

Structure refinements of LiCu_2O_2 and LiCu_3O_3 from neutron powder diffraction data

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Abstract

In its inherent ability to discern light elements in a heavy-atom matrix, neutron powder diffraction has been used at room temperature to confirm structure hypotheses of LiCu_2O_2 ($R_1=2.18\%$; $R_p=4.21\%$) and LiCu_3O_3 ($R_1=2.19\%$; $R_p=5.45\%$), inferred from previous X-ray diffraction studies. LiCu_2O_2 is orthorhombic, described by the space group $Pnma$ ($Z=4$), as suggested from a structure determination from twin-crystal data. The cell parameters found were $a=5.7260(4)$ Å, $b=2.8587(2)$ Å and $c=12.4137(7)$ Å. The apparent tetragonal symmetry independently advocated must be definitively discarded as an artifact from twinning. LiCu_3O_3 was successfully refined on a tetragonal cell—with $a=2.8142(1)$ Å and $c=8.8956(5)$ Å—in PA/mmm ($Z=1$) using a single-crystal model. The data were insufficient to test any superstructure model.

1. Introduction

In the course of the study of copper-oxide-based high-temperature superconductors, many theories have been put forward to explain the phenomena observed. Magnetic interactions or the presence of electron holes have been essential elements of such arguments. In this light, copper(II) oxide itself has come into focus with investigations concerning structural details [1], its magnetic transitions [2] and the possibility of creating electron holes in it, for instance by lithium doping [3]. Interest in the system Li–Cu–O also evolved from another angle, where a potential usage of Li/CuO primary cells was considered [4]. Two new phases with mixed-valence copper(I,II), LiCu_2O_2 and LiCu_3O_3 , were independently synthesized [3, 4].

As part of the crystallographic characterization of LiCu_2O_2 , electron diffraction was used which indicated [3] that the X-ray powder diffraction data could be successfully described on an orthorhombic cell, in contrast to the tetragonal symmetry assumed in an independent investigation [5]. Eventually, the structure was solved from two X-ray diffraction twin-crystal data sets [6] on a $Pnma$ model. The two reports on LiCu_3O_3 [3, 5] are more consistent on assigning a tetragonal cell. This symmetry is supported by convergent beam patterns and the fact that no deviation from the indexing model was found (such as line splittings) while the volume changed 1% in its homogeneity range [3]. Hibble *et al.* [5] performed a structure determination

where, in contrast to the situation in LiCu_2O_2 , lithium and copper partly occupy the same sites substitutionally.

Since the scattering factors of the constituent elements vary widely for the X-ray method, it was considered worthwhile to receive a confirmation of the structure proposals by using neutron diffraction instead, where the scattering powers are more compatible and, moreover, to perform a study on powder that is unaffected by twinning effects. The results are reported in this paper.

2. Experimental details

2.1. Sample preparation and X-ray diffraction

Mixtures of CuO and Li_2CO_3 ("Baker analysed Reagent", J. T. Baker, Deventer resp. Phillipsburg) according to the appropriate stoichiometries were ground together and compacted. They were reacted at $900\text{ }^\circ\text{C}$ for 1 h. According to X-ray powder diffraction analysis, the phases present were CuO , Li_2CuO_2 , LiCu_2O_2 and LiCu_3O_3 , indicating that all lithium carbonate had reacted but not to a phase equilibrium.

2.1.1. LiCu_2O_2

The product was again ground, compacted and reheated, this time at $970\text{--}980\text{ }^\circ\text{C}$. The phase set was monitored by X-ray diffraction, and it was found that this process of homogenization and heating had to be repeated several times. According to the phase analysis results, some lithium loss occurred (to give CuO , LiCu_2O_2 and LiCu_3O_3) which was compensated for by adding some extra lithium carbonate to the mixture before the final heating stage after which the product still consisted of three phases, now CuO , Li_2CuO_2 and LiCu_2O_2 . This three-phase set was considered more favourable than the former, for Li_2CuO_2 was now completely removable by treating the product with concentrated ammonia. Li_2CuO_2 reacts with water [7], but, instead of obtaining copper hydroxide as a solid, all decomposition products are water soluble in ammonia solution owing to complexation. The treatment was stopped when a fresh portion of ammonia was no longer coloured dark blue, and powder diffraction on the product now showed only CuO and LiCu_2O_2 .

