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The structure of $Li_3Cu_2O_4$, a compound with formal mixed valence

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Abstract

The structure of $Li_3Cu_2O_4$ was solved from X-ray powder diffraction data and refined from a multiphase specimen using the Rietveld method. The cuprate crystallizes in $C2/m$ with $Z=2$. The compound has a small homogeneity range. Typical parameters are $a=9.946(5)$ Å, $b=2.778(2)$ Å, $c=7.260(5)$ Å and $\beta=119.10(2)°$. The structure may be described as an ordered intergrowth of slabs of Li_2CuO_2 and hypothetical $LiCuO_2$ of $NaCuO_2$ type. The formula suggests a copper(II, III) mixture, but there is only one crystallographic copper site which implies a more appropriate formulation as $Li_3^+[Cu(II)O_2]_2^{-3/2}$ with parallel strands of edge-coupled CuO_4 units running along the *b* axis.

1. Introduction

Recent developments in superconductor research have focused on copper-oxide-based compounds in the search for the fundamental principles which determine the ultimate properties. The Li–Cu–O system has been re-investigated, including magnetic property measurements on known phases, such as Li_2CuO_2 [1, 2], and syntheses and property measurements of previously unknown phases such as $LiCu_2O_2$ and $LiCu_3O_3$ [3, 4]. The last two phases are interesting in the sense that the formulae suggest a mixed valence of copper. The structure determinations [3, 5, 6] disclosed a strict crystal site ordering of Cu(I) and Cu(II) in both, although there is a Cu(II)–Li(I) disorder in $LiCu_3O_3$.

Although some theories have proposed that the presence of trivalent copper is a fundamental property in cuprate superconductors, experimental observations have indicated that the electron hole is mainly situated on the oxygen network. The trivalency of copper must also be in doubt even for more simple stoichiometries, such as $NaCuO_2$ [7, 8]. In view of this, it is of interest to study other compounds in the Li–Cu–O system. In Li_3CuO_3 [9] and Li_5CuO_4 [10] copper is formally trivalent, whereas in $Li_3Cu_2O_4$ [11] and $Li_{1.5}CuO_2$ [12] an apparent Cu(II)–Cu(III) mixture occurs.

Although known for some decades, $Li_3Cu_2O_4$ was not crystallographically characterized until recently [4]. Its X-ray powder pattern was indexed on a C-centred monoclinic cell containing two formula units. A structure determination is essential to establish whether there are one or two crystallographic copper sites and to determine the coordination details. From crystal-chemical considerations Berger [4] anticipated a close structural relationship with Li_2CuO_2 which led to a structural model; this is confirmed in this paper using experimental X-ray powder data.

2. Experimental details

2.1. *Synthesis*

In the original synthesis of $Li_3Cu_2O_4$ by Klemm *et al.* [11], the reaction between Li_2O and CuO took place under flowing oxygen in the temperature range 250–300 °C. At higher temperatures a disproportionation was found to occur. By using this route, we found that the sample contained a large amount of unreacted CuO even after 1 month. Traces of Li_2CuO_2 and Li_2CO_3 were also noted. Part of the sample was used for thermal analysis. The results from thermogravimetry/differential thermal analysis (TG/DTA) showed that a mass loss started at about 330 °C. X-Ray diffraction of the phase mixture after TG/DTA still gave evidence of $Li_3Cu_2O_4$, but with a change in cell parameters indicating a homogeneity range.

Since Li_2O is seldom phase pure and the standard route gave heavy overlap with CuO, single-phase Li_2CuO_2 was first synthesized by reacting CuO and Li_2CO_3 in an alumina boat at 700 °C. The cuprate was

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heat treated in a stream of oxygen at 320 °C to enhance the kinetics. As anticipated, $Li_3Cu_2O_4$ began to form at the expense of the parent phase. Although far from being single phase after heat treating for 6 weeks, the sample (a black powder) was used for structural confirmation applying X-ray diffraction techniques.

The excess lithium was mainly found as LiOH together with traces as carbonate. The formation of the hydroxide (which may take up CO_2) may be a sign of deterioration on handling the sample, $Li_3Cu_2O_4$ and Li_2CuO_2 both being sensitive to moisture.

