LiCu₂O₂ and LiCu₃O₃: New Mixed Valent Copper Oxides

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Black, shiny crystals of $LiCu_2O_2$ (I) and $LiCu_3O_3$ (II) were prepared by melting a mixture of Li_2CO_3 and CuO (1 : 4) in a corundum crucible at 1150°C (I) or heating a mixture of Li_2CO_3 and CuO (1 : 5) in a corundum crucible at 825°C (II). Crystals of (I) had tetragonal symmetry and the structure was solved in $P4_2/nmc$ with $a = 571.9(1)$, $c = 1240.1 (4)$ pm, and $Z = 8$ (four-circle diffractometer CAD4, 201 $I_0(hkl)$, MoK_α, $R_W = 3.1\%$). Nearly identical but orthorhombic crystals (I') could be isolated from a different batch ((I'): $a = 571.4(3)$, $b = 572.7(3)$, $c = 1241.0(4)$ pm). The crystal structure of (II) was solved and refined in $P4/mmm$ with $a = 281.0(1)$, $c = 888.9(4)$ pm, and $Z = 1$ (four-circle diffractometer CAD4, 82 $I_0(hkl)$, MoK_α, $R_W = 1.9\%$). Characteristic building units in (I) and (II) are Cu^IO_2-dumbbells ($d_{Cu-O} = 185$ pm), LiO_5-pyramids, and $Cu^{II}O_4$-squares with one or two additional O atoms at about 242-259 pm. In (I) the $Cu^{II}O_4$-squares ($d_{Cu-O} = 198$ pm (4x)) are connected edge-shared to form infinite chains. The square-pyramidally surrounded Li atoms also form chains which, together with the Cu^{II}-O-chains, form double sheets separated by the CuO_2-dumbbells. In the orthorhombic crystal (I') Li and Cu^{II} are partially disordered. In (II) Li and Cu^{II} are completely disordered on centers of 4^4 nets of O atoms ($d_{Cu-O} = 199$ pm (4x)). Three sheets are packed in such a way that the coordination spheres of Cu^{II} or Li are completed by additional O atoms to form square pyramids ($d_{Cu-O} = 242$ pm) or elongated octahedra ($d_{Cu-O} = 259$ pm (2x)). A triple sheet of this type is connected via Cu^IO_2-dumbbells ($d_{Cu-O} = 185$ pm) to form a three-dimensional framework. (I) is an insulator and antiferromagnet (Néel temperature 40 K). At higher temperature it obeys the Curie–Weiss law with $\mu_{eff} = 1.93$ μ_B/Cu atom and $\Theta = -75$ K; (II) is a paramagnetic semiconductor with $\rho = 0.1$ $\Omega \cdot$ cm, $\mu_{eff} = 1.83$ μ_B/Cu₂ formula unit at 293 K; this is about half of the moment one would expect for two Cu^{II} atoms. © 1990 Academic Press, Inc.

1. Introduction

A study of Li/CuO electrochemical cells showed the formation of a new phase of approximate composition $Li_{0.5}CuO$ (*1*).

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This composition did not correspond to any known phase in the Li–Cu–O system and we were curious to discover whether we could synthesize and characterize other new lithium copper oxides. An added impetus to this work was the interest shown in intermediate valence copper oxides after the discovery of high temperature superconductivity in a number of these systems. Examples

include $La_{2-x}Sr_xCuO_4$ (2), $YBa_2Cu_3O_{7-x}$ (3), $Ln_{2-x}Ce_xCuO_{4-y}$ (Ln = Pr, Nd, or Sm) (4), $Bi_2Sr_{2-x}CaCu_2O_8$ (5), $Bi_2(Sr_{2-x}Ca_x)_2$-$CuO_{8-\delta}$ (6), $Pb_2Sr_2M_{1-x}(AE)_xCu_3O_8$ (M = lanthanoid and AE = Ca or Sr) (7). As can be seen, both mixed Cu^{III}/Cu^{II} and $Cu^{II}Cu^I$ systems give rise to high T_c behavior.