2.1.2. LiCu_3O_3

The phase mixture was reheated a couple of times at $900\text{ }^\circ\text{C}$ including grinding and compacting. Phase analysis showed CuO and LiCu_3O_3 as main constituents and a trace of Li_2CuO_2 .

The cell parameters were determined using a Guinier–Hägg focusing camera with strictly monochromatic $\text{CuK}\alpha_1$ radiation and being calibrated by silicon as internal standard ($a = 5.431065\text{ \AA}$ at $25\text{ }^\circ\text{C}$). Individually weighted Q values were treated in least-squares refinements. The resulting cell of LiCu_2O_2 , with $a = 5.7260(4)\text{ \AA}$, $b = 2.8587(2)\text{ \AA}$ and $c = 12.4137(7)\text{ \AA}$, is in

excellent agreement with previous findings [3]. (To compare with the results of ref. 5 the b axis must be doubled.) Refinement on LiCu_3O_3 gave $a = 2.8142(1)$ Å and $c = 8.8956(5)$ Å. A certain homogeneity range has been noted [3, 5]. The cell of CuO in that sample was also refined, yielding $a = 4.6924(3)$ Å, $b = 3.4151(5)$ Å, $c = 5.1272(6)$ Å and $\beta = 99.628(9)^\circ$. These parameter values, being intermediate between those for pure CuO and for the maximum solubility [3], indicate that lithium of the order of 1% has gone into solid solution. Refinement of the cell parameter values of the lithium cuprates was formally performed initially in the Rietveld procedure, but the values so obtained were used for rescaling the wavelength until the X-ray parameters were retrieved, effectuating a refinement of the wavelength.

2.2. Neutron diffraction

Neutron powder diffraction data were recorded at the R2 reactor, Studsvik, Sweden. The neutron flux at the sample position is approximately $10^6 \text{ cm}^{-2} \text{ s}^{-1}$ when using the normal monochromatization by $\text{Cu}(220)$. Since the a/b axis ratio is 2.003 for LiCu_2O_2 , we chose the copper monochromator (331) reflection to increase the resolution for these profiles but thereby decreasing the intensity strongly. Table 1 presents some experimental parameters of the data collection. A multidetector system with ten separate detectors measured the intensities in 2θ steps of 0.08° . The sample was contained in a vanadium cylinder during data collection which occurred at 295 K. Absorption effects were later corrected for by using experimentally determined μR values from transmission measurements at $2\theta = 0$.

2.3. Structure refinement

The Rietveld method [8] was applied, as implemented in the multiphase LHPM1 program [9]. The diffraction peaks were described as being gaussian, and the linewidths (represented by the full width at half-maximum (FWHM)) were assumed to follow an angular dependence expressed as $\text{FWHM}^2 = U \tan^2\theta + V \tan\theta + W$, where θ is the Bragg angle and U , V and W are refinable parameters. The background was also described by a polynomial expression, where the coefficients were refined. The scattering lengths used were -2.03 fm, 7.718 fm and 5.805 fm for natural lithium, copper and oxygen respectively.

TABLE 1

Experimental parameters for recording the neutron diffraction data

Parameter	LiCu_2O_2	LiCu_3O_3
Monochromator plane	(331)	(220)
Wavelength (Å)	1.335(3)	1.469(3)
Absorption factor μR	0.474	0.455
2θ range (deg)	9.00–128.12	9.00–128.04
Time per step (min)	50	30

2.3.1. LiCu_2O_2

Assuming that the space group ($Pnma$) and structure parameters of LiCu_2O_2 , as obtained from the X-ray determination [6], were essentially correct, we started the refinement by adjusting the zero-point (2θ) and background parameters, treating the data as being single phase. After refining the corresponding scale factor, we allowed for the presence of CuO, refining its scale factor but keeping the positional (oxygen in 4e with $y=0.416$ [10]) and unit-cell parameters (from X-ray powder diffraction) constant. Eventually, we refined the ten LiCu_2O_2 positional parameters, three cell parameters and a total of three isotropic temperature factors (lithium, copper, oxygen), partly common for the two phases. We also allowed for a small asymmetry of the profiles, described by one refinable parameter, giving in total 29 parameters.

