

Room temperature synthesis and structural characterization of monoclinic LiCuO_2 by X-ray and neutron diffraction

Rolf Berger and Lars-Erik Tergenius

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala (Sweden)

(Received June 21, 1993)

Abstract

LiCuO_2 was synthesized at room temperature by delithiation of Li_2CuO_2 using bromine in acetonitrile. The product shows broad diffraction profiles which were analysed by the Rietveld refinement technique on X-ray and neutron powder data. The phase conforms to the NaCuO_2 structure type ($C2/m$, $Z=2$) with the cell $a=5.733(1)$ Å, $b=2.7176(3)$ Å, $c=5.622(1)$ Å, $\beta=120.68(2)^\circ$.

1. Introduction

A large number of alkali metal cuprates are known with variable oxidation states of copper, at least formally, from Cu(I) to Cu(III), sometimes also with mixed valence. The high ionization energy demanded to reach the trivalent state has initiated doubt in the credibility of many cuprates(III) with the argument that it would be energetically more favourable to create holes in the oxygen than in the copper band [1]. The indirect method of using the "bond valence" concept for determining local charges [2] is also inconclusive since for its calibration it utilizes interatomic distances obtained from "standard compounds". Cu(III)–O distances have been assessed from alkali cuprates of MeCuO_2 stoichiometry ($\text{Me} \equiv \text{Na, K, Rb, Cs}$), known for quite some time [3, 4]. However, it seems from recent X-ray photoelectron spectroscopy (XPS) measurements supported by cluster calculations [5] on NaCuO_2 that the electron holes are rather localized to peroxide-like oxygen states, implying an $\text{Na}^+[\text{Cu}^{2+}\text{O}_2^{-1.5}]^-$ charge formalism.

Recently the cuprates of MeCuO_2 stoichiometry of the alkali metals have been fully characterized crystallographically, where isostructurality occurs for $\text{Me} \equiv \text{K, Rb and Cs}$ while NaCuO_2 crystallizes in another structure type [6, 7]. Several unsuccessful attempts have been made to synthesize a lithium analogue either under flowing oxygen through high temperature [8] or medium temperature [9] techniques or by applying powerful oxidizing agents at ambient temperature [10]. LiCuO_2 was synthesized for the first time through a fairly mild oxidation of Li_2CuO_2 by iodine in boiling acetonitrile [11]. The product showed poor crystallinity but a structure proposal was still put forward based

on X-ray powder diffraction data (including a prominent texture). Despite the low R factors presented, the orthorhombic model deserves only a low credence since it yields unrealistic interatomic distances and peculiar temperature factors [12].

A formal mixed valence lithium cuprate, $\text{Li}_3\text{Cu}_2\text{O}_4$, was recently characterized crystallographically by X-ray [13, 14] and neutron [15, 16] diffraction. It was pointed out [14] that according to its structural characteristics it could be viewed as $\text{Li}_2\text{CuO}_2 \cdot \text{LiCuO}_2$ by ordered intergrowth between slabs of these respective compositions. The latter structural slab has the characteristics of the NaCuO_2 structure type. LiCu_2O_2 [17, 18] and NaCu_2O_2 [19] were recently found to be isostructural, both containing light alkali metals. It then seemed reasonable that if LiCuO_2 exists, it should be analogous to the sodium compound.

In this paper we report on the room temperature synthesis of LiCuO_2 and its subsequent crystallographic characterization by X-ray and neutron powder diffraction, claiming that our product is identical with that obtained previously [11, 12] but with its structure more correctly described by the NaCuO_2 type.

2. Experimental details

2.1. Synthesis

LiCuO_2 was prepared in two steps. First Li_2CuO_2 was synthesized by heating a 1:1 mixture of CuO and Li_2CO_3 in air at 1000 K. The phase purity was checked by the Guinier camera technique and a noted small loss of lithium, possibly through volatilization of LiOH, was compensated for to yield a single-phase specimen.

The next step, following the recommendations by Imai *et al.* [11], was a delithiation using iodine in acetonitrile (the addition of tetrabutylammonium iodide was considered uncalled for). Although the new phase did form by this procedure, a very low yield was obtained when powder was treated for 1 h. Therefore, being a more efficient oxidizing agent, bromine was tried instead. The delithiation now proceeded much more rapidly, even at room temperature, with gram quantities of the parent compound being completely transformed within a couple of hours.