Besides the well-known copper oxides CuO and Cu_2O, a binary oxide Cu_4O_3 (8) containing Cu^I and Cu^{II} is known. Only a few ternary mixed valent oxocuprates have been made, e.g., Cu_3TiO_4 (9) and the recently published $TlCu_2O_2$ (10). In the Li–Cu–O system only one mixed valence compound $Li_3Cu_2O_4$ (11), with Cu^{III} and Cu^{II}, is known. The other known lithium cuprates, LiCuO (12, 13) (Cu^I), Li_2CuO_2 (14) (Cu^{II}), and Li_3CuO_3 (15) (Cu^{III}) contain Cu in only one oxidation state. The last three compounds have been structurally characterized, whereas the structure of the first is still unknown. Two other phases, Li_6CuO_4 and $Li_2Cu_2O_3$ (16), have been reported but are not well-characterized. As part of our investigation of the Li–Cu–O system we attempted to prepare them.

2. Experimental

2.1. Preparation

The starting materials were Li_2CO_3 (Merck, 99%), CuO (Ventron, AR), and Cu_2O (EGA). Li_2CuO_2 was prepared by heating Li_2CO_3 and CuO in a 1 : 1 mixture in a corundum crucible for 2 days at 700°C.

Exploration of existing phases in the Li–Cu–O system was carried out as described in Table I. Mixtures with Li/Cu ratios from 6 : 1 to 2 : 6 were made up from Li_2CO_3 and CuO and heated at temperatures between 650 and 1200°C in air. A gold boat or an alumina crucible was used for reactions at 950°C and below and an alumina crucible at higher temperatures. Mixtures with Li/Cu ≤ 2 were first heated at 700°C to react Li_2CO_3. The mixtures were heated for

TABLE I

PREPARATIONS OF SAMPLES IN THE Li–Cu–O SYSTEM

Composition	Temperature	Copper-containing phases present
3 Li_2CO_3/CuO	685°C	Li_2CuO_2
	1050°C	Li_2CuO_2
	1150°C	Li_2CuO_2
	1250°C	Li_2CuO_2, LiCuO
Li_2CO_3/CuO	700°C	Li_2CuO_2
3Li_2CO_3/4CuO	870°C	$LiCu_2O_2$, Li_2CuO_2, CuO
Li_2CO_3/2CuO	685°C	Li_2CuO_2, CuO
	750°C	Li_2CuO_2, CuO
	840°C	$LiCu_2O_2$, Li_2CuO_2, CuO
	880°C	$LiCu_2O_2$, Li_2CuO_2, CuO
	920°C	$LiCu_2O_2$, Li_2CuO_2, CuO
	950°C	$LiCu_2O_2$, Li_2CuO_2, CuO
Li_2CO_3/3CuO	840°C	$LiCu_2O_2$, Li_2CuO_2, CuO
Li_2CO_3/4CuO	850°C	$LiCu_3O_3$, $LiCu_2O_2$, CuO, Li_2CuO_2
	870°C	$LiCu_2O_2$, Li_2CuO_2, CuO
	900°C	$LiCu_2O_2$, Li_2CuO_2, Li_3CuO_3
	950°C	$LiCu_2O_2$, Li_2CuO_2, CuO
	1150°C	$LiCu_2O_2$, Cu_2O
Li_2CO_3/5CuO	750°C	Li_2CuO_2, CuO
	800°C	$LiCu_3O_3$, CuO, Li_2CuO_2
	825°C	$LiCu_3O_3$, CuO
	850°C	$LiCu_3O_3$, CuO, Li_2CuO_2
	870°C	$LiCu_3O_3$, $LiCu_2O_2$, Li_2CuO_2, CuO
	900°C	$LiCu_2O_2$, $LiCu_3O_3$

periods of between 2 and 10 days for reactions at or below 950°C and for 6–12 hr at higher temperatures.