2.2. *Diffraction equipment and data collection*

A data set was collected for Rietveld profile analysis on a STOE STADI/P powder diffractometer in a symmetric transmission mode, covering the 2θ range 10°–100°. The sample, in powder form, was placed between two pieces of adhesive tape on a rotating sample holder in a beam of $CuK\alpha_1$ radiation from a germanium monochromator crystal. The intensity data were collected by a small position-sensitive detector (PSD) in steps of 0.02° (2θ) for a total of 13 h. The intensity was measured at $\theta=0°$ during a fixed time with and without the sample in the beam to give μt. The diffraction data were then corrected for absorption effects by the factor $\exp(\mu t/\cos\theta)$ derived for a $\theta/2\theta$ scan in transmission mode.

3. Solution and refinement of structure

The solution of the structure involved a non-standard procedure in which the structure of $Li_3Cu_2O_4$ was guessed (R. B.). The structure is rather simple, and an identical solution is obtained by applying conventional methods (extraction of individual intensities followed by Patterson synthesis or direct methods). The basis for the structural proposal is the fact that the three strongest reflections of $Li_3Cu_2O_4$ indicate crystal planes in orientations involving a high alignment of copper, which dominates the scattering. The cell size suggests the presence of only four copper atoms. Furthermore, the dimensions of the short axis (indicating a mirror plane) and the B-face diagonal of Li_2CuO_2 compared with the values of the axes of $Li_3Cu_2O_4$ lead to a crystal-chemically plausible model. The relationships to Li_2CuO_2 are further discussed below (see Fig. 3, Section 4).

The diffraction data were analysed in a multiphase Rietveld program LHPM1 [13] which could handle a maximum of only three phases. The refinement including $Li_3Cu_2O_4$, Li_2CuO_2 [2] and Li_2CO_3 [14] disclosed the presence of a fourth phase, identified as LiOH [15]. Another refinement was then made with LiOH as the third phase. From the scale factors it was judged that the carbonate content could be discarded. The diffraction peaks were described by a pseudo-Voigt function, with consideration of a gaussian deviation from the prominent lorentzian shape expected for X-ray data. Asymmetry was also allowed for. The angular dependence of the linewidths, represented by the full width at half-maximum (FWHM), was expressed as $FWHM^2=u\tan^2\theta+v\tan\theta+w$, where θ is the Bragg angle and u, v and w are refinable parameters. The background intensity was approximated by a polynomial expression, the parameters of which were refined. The procedure also contained refinements of the zero point, individual scale factors and cell parameters in addition to the structural parameters. The temperature factors of the respective elements were made equal in the two main component cuprates. Appropriate structural parameters were taken from the literature [2, 14, 15]. The scattering factors included in the program package were taken for neutral atoms with allowance for anomalous dispersion effects.

All four phases were included using the program FULLPROF [16]. No significant change in parameters was obtained, but the very low amount of carbonate marred the refinement. We therefore chose to present the results from the LHPM1 three-phase refinement.

4. Results and discussion

The data set of a phase mixture can be handled well in the Rietveld programs used. If the phases occur in compatible relative amounts, structural parameters are well refined. Phases in trace amounts are better totally disregarded. The heavy overlap prohibits a physically reasonable refinement of anisotropic temperature factors, especially since the absorption correction is rather approximate. The reliability indices (background not subtracted) of the profiles are rather good and the suggested structural model seems to be well confirmed, as seen in Table 1. The corresponding profile is given in Fig. 1. The structural parameters of $Li_3Cu_2O_4$ are given in Table 2, the interatomic distances in Table 3, and a projection of the structure along [010] in Fig. 2.

The structure contains only one copper site. Site ordering of Cu(II)–Cu(III) is thus not applicable. Lithium occurs in two kinds of coordination, tetrahedral and distorted octahedral. There are two oxygen sites which could allow for different charges, *e.g.* O(−I) and O(−II). Since the charge of lithium is not disputed, the Li–O distances may serve as a better probe for such charge ordering than the Cu–O distances. The four oxygen near-neighbours (O(1)) to Li(1) are at a reasonable distance for an Li–O(−II) bond. Li(2) has one slightly shorter distance to O(1).