2.3.2. LiCu_3O_3

As starting model we used the data obtained by Hibble *et al.* [5] who had refined only copper and oxygen positions, since lithium negligibly contributes to the scattering from the assumed statistical distribution on the copper(II) sites. In our treatment we had to put in lithium also, with the constraints that the partial occupation by copper in 1b and 2h of $P4/mmm$ is completely compensated for by lithium. When comparing the oxygen coordination taken by copper(II) and lithium in LiCu_2O_2 , one observes that, although both metals take five neighbours in a pyramidal arrangement, the metal–oxygen distances are rather similar (2.07–2.11 Å) for lithium while copper, owing to the Jahn–Teller effect, prefers four short distances with the apex oxygen further away. A corresponding pyramidal coordination occurs in LiCu_3O_3 where copper and lithium enter the same site. However, when lithium enters this site, it should adopt a slightly different position, reflected by an individual z parameter to adapt to its own requirements. This could not be taken care of in the previous X-ray work where only the copper parameters were refined [5]. Therefore, while fixing the sum of the occupancies of the 2h and 1b sites each at 100%, we allowed for different positional parameters for the two atom kinds on 2h. In order to avoid expected strong coupling between the occupancy, thermal parameter and z value, we let lithium have the same B factor as copper on 2h. Moreover, the stoichiometry obtained by Hibble *et al.* [5] suggested strict ionic charge rules. Therefore we also put in the constraint that we would obtain an Li:Cu(II) ratio of 1:2, leading to one refineable occupation parameter.

3. Results and discussion

The refinements converged satisfactorily within the models for the two cuprates. Judging from the scale factors, the first sample contained 66(1)% LiCu_2O_2 , the rest being CuO. The second sample similarly contained 88(1)% LiCu_3O_3 . We also found a minute (0.2%) contribution of Li_2CO_3 , a decomposition product of a trace of Li_2CuO_2 (which had disappeared during the

interval between the synthesis and the neutron data collection). Since the solid solubility of lithium in CuO amounted only to approximately 1%, any deviation in stoichiometry was not refinable.

3.1. LiCu_2O_2

The reliability indices of the profiles $R_p=4.21\%$ and $R_{wp}=5.52\%$, correspond to an excellent general fit. As regards the structure models, the Bragg reliability indices were $R_1(\text{LiCu}_2\text{O}_2)=2.18\%$ and $R_1(\text{CuO})=3.02\%$, calculated for 309 and 114 reflections respectively. The overall fit obtained from the refinement is illustrated in Fig. 1.

The refined structural parameters are found in Table 2, including the corresponding data from the X-ray twin-crystal data refinement [6]. The standard deviations are larger for the powder profile data. The temperature factor of lithium comes out rather high and with a large spread. A smaller value, more in line with that obtained from the X-ray refinement, may be obtained if one allows for a deviation in occupation on that site. Correlation effects preclude a decisive interpretation, but we are rather in favour of a situation where we have some kind of disorder as indicated from the somewhat broader reflections with h odd as previously commented upon [6]. The covariance matrix discloses that, apart from strong correlations between the parameters for each polynomial expression describing the background and the line width, relatively large correlations (-0.74 and 0.77) are found