Two new phases, subsequently identified as $LiCu_2O_2$ and $LiCu_3O_3$, were found in a number of these preparations. In an earlier study (16), the first of these phases had been incorrectly assigned the formula $LiCu_2O_3$. No evidence was found for the existence of Li_6CuO_4 (16) under the conditions described in Table I. Both phases, $LiCu_2O_2$ and $LiCu_3O_3$, appear only above 800°C in mixtures heated in air.

2.1.1. $LiCu_2O_2$

(a) *Crystals.* $LiCu_2O_2$ was prepared by melting a mixture of Li_2CO_3 and CuO (1 : 4) at 1150°C in a corundum crucible. After cooling rapidly to room temperature, black, shiny crystals of (I) were found in the broken regulus. Precession photographs of these crystals showed tetragonal symmetry. Orthorhombic plate-like single crystals (I′) of $LiCu_2O_2$ were grown in another batch by cooling the melt slowly (10°C/hr) from 1150 to 900°C and then rapidly to room temperature. According to Laue and precession photographs these crystals (I′) exhibit only two-fold axes.

(b) *Powder samples.* Dark brown powders of $LiCu_2O_2$ were prepared in the same way as the single crystals. Some Li_2O was lost during prolonged heating to give $LiCu_3O_3$, containing trace quantities of CuO.

2.1.2. $LiCu_3O_3$

(a) *Single crystals.* $LiCu_3O_3$ was prepared by heating a mixture of Li_2CO_3 and CuO (1 : 5) at 825°C in a corundum crucible. Very small, black, shiny crystals (II) were found in a sample cooled rapidly to room temperature.

(b) *Powder samples.* Black powders of $LiCu_3O_3$ were prepared by heating a pellet of $LiCu_2O_2$, CuO, and Cu_2O in a 1 : 1 : 1 ratio

in a sealed, silica tube filled with argon at 700°C. These samples always contained by-products.

2.2. Characterization

$LiCu_2O_2$ (prepared at 750°C) is described by the following characteristic lines of a Guinier diagram at the resolution for $CuK\alpha_1$ radiation (calculated d-values [pm], intensities in parentheses): 620(20), 590(50), 420(40), 279(30)*, 250(10), 236(15), 235(100), 228(10), 206.7(40), 202.2(80), 187.4(10), 178.1(10), 144.5(40), 143.0(20)*, 124.1(15), 122.2(30)*, 117.6(25)*. The reflections marked with an asterisk are broadened or even split (see below).

$LiCu_3O_3$ is described by the following characteristic lines of Guinier diagram (calculated d-values [pm], intensities in parentheses): 888(10), 444(5), 296(10), 281(10), 268(5), 237(100), 222.1(40), 198.7(70), 148.1(45), 142.5(20), 131.1(20), 120.9(30), 118.8(25).

Close inspection of the Guinier pattern of a well-crystallized sample of $LiCu_2O_2$ (prepared at 1150°C) showed that the 2 0 1, 4 0 0, 4 2 3, and 4 0 6 reflections were split. This splitting was very small at room temperature (0.15° in 2θ for the 4 0 0 reflection, $CuK\alpha$ radiation) and could not be seen on Guinier patterns of all samples. A variable temperature Guinier photograph (100 to 610 K) showed that the splitting increases with temperature (0.30° in 2θ for the (4 0 0) reflection at 500 K). We could index this pattern on the basis of an orthorhombic cell (a = 5.714(3), b = 5.724(3), c = 12.406(2) pm at room temperature). This result prompted a reinvestigation leading to a sample (I′) with similar lattice constants a = 5.714(3), b = 5.727(3), and c = 12.410(4) pm from powder.