TABLE 1. Summarized profile-fitting results. In addition to the common residuals and halfwidth parameters, the goodness of fit and Durbin–Watson *d* index are given

Overall or common parameters		
R_P	0.076	
R_{wP}	0.101	
χ^2	2.6	
d	0.24	
Phase dependent		
$R_I(Li_3Cu_2O_4)$	0.035 (118 refl.)	u: 0.065(8), v: 0.044(5), w: 0.0139(8)
$R_I(Li_2CuO_2)$	0.020 (41 refl.)	u: 0.14(1), v: −0.061(8), w: 0.028(1)
$R_I(LiOH)$[a]	0.031 (26 refl.)	

[a]The same *u*, *v* and *w* parameters as for Li_2CuO_2

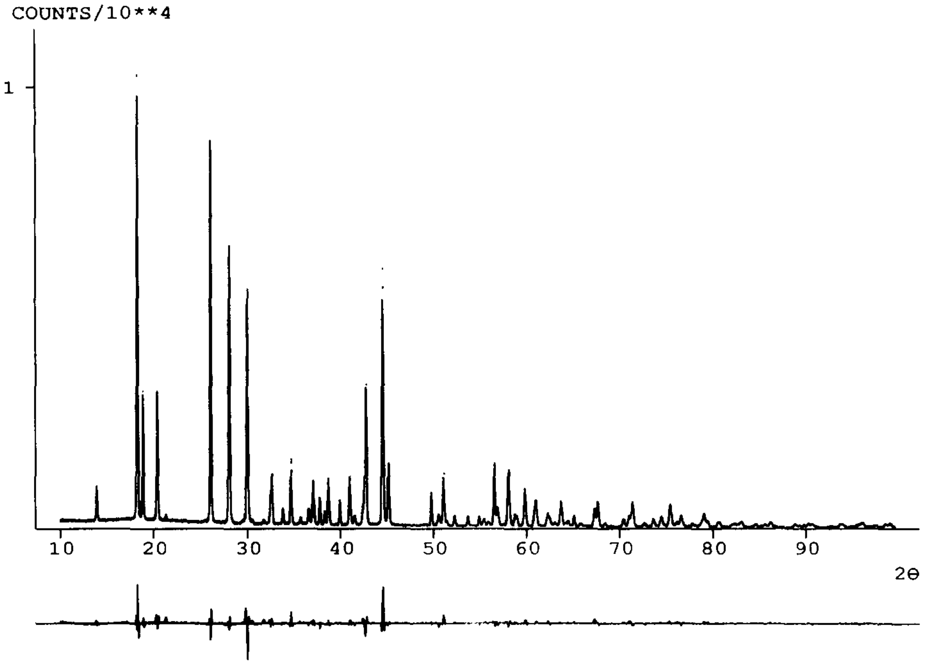

Fig. 1. X-ray powder diffraction data on $Li_3Cu_2O_4$ in a mixture with Li_2CuO_2 and LiOH. A trace amount of Li_2CO_3 was also present, the strongest line of which is seen at a scattering angle of 21°. The top part illustrates the observed intensities (dots) and Rietveld refined profiles (full line) and the bottom part gives their difference on the same scale.

TABLE 2. Structural data for $Li_3Cu_2O_4$ described on *C2/m* (all atoms in $y=0$)

Atom	Site	x	z	B_{iso} (Å^2)
Li(1)	2c	0	1/2	3.2(2)
Li(2)	4i	0.362(2)	0.132(2)	3.2(2)
Cu	4i	0.1609(1)	0.2729(3)	2.07(3)
O(1)	4i	0.5671(6)	0.3442(8)	1.90(7)
O(2)	4i	0.2564(5)	0.8211(8)	1.90(7)

The observation that the four shortest Cu–O distances are shorter than expected for Cu(II)–O(−II) does not necessarily imply a higher charge on copper, since the same tendency is seen for Li(2)–O(1). Thus the electron hole is probably associated with oxygen rather than with copper which, consequently, should be considered to be primarily divalent in character. In this hypothesis, the "electron deficit" cannot be associated with one of the oxygen sites but must be localized over the whole oxygen network giving an effective attraction to the O–O bonds, as reflected in the O(1)–O(2) distance of 2.56 Å and the short *b* axis. Charge ordering to a similar network [8] explains the properties of $NaCuO_2$ in a formal picture as $Na^+[Cu(II)O_2]^-$. A corresponding formulation devised for $Li_3Cu_2O_4$ yields $Li_3{}^+[Cu(II)O_2]_2{}^{-3/2}$.