On bromine treatment of single-phase Li₂CuO₂, the final synthesis product often contained residual parent phase. However, a longer soaking time promoted the formation of CuO. The parameters were not optimized for obtaining single-phase material. For retrieving the product that had been immersed in the bromine solution, it was washed a couple of times with pure solvent (acetonitrile) to avoid precipitation of LiBr that stayed in solution during the treatment.

2.2. X-Ray powder characterization

The powder pattern (Guinier-Hägg camera, Cu K α ₁ radiation) of the product shows rather broad lines. By using preliminary cell parameters obtained from the Li₃Cu₂O₄ subcell of LiCuO₂ stoichiometry [14] and NaCuO₂ positional parameters [6], intensity calculations were performed (LAZY PULVERIX [20]) from which the pattern was successfully indexed and the cell parameters refined. The pattern was also correspondingly analysed using the orthorhombic model advocated by Imai *et al.* [11], but it yielded a less satisfactory fit regarding the cell parameters, although the calculated intensities were almost identical. This latter fact indicates that the cells of the NaCuO₂ type (*C2/m*) and that proposed by Imai *et al.* [11] (*Cmmm*) might be interrelated.

The cell volume of the orthorhombic cell (*Z*=4) is twice that of the monoclinic one (*Z*=2) and the cell matrix relations are

$$\begin{pmatrix} 1 & 0 & 0 \\ 1 & 0 & 2 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{\text{mon}} = \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{\text{orth}}$$

However, the larger cell only shows orthorhombic pseudosymmetry when that of NaCuO₂ is taken as the true cell: the γ angle is about 90.25° and there is only one mirror plane. The crucial difference between the two structure proposals occurs for the oxygen atoms, while the copper and lithium positions are practically identical. The scattering power by copper dominates in the X-ray case, which explains why two different models may give "identical" results.

2.3. Diffraction intensity data collection

Several sets of X-ray powder profile data were recorded by scanning Guinier-Hägg films (strictly monochromatic Cu K α ₁ radiation) with a microdensitometer [21], computer programmes translating the transmission into intensity values with a step scan size (2θ) of 0.023°. The variation in the background was taken care of by manual corrections through a spline function.

Six data sets were also collected on a Stoe STADI/P powder diffractometer in a symmetric transmission mode. Each set was collected for 1.5 h by a position-sensitive detector in steps of 0.02° (2θ). Since the sets were principally similar, only differing in contents CuO and Li₂CO₃ which seemed to increase with time owing to specimen degradation, the sets were at the end just merged into a single set by addition.

After completion of the refinements on X-ray data, the opportunity suddenly arose to use neutron diffraction, albeit on an instrument with low resolution. It was still considered worthwhile in order to fully establish the positions of the light elements. The data were collected at Studsvik, Sweden, using the SLAD ("Studsvik liquids and amorphous materials diffractometer") with a flux of 10⁶ cm⁻² s⁻¹ at 1.1 Å, monochromatized by Cu(220) and with a step size of 0.1° yielding an angular resolution of 0.6°.

2.4. Refinement procedure

The film and diffractometer data (of different phase sets) were analysed using a multiphase Rietveld programme LHPM1 [22] capable of simultaneously refining up to three phases. For the films the unrealistic "zero background" obtained as a result of subtracting the background was compensated for by adding an overall constant to the whole range in a manner mimicking diffractometer data, its value chosen so as to bring the weights to a reasonable level governed by the value of χ^2 .

One problem in the X-ray refinements arose from the variation in halfwidth for LiCuO₂ where a structural dependence – (00*l*) reflections having a smaller halfwidth – seemed to compete with the common angular dependence. Still, a refinement was accepted using the common *u*, *v*, *w* parameters even for unrealistic values of these. On the other hand, the neutron data were hardly affected through a larger dominating instrumental broadening. In the first refinement stages the zero point and individual scale factors were refined followed by individual cell parameters and finally by positional parameters (using NaCuO₂ as a starting model [7]) for LiCuO₂ and temperature factors for each element irrespective of phase. Positional parameters for accompanying minority phases (CuO, Li₂CuO₂ or Li₂CO₃) were taken from the literature and were not refined.