Single crystals of $LiCu_2O_2$ (I) were separated mechanically for analysis and magnetic studies. Analysis (average of two determinations) gave Li 4.08% and Cu 76.5%,
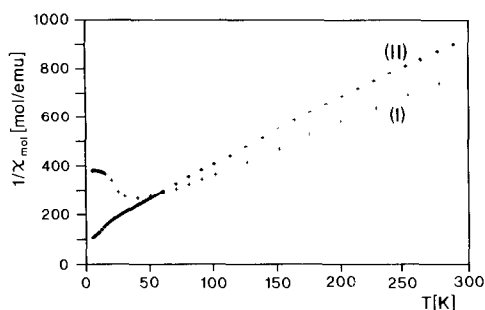
FIG. 1. Reciprocal magnetic susceptibilities of Li-Cu$_2$O$_2$ (I) and LiCu$_3$O$_3$ (II).

TABLE II

SUMMARY OF SINGLE-CRYSTAL DATA AND X-RAY INTENSITY COLLECTION FOR LiCu$_2$O$_2$ (I) (TETRAGONAL CRYSTAL) (LiCu$_3$O$_3$) (II)

Formula	LiCu$_2$O$_2$ (LiCu$_3$O$_3$)
Molar weight	166.0 (245.6) (amu)
Lattice constants[a]	a = 571.9(1) (281.1(2)),
	c = 1240.1(4)
	(888.8(4)) pm
Space group	$P4_2/nmc$ ($P4/mmm$), Z
	= 8(1)
d_{calcd}	3.35 (3.50) g cm^{-3}
μ(Mo$K\alpha$), λ	151.01 (217.7) cm^{-1},
	71.069 pm
Dimensions of the	0.1 × 0.1 × 0.1 (0.05
single crystal	× 0.05 × 0.05) mm
Data collection	Four-circle
	diffractometer CAD4
	graphite
	monochromator,
	scintillation counter
Range of data, method	3°(3°) ≤ 2θ ≤ 58°(55°),
	ω scan, ω 0.75θ scan
Scan speed	Variable depending on I
Number of reflections	571 (360)
Independent	201 (82) of 259 (85) with
	$F \geq 3\sigma(F)$
Absorption correction	Ψ-scan with 6 (4)
	reflections
Refinement	SHELX program, full
	matrix, least-squares
Number of parameters	29 (15)
R(aniso)	4.4 (2.3)%
R_w(aniso)	3.1 (1.9)%

Note. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein–Leopoldshafen (FRG), on quoting the depository No. CSD-54537, the names of the authors, and the journal citation.

[a] Modified Guinier technique.

compared to calculated values of 4.18 and 76.5% respectively for the formula LiCu$_2$O$_2$.

The magnetic susceptibility of LiCu$_2$O$_2$ (I) was measured between 4.6 and 300 K in a SQUID magnetometer employing a field of 10 kG (see Fig. 1). LiCu$_2$O$_2$ is an antiferromagnet with a Néel temperature at 40(3) K. It obeys the Curie–Weiss law well above the ordering temperature. The high temperature part of the curve yielded μ_{eff} = 1.93(5) μ_B, which is typical for Cu(II) (17), and Θ = −75(3) K.

The purest sample of LiCu$_3$O$_3$ (II) contained only traces of CuO, which was detected on Guinier patterns with long exposure times. The analysis of this sample gave Li 2.71% and Cu 78.2%, compared to calculated values of 2.78 and 78.1% respectively for the formula LiCu$_3$O$_3$.

The magnetic susceptibility of LiCu$_3$O$_3$ (II) was measured like that of LiCu$_2$O$_2$ (see Fig. 1). The magnetic moment per formula unit is μ_{eff} = 1.83(5) μ_B at room temperature and decreases to 0.32 μ_B at 4 K. This is quite low (as (II) contains two Cu^{II}) atoms but comparable to that found for CuO.

