}$. Atomic parameters are given in Tables IV and V, and structure amplitudes are given in Table VI.[3]

TABLE II

ANISOTROPIC THERMAL PARAMETERS FOR $\mathrm{NaCuO_2}$[a]

Atom	U_{11}	U_{22}	U_{33}	U_{13}
Na	0.74(7)	1.22(8)	0.75(7)	0.28(5)
Cu	0.58(5)	0.27(4)	0.39(5)	−0.06(3)
O	0.84(5)	0.33(4)	0.62(4)	0.05(3)

[a] All values to be multiplied by 10^{-2} Å^2. $U_{12} = U_{23} = 0$.

Discussion

The structure of $\mathrm{NaCuO_2}$ is shown in clinographic projection in Fig. 3. The salient features of the structure are the isolated chains of edge-sharing $\mathrm{CuO_4}$ rectangles running along *b* and the layers of edge-sharing $\mathrm{NaO_6}$ octahedra. The structure is in fact closely related to that of α-$\mathrm{NaFeO_2}$ (itself a superstructure of the NaCl structure) as can be seen from Fig. 4 in which (on the left) the structure is shown projected on (010). In the center of the figure the same projection is shown but now the next-nearest oxygen neighbors of copper are included to form a very distorted octahedron around the copper atoms. On the right of the figure the structure of $\mathrm{NaCoO_2}$ is shown

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[3] See NAPS Document No. 4713 for 39 pages of supplementary materials. Ordering information in footnote 2.

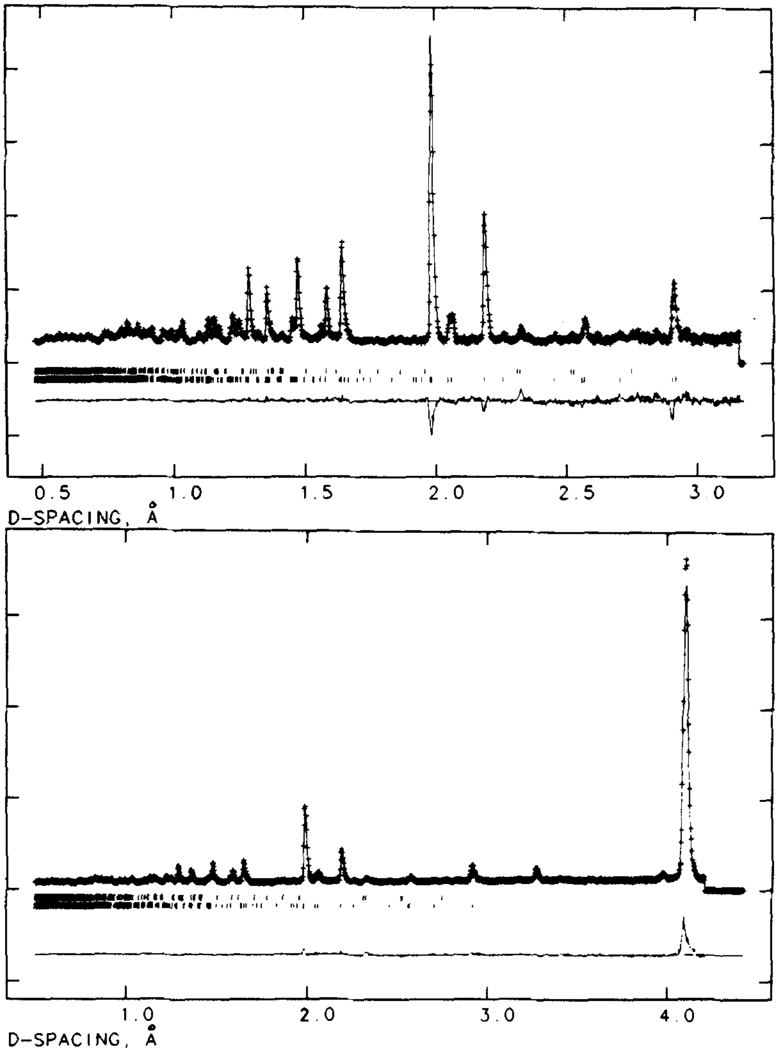

FIG. 2. Neutron diffraction profile fit for $KCuO_2$. The data points are shown as "+" and the calculated profile is the solid line. The difference curve at the bottom is on the same scale as the data. The lower tick marks indicate peak positions for $KCuO_2$ and the upper marks show the positions of peaks due to CuO.

for comparison (*12*): it can be seen that the octahedra around the transition metal are now much more regular at the expense of the octahedra around the sodium atoms.