Only a very slight texture was noted, in strong contrast with the previous investigation [11].

3. Results and discussion

A consistent picture was obtained concerning the positional parameters of LiCuO₂ even though different phase sets and radiations were used. Parameter data are given in Table 1. The diffractometer data seem more internally in line than those from the film, partly owing to background problems alluded to in the previous paragraph. Representative X-ray and neutron profiles are given in Figs. 1 and 2 respectively. Since the compound is not very stable, no improvement in line quality can be obtained by heat treatment of powder

obtained in this manner. The structure is depicted in projection in Fig. 3, also with a comparison with the model previously suggested [11]. Corresponding interatomic distances are presented in Table 2.

We find, not least from the supplementary neutron data, that the LiCuO₂ structure without doubt conforms to the NaCuO₂ type. For comparison, the Bragg residuals described by R_1 were 1.84% (X-ray film data), 3.51% (X-ray diffractometer data) and 2.75% (neutron data) using our model. The relatively great success of the previous orthorhombic model applied to X-ray data is due to the special circumstance that copper is a stronger scatterer than the other atoms and thus dominates the structure factor. Consequently, we tested the $Cmmm$ model validity for our neutron data, which should discriminate the models better owing to the significant

TABLE 1. Structural parameters of LiCuO₂ refined in $C2/m$ (NaCuO₂ type, $Z=2$). All atoms are at $y=0$

Atom	Site	x	z	R_{wP} (%)	R_1 (%)
Cu	2a	0	0		
Li	2b	$\frac{1}{2}$	$\frac{1}{2}$		
O	4i	0.303(1)	0.737(1)	3.2	1.8 (X-ray film data) ^a
		0.312(2)	0.744(1)	8.5	3.5 (X-ray diffractometer data) ^b
		0.3130(7)	0.7567(7)	6.8	2.8 (neutron data) ^c

^aContained Li₂CuO₂.

^bContained CuO and Li₂CuO₂; inadequate "amorphous background" description.

^cContained Li₂CuO₂ and Li₂CO₃.

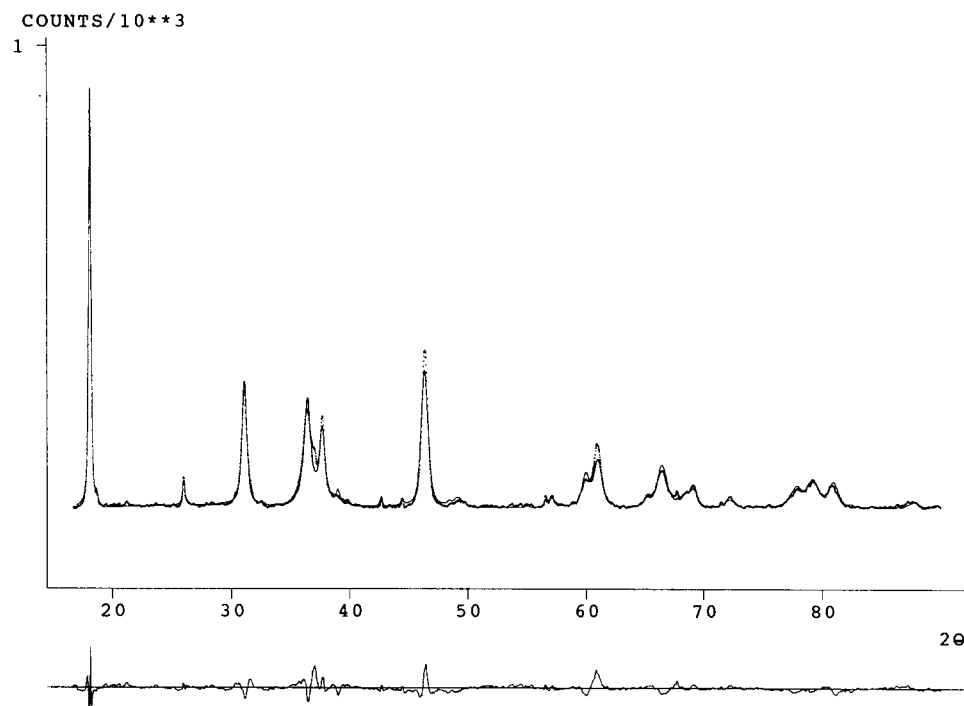


Fig. 1. A representative profile from a Guinier-Hägg camera from a sample also containing a residue of Li₂CuO₂ (its strongest line is at 26.1°). The difference between the observed and calculated intensities is given at the bottom on the same scale.