The measurements of the electric conductivity of pressed pellets from room temperature down to 4 K show that LiCu$_2$O$_2$ is an insulator ($\rho_{293 K}$ ≈ 10^6 Ω · cm whereas LiCu$_3$O$_3$ is semiconducting: $\rho_{293 K}$ = 0.1 Ω · cm and $\rho_{4 K}$ = 100 Ω · cm.

The structures of LiCu$_2$O$_2$ (I) and LiCu$_3$O$_3$ (II) were determined from single crystals. Details concerning the structural investigations are summarized in Table II. The positional parameters and the anisotropic temperature factors of (I) and (II) are given in Tables IIIa and IIIb. In LiCu$_2$O$_2$ the Li atoms could be located and isotropically re-

TABLE IIIa

POSITIONAL PARAMETERS AND U_{ij} VALUES OF THE ANISOTROPIC TEMPERATURE FACTORS $[pm^2]$ FOR $LiCu_2O_2$
(I) (STANDARD DEVIATIONS)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}
Cu1	$8g$	0.4947(1)	3/4	0.9949(1)	146(7)	32(5)	81(5)	8(25)
Cu2	$8g$	1/4	0.5004(3)	0.1557(1)	46(4)	39(5)	96(5)	10(33)
O2	$8g$	0.011(2)	1/4	0.1551(5)	64(27)	122(25)	10(33)	6(98)
O1	$8g$	0.487(2)	3/4	0.1436(5)	32(27)	100(24)	80(22)	4(83)
Li1	$8g$	3/4	0.989(3)	0.179(1)	65(25)^a		73(23)	

Note. The U_{ij} are defined for $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^*)]$. $U_{12} = U_{13} = 0$ for all Cu and O.
^{a} The position of Li has been refined isotropically.

fined. In $LiCu_3O_3$ (II), the Cu2 and Cu3 sites are partially occupied by both Cu and Li atoms and no out of plane positions could be found for the Li atoms. Precession photographs show no indication for any superstructure, and therefore a statistical distribution of Li on the two copper sites seems reasonable. The refined occupancy, corresponding to $Li_{1.004}Cu_{2.996}O_3$, is in agreement with the given formula $LiCu_3O_3$ and the chemical analysis. The refinement of a data set of a second crystal, picked from a different sample, gave exactly the same fractional occupancy for Cu2 and Cu3. A difference Fourier map did not indicate any dislocation of Li from the refined Cu2 and Cu3 positions.

There is no evidence for any deviation from tetragonal symmetry in the intensities of corresponding symmetry related reflections for the $LiCu_2O_2$ crystal (I) ($R_{merge} = 3.1\%$ in $P4_2/nmc$). This changed with a crystal taken from a different sample (I') which gave $R_{merge} = 25.2\%$ in $P4_2/nmc$. Space group ambiguities due to pseudo-extinctions (nonobserved: $hk0$ with $h,k = 2n + 1$ and $00l; = 2n + 1$) are problematic in the structural refinement. We refined a model in $Pmmn$ (601 independent reflections, $R_W = 5.1\%$). Like refinements in other space groups the results are still unsatisfying due to unreasonable temperature factors of the Cu^{II} atoms in the layers (see below) and the light atoms (O and Li).

TABLE IIIb

POSITIONAL PARAMETERS AND U_{ij} VALUES OF THE ANISOTROPIC TEMPERATURE FACTORS $[pm^2]$ FOR $LiCu_3O_3$
(II) (STANDARD DEVIATIONS)

Atom	Site	x	y	z	Occupation	$U_{11} = U_{22}$	U_{33}
Cu1	$1a$	0	0	0	0.0625	104(4)	107(6)
Cu2	$1b$	0	0	1/2	0.0505(2)	51(5)	99(7)
Cu3	$2h$	1/2	1/2	0.2283(2)	0.0743(2)	57(4)	128(7)
O1	$1d$	1/2	1/2	1/2	0.0625	83(18)	186(20)
O2	$2g$	0	0	0.2088(6)	0.1250	77(12)	167(17)