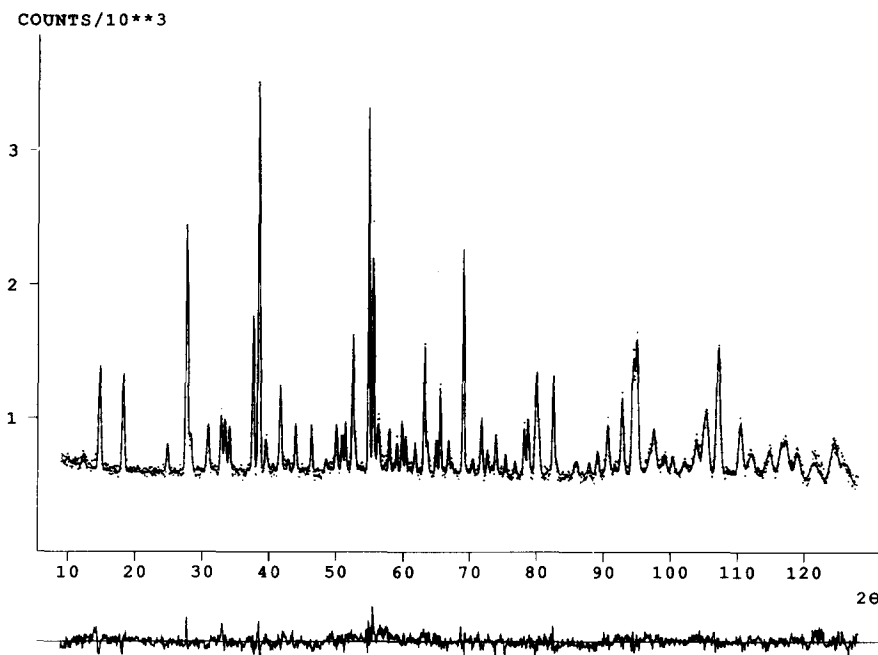


Fig. 1. Neutron powder diffraction data for $\text{LiCu}_2\text{O}_2\text{-CuO}$: top, the observed intensities (\cdot) and Rietveld-refined profiles; bottom, their difference on the same scale.

TABLE 2

Comparison between the structural parameters of LiCu_2O_2 , as obtained from a previous X-ray refinement from twin-crystal data [6] and the current neutron diffraction powder data^a

Atom	x	z	B (\AA^2)	Technique
Li	0.130(3) ^b	0.5719(9)	0.48(8)	X-ray ^c
	0.150(7)	0.572(1)	1.5(4)	Neutron ^d
Cu(1)	0.1194(3)	0.25490(7)	0.67(2)	X-ray
	0.128(2)	0.2548(4)	0.52(4)	Neutron
Cu(2)	0.1244(2)	0.90548(6)	0.45(1)	X-ray
	0.120(1)	0.9049(3)	0.52(4)	Neutron
O(1)	0.137(1)	0.4052(4)	0.49(3)	X-ray
	0.137(2)	0.4063(5)	0.25(6)	Neutron
O(2)	0.115(1)	0.1049(4)	0.61(3)	X-ray
	0.113(2)	0.1058(5)	0.25(6)	Neutron

^aAll atoms at $4c$ with $y=1/4$ in $Pnma$.

^bStandard deviations are given in parentheses.

^cIndividual thermal parameters were used in refinement, even anisotropic values for the two copper sites, although the values given here are the equivalent isotropic values.

^dIn the neutron refinement each kind of atom was assigned a temperature factor.

between the x parameters of lithium and copper(II), and between the oxygen x parameters, respectively. It seems too far fetched to draw any decisive conclusions from these not too disturbing values. Moreover, the Durbin–Watson d index of 1.1 indicates a series correlation [11] to some extent that leaves the parameter estimates unbiased but affects the standard deviations. These tend to become slightly underestimated from which we conclude that the parameter values are not significantly different between the two determinations.

3.2. LiCu_3O_3

The residuals for the profiles were slightly higher here, $R_p=5.45\%$ and $R_{wp}=7.10\%$, probably reflecting the difference in monochromator settings. The corresponding Bragg reliability indices were $R_1(\text{LiCu}_3\text{O}_3)=2.19\%$ and $R_1(\text{CuO})=2.67\%$, calculated for 67 and 85 reflections respectively. The overall fit from the profile refinement, as seen in Fig. 2, is quite satisfactory.

The largest covariance between the structural parameters was 0.77, found for the z parameters of lithium and copper on 2h. The Durbin–Watson d index was 0.70. Again, remembering that such a value implies that the standard deviations are underestimated, we see from Table 3 that the model by Hibble *et al.* [5] is verified. Previous indications from electron diffraction that the tetragonal a axis should be modified to yield a larger tetragonal cell [3] were not put to the test. We cannot totally rule out that the compound also changes in the electron beam so as to produce artifacts.

While also properly taking account of the lithium scattering which is negligible in the X-ray case, we arrived at the same distribution of copper and lithium as that obtained by Hibble *et al.* [5]. They reproduced their