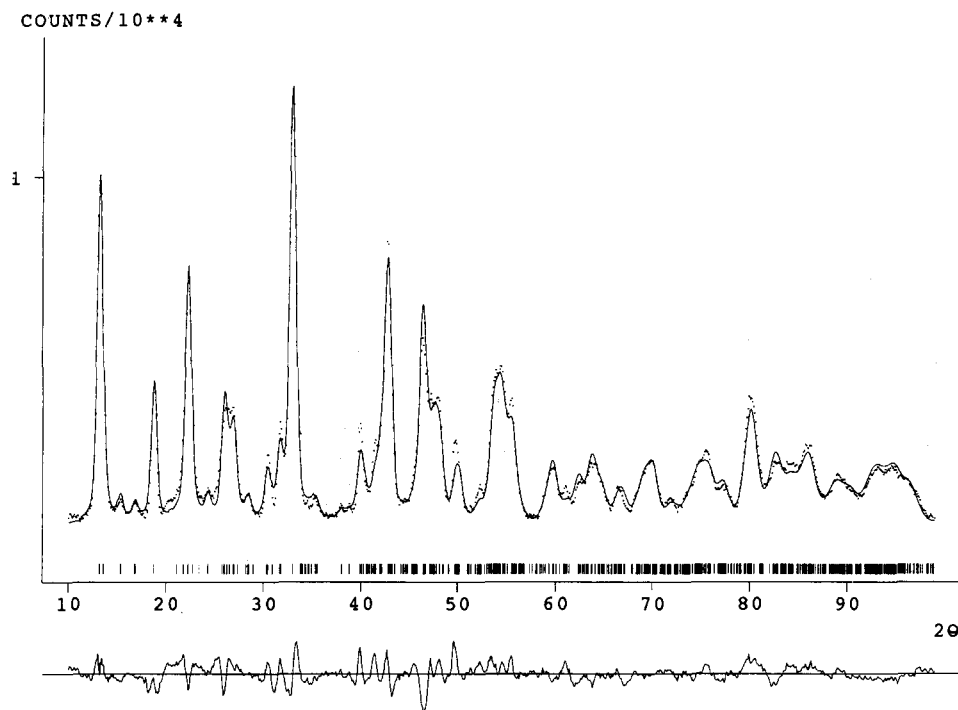


Fig. 2. A neutron diffraction profile from a sample with a high content of residual Li_2CuO_2 . The Li_2CO_3 contribution also seen here clearly (strongest peaks at 16° and 17.5°) would in the X-ray case be negligible owing to the weak scattering.

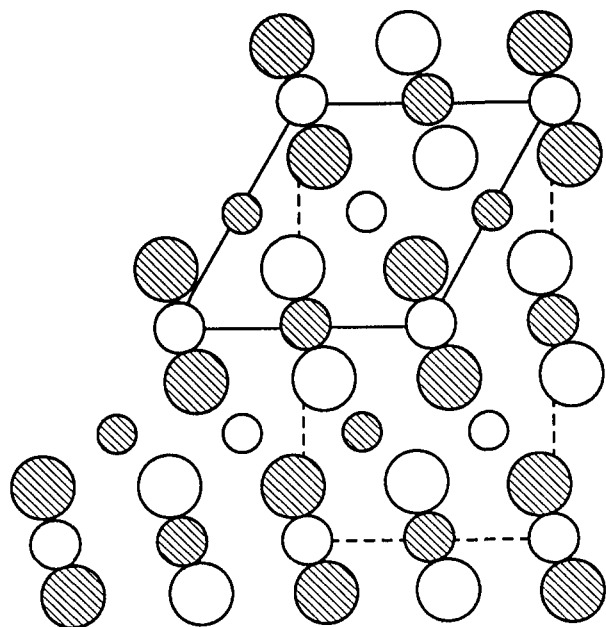


Fig. 3. The structure of LiCuO_2 in a $[010]$ projection. In addition to the true monoclinic cell, the pseudo-orthorhombic cell of double volume is outlined, illustrating that the copper partial structure very nearly adopts the orthorhombic symmetry previously suggested for the whole structure. Large circles, oxygen; medium circles, copper; small circles, lithium. The coordinates along the b axis are differentiated as: unfilled, $y=0$; shaded, $y=\frac{1}{2}$.