Note. Lithium atoms presumed to complete the occupancy of the Cu2 and Cu3 sites. The U_{ij} are defined for $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^*)]$. $U_{12} = U_{13} = U_{23} = 0$ for all Cu and O.
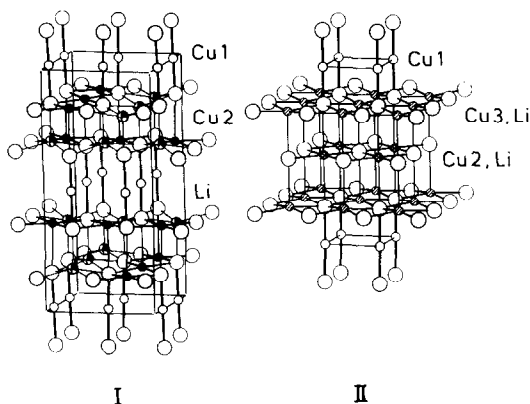
I   II

FIG. 2. Projections of the crystal structures of Li-Cu_2O_2 (I) and $LiCu_3O_3$ (II). ○ represents O atoms and ○ Cu^I atoms in (I) and (II); ● represents Cu^{II} and ⊕ Li in (I); in (II), ○ and ● represent sites for both kind of atoms, Li and Cu^{II}. Cu^IO_2-dumbbells are graphically emphasized.

3. Discussion of the Crystal Structures

The new structures of $LiCu_2O_2$ (I) and $LiCu_3O_3$ (II) are shown in Fig. 2. Both compounds are class I (18) mixed valence compounds containing Cu^I (site Cu(1)) and Cu^{II} (Cu(2) in (I) and Cu(2), Cu(3) in (II), respectively) on distinct sites. Cu^I is coordinated to two O atoms to form CuO_2-dumbbells, which are arranged in square nets in $LiCu_3O_3$ and almost square nets in $LiCu_2O_2$ (I). Cu^{II} exhibits its proclivity to adopt square-planar coordination in both structures (v.i.). All O atoms in $LiCu_2O_2$ and $LiCu_3O_3$ are octahedrally surrounded by cations. Motifs of mutual adjunction (19) and bond order sums (20) are given in Table IV, important bond lengths in Table V. The interatomic distances are given for the tetragonal structure of $LiCu_2O_2$.

The Cu(2) site in $LiCu_3O_3$ has perfect square-planar coordination with two additional O atoms completing a very elongated octahedron. Cu(3) lies just above the plane of four O-atoms with a fifth at 241 pm completing a square pyramid. Similar coordination is found for Cu^{II} in $LiCu_2O_2$, although

in this case the base of the square pyramid is distorted.

An interesting difference between the two structures is that in $LiCu_2O_2$ (I) Li and Cu lie on distinct sites, whereas in $LiCu_3O_3$ (II) the metal atoms are disordered on the Cu(2) and Cu(3) sites. The coordination geometry for Li in $LiCu_2O_2$, with five O-atoms at approximately the same distance, is different from that of Cu. In $LiCu_3O_3$ lithium is presumed to complete the occupation of the two Cu(2) and Cu(3) sites and has the same positional parameters and therefore coordination geometry as the Cu^{II} atoms. Lithium displacements from the Cu sites, if any, must be small, since there is no indication for this in the structure refinement, and it should be noted that bond-length bond-strength calculations suggest both sites are suitable for lithium. The fractional occupancies of the two sites, Cu(2) 80% Cu and Cu(3) 59% Cu, lead to the formula $Li(2)_{0.2}Li(3)_{0.8}Cu(1)_1Cu(2)_{0.8}Cu(3)_{1.2} = LiCu_3O_3$. Cu^{II} appears to prefer the square-planar coordination of the Cu(2) site. However, there are