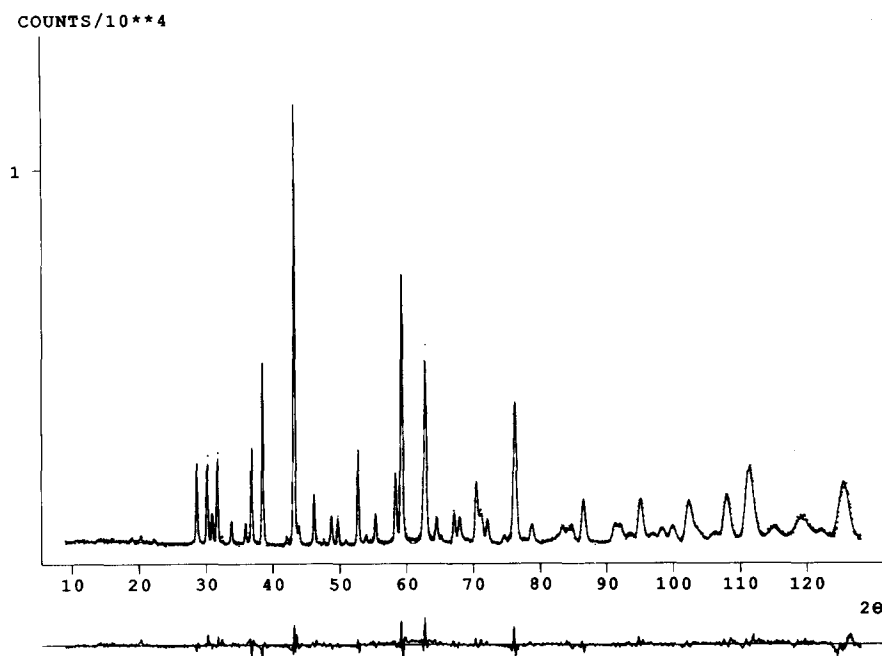


Fig. 2. Neutron powder diffraction data for $\text{LiCu}_3\text{O}_3\text{-CuO}$: top, the observed intensities (·) and Rietveld-refined profiles; bottom, their difference on the same scale.

result on a second single crystal while we measured an average from powder. The cell parameter variation found [3], more decisive for the c axis, could reflect a homogeneity range or different Li:Cu distributions. Since the lattice is spanned by metal–oxygen pyramids, apex to apex in the c direction, a larger fraction of copper on 2h might result in an elongation of the c axis, for our refinement clearly shows that lithium tends to take a slightly different position within the oxygen pyramid compared with copper in order to obtain more even distances ($4 \times 2.02 \text{ \AA}$ and $1 \times 2.23 \text{ \AA}$) to oxygen than copper does ($4 \times 2.00 \text{ \AA}$ and $1 \times 2.41 \text{ \AA}$).

4. Conclusions

Our investigation is a solid confirmation of the previous X-ray results, now obtained with a technique that better discerns the atomic positions and which is unmarred by twinning effects. Since there are no fundamentally new structural aspects gained, we refrain from discussing the structures here but rather refer to the previous reports on LiCu_2O_2 [6] and LiCu_3O_3 [5]. We intend further research using neutron diffraction for surveying the low-temperature magnetic interactions in these lithium cuprates(I,II) as indicated from the magnetic susceptibility data [5].

TABLE 3

Comparison between the structural parameters of LiCu_3O_3 , as obtained from previous X-ray single-crystal data [5] and the current neutron diffraction powder data, refined in $P4/mmm$

Atom Site	x	y	z	G	B (\AA^2)	Technique
Cu(1) 1a	0	0	0	0.0625	0.82(3) ^a	X-ray ^b
	0	0	0	0.0625	0.65(5)	Neutron
Cu(2) 1b	0	0	1/2	0.0505(2)	0.53(3)	X-ray
	0	0	1/2	0.0508(3)	0.35(5)	Neutron
Cu(3) 2h	1/2	1/2	0.2283(2)	0.0743(2)	0.64(3)	X-ray
	1/2	1/2	0.2265(6)	0.0742(3) ^c	0.35(5) ^c	Neutron
Li(1) 1b	0	0	1/2	0.0120(2) ^c		X-ray
	0	0	1/2	0.0117(3) ^c	0.35(5) ^c	Neutron
Li(2) 2h	1/2	1/2	0.2283(2) ^c	0.0507(2) ^c		X-ray
	1/2	1/2	0.250(4)	0.0508(3) ^c	0.35(5) ^c	Neutron
O(1) 1d	1/2	1/2	1/2	0.0625	0.9(1)	X-ray
	1/2	1/2	1/2	0.0625	0.61(4)	Neutron
O(2) 2g	0	0	0.2088(6)	0.125	0.84(8)	X-ray
	0	0	0.2091(3)	0.125	0.61(4) ^c	Neutron

^aStandard deviations are given in parentheses.

^bLithium atoms were omitted from the X-ray refinement and assumed to complete the occupancies at the copper(II) sites; individual anisotropic temperature factors were used, but in the table these are replaced by their equivalent isotropic parameters, taking B as equal to the trace of the U_{ij} tensor times the factor $8\pi^2/3$.

^cConstrained value.

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