TABLE 2. Interatomic distances up to 3.0 \AA in LiCuO_2 using $a = 5.733(1) \text{ \AA}$, $b = 2.7176(3) \text{ \AA}$, $c = 5.622(1) \text{ \AA}$, $\beta = 120.68(2)^\circ$ from Guinier-Hagg data and positional parameters from neutron data

Li-O	2.123(3)	Cu-O	1.836(2)	O-Cu	1.836(2)
2O	2.193(3)	2Cu	2.718(0)	2Li	2.123(3)
2Li	2.718(0)	2O	2.756(3)	Li	2.193(3)
2Cu	2.810(1)	2Li	2.810(0)	O	2.469(7)
				2O	2.718(0)
				Cu	2.756(3)
				2O	2.928(6)

oxygen contribution, and obtained $R_I = 13.2\%$ ($R_{WP} = 17.5\%$). The previous refinement gave unrealistic Cu-O distances at variance with edge X-ray absorption fine structure (EXAFS) measurements [11, 12], while our results using the monoclinic model are in good agreement with these.

The interatomic distances for Li-O are similar to those found in other cuprates. The Cu-O distances are quite compatible with those found in NaCuO_2 and KCuO_2 [6] but are not too different either from those found in $\text{Li}_3\text{Cu}_2\text{O}_4$, where there is only one site for the supposed mixed valence Cu(III)/Cu(II). Interestingly, the two copper sites in mixed valence $\text{NaBa}_2\text{Cu}_3\text{O}_6$ [23], with Cu-O distances of 1.85 and 1.95 Å respectively, would suggest a site localization for Cu(II) and Cu(III). However, Madelung calculations supported a random distribution of such states over the two sites, which

might be an indication that instead oxygen charge localization over the network is at play.

The view that the MeCuO₂ stoichiometry necessarily implies trivalent copper is currently being challenged [1, 5]. Considering that even iodine is capable of delithiating Li₂CuO₂ through oxidation makes Cu(III) species unlikely, while "peroxide-like states" might be formed more easily. LiCuO₂ decomposes instantaneously in aqueous sulphuric acid, dissolving under the formation of oxygen. If iodide is present, free iodine forms together with a CuI precipitate. The iodide oxidation is commonly used for experimentally determining the hole concentration in cuprate superconductors. However, it is not possible by this technique to determine where the holes are situated, in a Cu(II) or an O(-II) band. We are in favour of electron holes being created in a localized oxygen band assigned to the oxygen network. Their effect is reflected in the short O-O distances discussed by Mehta *et al.* [1], 2.5 Å found in the MeCuO₂ compounds and 2.6–2.7 Å in Li₃Cu₂O₄ and NaBa₂Cu₃O₆. These compounds illustrate a gradual change in bond order by an increasing condensation of CuO₄ units through edge sharing to form charged [Cu(II)O₂]₂ species, formally written as Me⁺[CuO₂]⁻, Li₃⁺[CuO₂]₂^{-3/2} and Na⁺Ba₂⁺[CuO₂]₃^{-5/3} respectively. The coupled CuO₄ units occur as infinite parallel strands in the first two, while in the third a hexagonal ring is formed to accommodate the holes through charge localization.

4. Conclusions

We have modified the previous method of obtaining LiCuO₂ by lithium deintercalation through "chimie douce", now by using bromine in acetonitrile at room temperature. From crystal chemical considerations, and with support from Rietveld refinements on X-ray as well as neutron powder data, we conclude that LiCuO₂ crystallizes in the monoclinic NaCuO₂ structure type [6] rather than in *Cmmm* [11, 12].