TABLE IV

MOTIFS OF MUTUAL ADJUNCTION (19) AND BOND ORDER SUMS (20) IN $LiCu_2O_2$ (I) AND $LiCu_3O_3$ (II)

Atom	O(1)	O(2)	C.N.[a]	Σs_i
		(I)		
Li	2/2	3/3	5	0.91
Cu1	1/1	1/1	2	1 (fixed)
Cu2	3/3	2/2	5	1.9
C.N.[a]	6	6		
Σs_i	1.903	1.913		
		(II)		
Cu1	—	2/1	2	1 (fixed)
Cu2(Li)	4/4	(2/1)	4 + 2	Cu 1.91, Li 1.07
Cu3(Li)	1/2	4/4	4 + 1	Cu 1.84, Li 1.03
C.N.[a]	4 + 2	5 + 1		
Σs_i	1.82[b]	2.12[b]		

[a] Coordination number.
[b] Calculated assuming ratios Cu2 : Li = 4 : 1 and Cu3 : Li = 3 : 2.

TABLE V

Important Interatomic Distances in $LiCu_2O_2$ (I) and $LiCu_3O_3$ (II) (pm)

(I)

Cu1–O1	184.5		Cu2–O1	197.4	(2×)
–O2	186.2		–O2	198.0	(2×)
–Cu2	277.0	(2×)	–O1	249.0	
–Cu1	279.9		–Cu1	277.0	(2×)
–Cu2	282.4	(2×)	–Cu1	282.4	(2×)
–Cu1	286.3	(2×)	–Cu2	285.2	(2×)
–Cu1	292.0		–Cu2	287.5	(2×)
–O2	205.7				
Li –O1	208.3	(2×)			
–O2	212.8	(2×)			

(II)

Cu1–O2	185.4	(2×)	Cu3–O2	199.6	(4×)
–Cu1	281.2	(4×)	–O1	241.3	
–Cu2	284.0	(8×)	–Cu1	284.0	(4×)
Cu2–O1	198.8	(4×)	–Cu2	312.6	(4×)
–O1	258.6	(2×)	–Cu3	281.2	(4×)
–Cu2	281.2	(2×)			
–Cu3	312.6	(8×)			

Note. The distances Li–O should be similar to the Cu2–O and Cu3–O distances.

other factors which must affect the Li/Cu ratio on the two sites. If, for example, Cu(2) were 100% Cu^{II}, then the central sheet would have the composition CuO and be virtually unattached to the rest of the structure. The occupation of such a large fraction (80%) of the cation sites in a square oxygen net by Cu^{II} is very unusual.

The structures are closely related, with two and three sheets of 4^4 nets of oxygen, for $LiCu_2O_2$ and $LiCu_3O_3$ respectively, between the sheets of Cu^I. The problem of accommodating Li and Cu^{II} in these sheets, and of satisfying their bonding requirements and those of oxygen, is solved in different ways. In $LiCu_2O_2$ (I), the ratio of Li/Cu^{II} in the two identical sheets is 1 : 1, and it is easy to envisage ways of ordering Li and Cu on square nets. The actual ordering observed in (I) is rather curious, with CuO_4 groups sharing opposite edges to form CuO_2 chains separated by LiO_2 chains running at 90° in successive sheets. These CuO_2 chains, tilted or distorted, are also found in CuO, Cu_4O_3,

$TlCu_2O_2$, and Li_2CuO_2. Ordering across the intervening Cu^I layers is maintained by the unsymmetrical coordination of the dumbbells.

In the case of $LiCu_3O_3$ a disordered structure is produced, which may result from the difficulty of ordering the lithium and copper on a square net in the observed ratio of 4 : 1, further complicated by the presence of two neighboring square nets with a Li/Cu2 ratio of 3 : 2.