Also apparent from Fig. 4 (left) is the fact that the positions of the Na and Cu atoms in $NaCuO_2$ have transformed to an arrangement that is now more nearly hexagonal eutaxy ("close packing") than the cubic arrangement in the parent NaCl structure. This observation can be made more quantitative by transforming the original cell to the one appropriate for hexagonal packing. The axes are transformed according to the matrix ($\frac{1}{2}$ $\frac{1}{2}$ 0/$-\frac{1}{2}$ $\frac{1}{2}$ 0/$\frac{1}{2}$ 0 1); the new "unit cell" has parameters (with values for ideal hexagonal eutaxy in parentheses) $a = b$, $c/a = 1.52(1.63)$, $\alpha = 90.5°(90.0)$, $\beta =$

TABLE IV

POSITIONAL PARAMETERS[a] FOR $KCuO_2$

Atom	Site	x	y	z	$100U_{iso}$ (Å^2)
K	4c	0	0.3008(2)	$\frac{1}{4}$	1.27(4)
Cu	4c	0	0.0033(1)	$\frac{1}{4}$	0.70(3)
O	8f	0	0.10522(5)	−0.0072(3)	1.37(2)

[a] Space group *Cmcm*, a = 4.3742(1) Å, b = 11.6859(4) Å, c = 5.4124(2) Å.

TABLE V

ANISOTROPIC THERMAL PARAMETERS FOR $KCuO_2$[a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}
K	1.5(1)	1.1(1)	1.22(8)	0.0
Cu	1.50(7)	0.55(6)	0.05(4)	0.0
O	3.28(8)	0.56(5)	0.26(4)	0.13(5)

[a] All values to be multiplied by 10^{-2} Å^2. $U_{12} = U_{13} = 0$.

89.5°(90.0), γ = 133.2°(120.0). The new c-axis runs from bottom to top in the plane of Fig. 4 (left).

The structure of $KCuO_2$ is shown in clinographic projection in Fig. 5. Again there are isolated parallel strings of edge-sharing CuO_4 rectangles. The coordination of potassium is that of an almost-regular triangular prism. Such coordination (*uncapped* trigonal prisms) is quite rare in oxides.

Selected bond lengths and angles are reported in Table VII. Of most immediate interest are the bond lengths to oxygen from copper. This is due to the interest (*5*) in having reliable values of the bond valence parameters for Cu(III)–O bonds. The average Cu–O bond length is d = 1.834 Å for a bond valence $v = \frac{3}{4}$. Accordingly in the Brown–Altermatt (*13*) form for the bond-length–bond-valence relation,

$$v = \exp[(R - d)/0.37\ \text{Å}], \qquad (1)$$

one has R = 1.728 Å. This value of R is close to the one assumed earlier (*5*).

Also of some interest are the Na–O and K–O bond lengths in these compounds with fairly regular 6-coordination. The average bond lengths are ⟨Na–O⟩ = 2.377 Å and

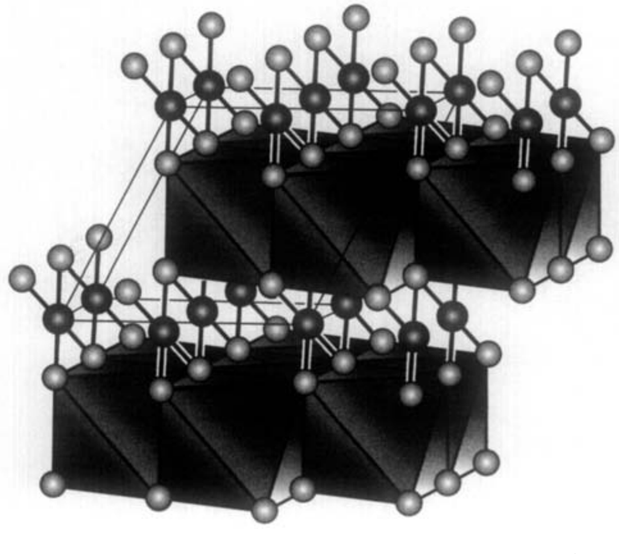

FIG. 3. Clinographic projection of the structure of $NaCuO_2$. The larger circles represent Cu atoms and the smaller ones O atoms. Na atoms center the octahedra.

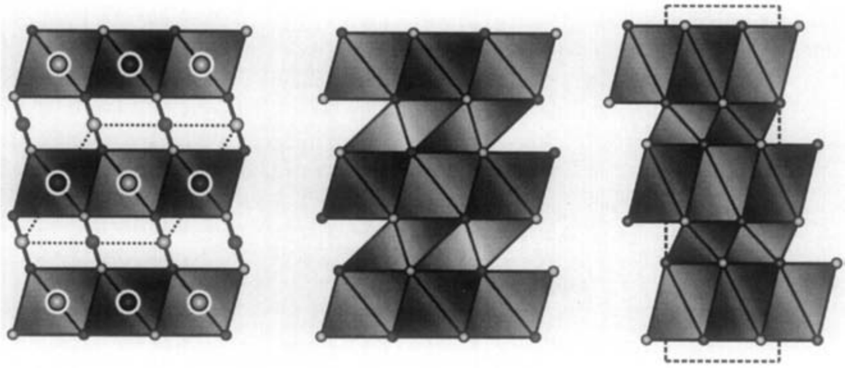

FIG. 4. Left: projection of the $NaCuO_2$ structure on (010). The largest circles represent Na atoms and the smallest represent O atoms. Lighter and darker circles represent atoms at $y = 0$ and $\frac{1}{2}$, respectively. Center: as on the left, with CuO_6 octahedra outlined. Right: the structure of $NaCoO_2$, projected on $(11\bar{2}0)$ with c vertical on the page. The broken line outlines an orthohexagonal cell.