The oxygen coordination about copper is practically square with the copper slightly shifted from the centre. These CuO_4 units are edge-connected into strands that run parallel with the *b* axis. In Li_2CuO_2 (Fig. 3) such strands (with slightly more irregular CuO_4 geometry) are stacked parallel on top of one another (as in $KCuO_2$ [17]). In $Li_3Cu_2O_4$ the situation is partly similar to that

TABLE 3. Interatomic distances (Å) up to 3 Å

Li(1) octahedron		Li(2) tetrahedron	
Li(1)–4O(1)	2.093(5)	Li(2)–O(1)	1.86(2)
Li(1)–2O(2)	2.481(4)	Li(2)–2O(2)	1.96(2)
		Li(2)–O(2)	1.98(2)
Cu square plane			
Cu–2O(1)	1.882(5)		
Cu–2O(2)	1.900(5)		
Cu–O(1)	2.777(4)		
Shortest O–O distances			
O(1)–O(2)	2.563(9)		
O(*i*)–O(*i*), *i*=1,2	2.778(2)		
Shortest intercationic distances			
Li(2)–2Li(2)	2.55(2)		
Li(2)–Cu	2.66(2)		
Li(1)–4Li(2)	2.71(1)		

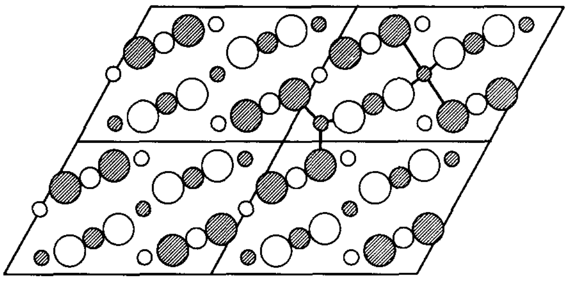

Fig. 2. The structure of $Li_3Cu_2O_4$ given as four unit cells projected along the monoclinic *b* axis. Large circles: oxygen; medium-sized circles: copper; small circles: lithium. The atoms are situated at $y=0$ (open circles) or at $y=\frac{1}{2}$ (filled circles). The two different oxygen coordinations taken by lithium are accentuated by a thick line ball-and-stick notation.

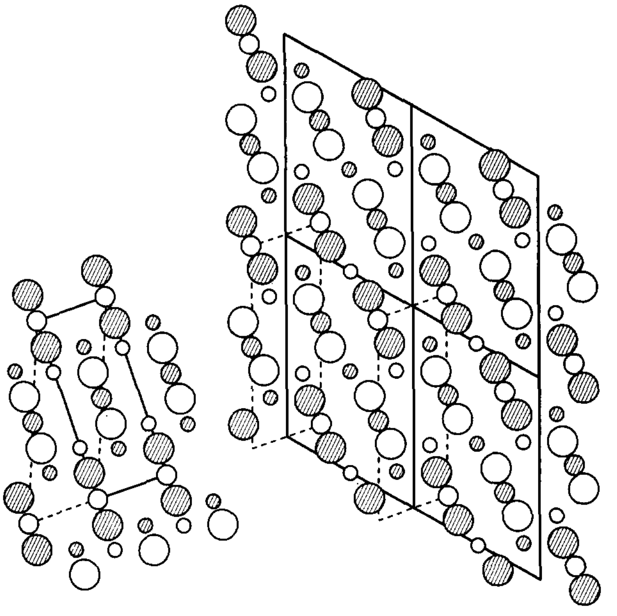

Fig. 3. A comparison between the structures of Li_2CuO_2 (left) and $Li_3Cu_2O_4$ (right), both projected along their respective *b* axes. The conventional unit cells are given by full lines. A common building block of monoclinic symmetry is shown by broken lines. This block constitutes an alternative unit cell in Li_2CuO_2 whereas in $Li_3Cu_2O_4$ it forms part of the parallel slabs that are intercalated with slabs of composition $LiCuO_2$. The atom symbols are the same as in Fig. 2. The relative orientation of the structures (*cf.* Fig. 2) has been chosen so that the common building blocks may be identified more easily.

in Li_2CuO_2, but a vague resemblance to the stacking principles of LiCu(I)Cu(II)O_2 [5] may also be discerned. In this compound, the divalent copper has five oxygen near-neighbours in a pyramidal arrangement so that the apex oxygen of one pyramid is a base oxygen of another. This is achieved by displacing strands pairwise. Such shifted double strands are also found in $Li_3Cu_2O_4$, but the apex atom of the pyramids is too far away (2.78 Å) to be considered for coordination.