$LiCu_2O_2$ is related to KNa_2CuO_2 (21), and both of these structures can be derived by filling vacancies in the XeF_2 structure. The formation of a number of structures of the type containing $Hg^{II}O_2$, $Ni^{II}O_2$, and $Ag^{I}O_2$ dumbbells and alkali metal cations has been derived by Hoppe (22).

As described above, the structure of $LiCu_2O_2$ (I), which contains Li and Cu^{II} ordered in chains, has tetragonal symmetry. It consists of sheets with orthorhombic symmetry which are alternatingly rotated by 90° so that a 4_2 axis results. When this rotation is lost, an orthorhombic structure results. In the preliminary structure of (I') a parallel orientation of CuO_2 chains in adjacent sheets seems to be partially verified.

We have calculated MAPLE (23) (Madelung Part of Lattice Energy) for $LiCu_2O_2$ (I) and $LiCu_3O_3$ and compared these values with the sum of MAPLE for the binary oxides (see Table VI). The difference is approximately 3% in both cases and is large compared with other copper oxides, such as Cu_4O_3, LiCuO, or Li_2CuO_2, where a deviation of less than 1% is found. The larger deviation in the case of $LiCu_2O_2$ (I) is surprising but not in the case of $LiCu_3O_3$, because MAPLE has been calculated using a homogeneous charge distribution corresponding to the fractional occupation of the Cu^{II} sites and assuming that Li is exactly on the same position as Cu^{II}. Any ordering within that phase should raise MAPLE a little and would lead to a better agreement with the $MAPLE_{binary}$.

TABLE VI

CONTRIBUTION OF ATOMS TO THE MADELUNG PART OF LATTICE ENERGY (MAPLE [kcal/mole]) IN $LiCu_2O_2$ (I) AND $LiCu_3O_3$ (II)

(I)				(II)			
Atom	MAPLE		ΣMAPLE	Atom	MAPLE		ΣMAPLE
Li	192.1	1×	192.1	Cu(1)	82.2	1×	82.2
Cu(1)	110.3	1×	110.3	Cu(2)(Li)[a]	535.3	1×	535.3
Cu(2)	541.4	1×	541.4	Cu(3)(Li)[b]	367.5	2×	735.0
O(1)	527.8	1×	527.8	O(1)	455.4	1×	455.4
O(2)	503.5	1×	503.5	O(2)	551.8	2×	1103.6
		Σ =	1875.2			Σ =	2911.5	kcal/mole

Note. $0.5\ MAPLE_{Li_2O} + 0.5\ MAPLE_{Cu_2O} + MAPLE_{CuO} = MAPLE_{LiCu_2O_2 calcd.}$
417.9   398.7   1105.4   1922.0

$0.5\ MAPLE_{Li_2O} + 0.5\ MAPLE_{Cu_2O} + 2\ MAPLE_{CuO} = MAPLE_{LiCu_3O_3 calcd.}$
417.9   398.7   2210.8   3027.4

[a] The value has been calculated assuming a charge of $+2(Cu) \times 0.8 + +1(Li) \times 0.2 = +1.8$.
[b] This value has been calculated assuming a charge of $+2(Cu) \times 0.6 + +1(Li) \times 0.4 = +1.6$.

4. Final Remarks

The exploration of the system Li–Cu–O was complicated by loss of oxygen at higher temperature. One of the phases formed, $LiCu_3O_3$, decomposes with further loss of oxygen and formation of Cu_2O as the temperature is raised.

The structural principle of $LiCu_2O_2$ is such that the O atoms of the CuO_2-dumbbells are arranged in layers with Li^+ and Cu^{2+} cations establishing a rock salt-type sheet. Inserting an additional (Cu,Li) sheet leads to the arrangement in $LiCu_3O_3$, which is the first step to extending the rock salt part of the structure. It would be interesting to seek further members of the series $LiCu_nO_n$ in the direction toward CuO with increasing n. Is there a critical composition, at which the highly symmetric arrangement breaks down to adopt a CuO-like structure?

Acknowledgments

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