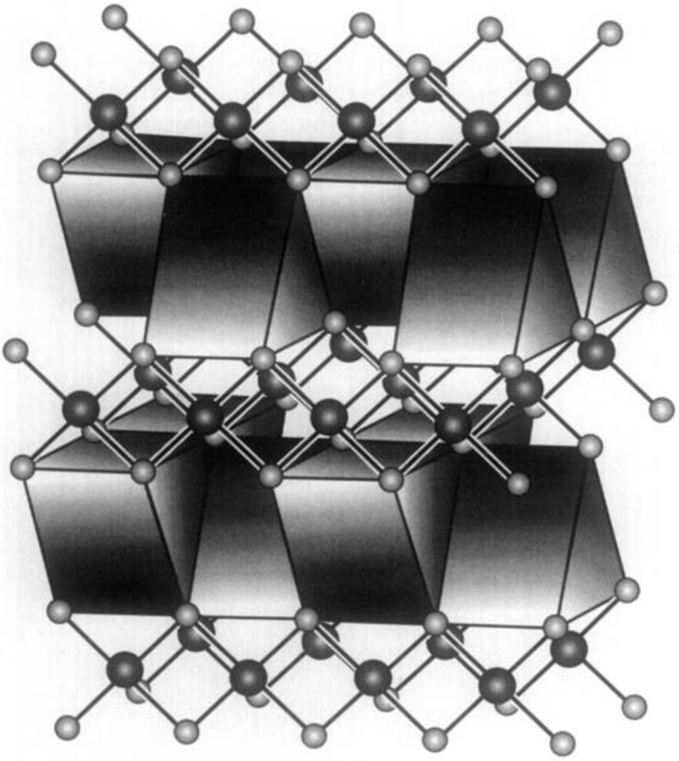

FIG. 5. Clinographic projection of the structure of $KCuO_2$. The smaller circles represent O atoms and the larger ones Cu atoms. K atoms center the prisms.

TABLE VII

SELECTED BOND LENGTHS (Å) AND ANGLES (DEG) FOR $NaCuO_2$ AND $KCuO_2$

$NaCuO_2$		$KCuO_2$	
Na–O (*2*)	2.411(1)	K–O (*4*)	2.778(1)
Na–O (*4*)	2.360(3)	K–O (*2*)	2.676(2)
Cu–O (*4*)	1.839(1)	Cu–O (*2*)	1.832(3)
		Cu–O (*2*)	1.826(2)
O–Cu–O (*2*)	180.00(0)	O–Cu–O (*2*)	176.6(1)
O–Cu–O (*2*)	96.64(9)	O–Cu–O	98.9(1)
O–Cu–O (*2*)	83.36(9)	O–Cu–O	92.1(1)
		O–Cu–O (*2*)	84.53(3)

⟨K–O⟩ = 2.744 Å. In both cases these are *shorter* than the bond lengths in the 4-coordinated compounds Na_2O (d = 2.403 Å) and in K_2O (d = 2.792 Å). These data strongly support the contention (*14*) that the bond lengths in the binary compounds are anomalously long.

We have some interest in Madelung potentials in transition metal oxides (*4*), experience showing that the potential at an ion site (calculated assuming nonoverlapping spherical ions of integral charges) scales approximately as the formal charge. The structures of $NaCuO_2$ and $KCuO_2$ allow a test in the case of copper oxides of unambiguous valence. Table VIII gives the potential at Cu and O in some simple oxides. The last row of the table shows that this hypothesis is fairly well obeyed, and suggests that Madelung potentials may be used as a diagnostic for valence in copper oxides where valences are ambiguous.

Acknowledgments

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TABLE VIII

MADELUNG POTENTIALS (V) AT Cu AND O IN SOME OXIDES

Oxide	Cu(I)	Cu(II)	Cu(III)	O
Cu_2O	−12.8			21.8
CuO^a		−25.3		24.9
$Cu_4O_3{}^b$	−12.2	−24.7		23.0 (av.)
$NaCuO_2$			−32.7	24.8
$KCuO_2$			−33.1	24.2
$-\langle\phi/z\rangle$	12.5	12.5	11.0	11.9

Note. Entries in the last row show the average potential (ϕ) divided by the formal valence (z).

[a] Structure Ref. (*15*).

[b] Structure Ref. (*16*).

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