Wizansky *et al.* [10] used more powerful oxidizing agents for delithiating various ternary lithium oxides. They were unable to interpret the X-ray powder data obtained for the product on oxidizing Li₂CuO₂ with NO₂PF₆. Their *d* values given tempted us recently to propose [14] that some kind of alternative intergrowth phase had formed based on the structural themes of Li₃Cu₂O₄. Considering the new data, we cannot exclude that the product was a phase mixture containing at least both LiCuO₂ and Li₃Cu₂O₄. On bromine treatment (room temperature) the latter phase is incompletely delithiated further to yield LiCuO₂.

Acknowledgments

Financial support was granted by the Swedish Natural Science Research Council (NFR). Neutron data were collected at the Studsvik reactor through the aid of A. Wannberg and Dr. R. Delaplane. Mrs. C. Lampe-Önnerud kindly assisted in collecting the X-ray diffractometer data. We are also grateful to Dr. K. Imai for supplying unpublished data on the previous structure investigation of LiCuO₂.

References

- 1 A. Mehta, J. DiCarlo and A. Navrotsky, *J. Solid State Chem.*, **101** (1992) 173.
- 2 I.D. Brown and D. Altermatt, *Acta Crystallogr. B*, **41** (1985) 244.
- 3 K. Hestermann and R. Hoppe, *Z. Anorg. Allg. Chem.*, **367** (1969) 249.
- 4 K. Hestermann and R. Hoppe, *Z. Anorg. Allg. Chem.*, **367** (1969) 261.
- 5 T. Mizokawa, H. Namatame, A. Fujimori, K. Akayama, H. Kondoh, H. Kuroda and N. Kosugi, *Phys. Rev. Lett.*, **67** (1991) 1638.
- 6 N. Brese, M. O'Keeffe, R.B. von Dreele and V. Young Jr., *J. Solid State Chem.*, **83** (1989) 1.
- 7 J. Pickardt, W. Paulus, M. Schmalz and R. Schöllhorn, *J. Solid State Chem.*, **89** (1990) 308.
- 8 T.A. Hewston and B.L. Chamberlain, *J. Phys. Chem. Solids*, **48** (1987) 97.
- 9 W. Klemm, G. Wehrmeyer and H. Bade, *Z. Elektrochem.*, **63** (1959) 56.
- 10 A.R. Wizansky, P.E. Rauch and F.J. Disalvo, *J. Solid State Chem.*, **81** (1989) 203.
- 11 K. Imai, M. Koike, H. Takei, H. Sawa, D. Shiomi, K. Nozawa and M. Kinoshita, *J. Phys. Soc. Jpn.*, **61** (1992) 1819.
- 12 K. Imai, personal communication, 1992.
- 13 M.T. Weller, D.R. Lines and D.B. Currie, *J. Chem. Soc., Dalton Trans.*, (1991) 3137.
- 14 R. Berger, P. Önnerud, Y. Laligant and A. LeBail, *J. Alloys Comp.*, **190** (1993) 295.
- 15 R. Berger, P. Önnerud and R. Tellgren, *Abstracts of IVth Eur. Conf. on Solid State Chemistry, Dresden, 1992*, p. 334.
- 16 D.B. Currie and M.T. Weller, *J. Mater. Chem.*, **3** (1993) 229.
- 17 R. Berger, A. Meetsma, S. van Smaalen and M. Sundberg, *J. Less-Common Met.*, **175** (1991) 119.
- 18 R. Berger, P. Önnerud and R. Tellgren, *J. Less-Common Met.*, **184** (1992) 315.
- 19 G. Tams and Hk. Müller-Buschbaum, *J. Alloys Comp.*, **189** (1992) 241.
- 20 K. Yvon, W. Jeitschko and E. Parthé, *J. Appl. Crystallogr.*, **10** (1977) 73.
- 21 K.-E. Johansson, T. Palm and P.-E. Werner, *J. Phys. E: Sci. Instrum.*, **13** (1980) 1289.
- 22 R.J. Hill and C.J. Howard, *Rep. m112*, 1986 (Australian Atomic Energy Commission, Lucas Heights Research Laboratories, Sutherland, N.S.W.).
- 23 G. Tams and Hk. Müller-Buschbaum, *Z. Anorg. Allg. Chem.*, **617** (1992) 19.