It is interesting to make a topological comparison between Li_2CuO_2 and $Li_3Cu_2O_4$. In Fig. 3 the structure of the former is included (projection along [010]) with the conventional *Immm* orthorhombic unit cell as well as an alternative *C2/m* cell (with the monoclinic *a* axis being the orthorhombic ⟨101⟩ direction and the *c* axis common to the orthorhombic *a* axis). This cell can be identified as a building block forming slabs within $Li_3Cu_2O_4$. These slabs are displaced $\frac{1}{2}b$ in $Li_3Cu_2O_4$ by the inclusion of slabs of composition $LiCuO_2$. A structure built only by the latter slabs would be of $NaCuO_2$ type (also described in *C2/m*). From the crystal chemistry, $Li_3Cu_2O_4$ may thus be seen as an ordered intergrowth of Li_2CuO_2 and fictitious $LiCuO_2$. This part of the structure demands an irregular octahedral coordination by lithium with only four oxygen near-neighbours in a square, maybe explaining why pure $LiCuO_2$ does not exist? However, similar deviations from regular octahedral symmetry around lithium are found in $LiScO_2$ [18] and $LiMnO_2$ [19], in the latter case enforced by the Jahn–Teller effect of Mn(III).

In view of the structural similarities between $Li_3Cu_2O_4$ and Li_2CuO_2, the experiment by Wizansky *et al.* [12] is very interesting. They tried to remove half of the lithium in Li_2CuO_2 by strongly oxidizing it, but only succeeded in reaching the composition $Li_{1.5}CuO_2$. However, the *d* values given do not imply the same structure as that presented here. On the other hand, the *d* value of the strongest line of the product, 4.84 Å, is suggestive of a similarity with the current $Li_3Cu_2O_4$ structure. It is tempting to compare this with the experimental evidence of topotaxy between $TlCu_3S_2$ and $TlCu_2S_2$ where, on oxidation of the former, the latter compound is obtained [20]. Whole $TlCu_2S_2$ slabs are conserved while copper is depleted. Intermediate ordering with regard to the stacking sequences of two kinds of slabs

($TlCu_2S_2$ and $TlCu_4S_2$ in this case) may be structurally realized; this model can easily be applied to compounds such as $Na_3Cu_8S_6$ and $Tl_5Cu_{14}Se_{10}$. Therefore the oxidation product obtained by Wizansky *et al.* [12] may contain the same kinds of slabs (Li_2CuO_2 and $LiCuO_2$) as found in $Li_3Cu_2O_4$, but with a modulation in order giving it a composition very close to that claimed.

5. Conclusions

We have determined and refined the structure of $Li_3Cu_2O_4$. The refinement was obtained using multiphase X-ray powder data applying the Rietveld method. On crystal-chemical grounds the structure may be considered as an ordered intergrowth between $Li_2Cu(II)O_2$ and (fictitious) $LiCu(III)O_2$. However, from bonding considerations we are inclined to view the compound as a cuprate formally written as $Li_3{}^+[Cu(II)O_2]_2{}^{-3/2}$, the electron hole being of oxygen character and localized over the oxygen network as in $NaCuO_2$ [8].

According to Klemm *et al.*[11] there is a strong antiferromagnetic coupling in the compound with a large negative temperature intercept to a Curie–Weiss law. The paramagnetic moment found ($p_{eff}=1.9\ \mu_B$) need not be in contradiction with a picture of divalent copper only. At present, we are unable to draw any decisive conclusions from the difference in cell parameters noted for the compound; it seems that, from the TG/DTA experiment and X-ray powder diffraction, the cell became larger after the mass loss on heating. The X-ray intensity data are not sufficient to fully support a homogeneity range in the form of partial oxygen occupancies. Neutron diffraction measurements are to be performed in the near future, partly to confirm the X-ray data and partly to elucidate the magnetic interactions.

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Note added in proof

After submitting our paper we came across a reference that evaded our literature search, concerning an independent determination and refinement of the structure [21]. Our results are a solid confirmation of that work but are based on more data yielding a higher precision of the parameters determined.

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