

# Investigations on a New Copper Niobium Oxide of $\text{LiNb}_3\text{O}_8$ Type Using Chemical Analysis and X-Ray Powder Diffraction Profile Analysis

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The compound  $\text{Cu}_{0.98 \pm 0.02}\text{Nb}_{2.97 \pm 0.03}\text{O}_8$  has been characterized by means of phase analysis, chemical analysis, density and magnetic measurements. Its crystal structure has been determined and refined by full-profile analysis of microdensitometer-measured Guinier-Hägg powder diffraction data. The black, weakly paramagnetic compound is isomorphous with  $\text{LiNb}_3\text{O}_8$ . The structural refinement, which included 36 positional parameters, led to an  $R_F$ -value=0.127. The following formula of the compound is suggested:  $\text{Cu}_{0.81}^{2+}\text{Cu}_{0.14}^{2+}(\text{Cu}_{0.03}^{2+}\text{Nb}_{2.97}^{5+})\text{O}_8$ .

A recently commenced study of phases formed by solid state reactions in the copper-niobium-oxygen system has revealed a number of compounds not previously reported.<sup>1</sup> Among these is one which forms very small black crystals. Its unit cell parameters show a close resemblance to those of  $\text{LiNb}_3\text{O}_8$  (cf. Table 1), the structure of which was determined a few years ago.<sup>2</sup> This paper deals with the preparation and stoichiometry of the new com-

pound and with the determination and refinement of its crystal structure by the application of a profile analysis to the data obtained from its Guinier-Hägg powder pattern. Following the nomenclature adopted by Young *et al.*<sup>3</sup> the profile analysis is a pattern-fitting structure refinement.

## PREPARATION AND ANALYSIS OF THE COMPOUND

The compound was prepared from various mixtures of copper, copper(I) oxide, copper(II) oxide,

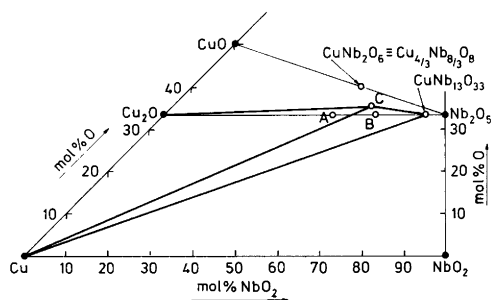


Fig. 1. Part of the phase diagram of the system Cu–Nb–O at around 770 °C. A and B correspond to the compositions  $x\text{Cu}_2\text{O} \cdot (1-x)\text{Nb}_2\text{O}_5$  with  $x=0.286$  for A and  $x=0.250$  for B (i.e.  $\text{CuNb}_3\text{O}_8$ ). C corresponds to  $\text{Cu}_{1+y/3}\text{Nb}_{3-y/3}\text{O}_8$ .  $y=0.06$  gives the composition for a weighed-in sample  $\text{Cu}_{1.02}\text{Nb}_{2.98}\text{O}_8$ . Note that in reality compositions A, B and C are closer to each other than they are represented in the figure.

Table 1. Comparison of unit cell parameters for  $\text{CuNb}_3\text{O}_8$  and  $\text{LiNb}_3\text{O}_8$ .

|                       | $\text{CuNb}_3\text{O}_8$ | $\text{LiNb}_3\text{O}_8$ |
|-----------------------|---------------------------|---------------------------|
| $a$ (Å)               | 15.365(2)                 | 15.262(2)                 |
| $b$ (Å)               | 5.0717(5)                 | 5.033(1)                  |
| $c$ (Å)               | 7.5266(6)                 | 7.457(1)                  |
| $\beta$ (°)           | 107.18(1)                 | 107.34(1)                 |
| $V$ (Å <sup>3</sup> ) | 560.34                    | 546.77                    |

niobium(IV) oxide and niobium(V) oxide in proportions giving a copper(I)–niobium(V) ratio close to 1:3.

The mixtures were reacted in evacuated silica tubes. The heating time varied from two days to several weeks. The reaction temperature was about 770 °C.

The phase analysis results showed that the stoichiometry of the new phase (denoted *C* in Fig. 1) deviates somewhat from  $\text{CuNb}_3\text{O}_8$  ( $=B$ ). For the latter composition of the starting mixture the product was contaminated with  $\text{CuNb}_{13}\text{O}_{33}$ , a phase isomorphous with  $\text{NaNb}_{13}\text{O}_{33}$ ,<sup>4</sup> and copper metal. If the amount of  $\text{Nb}_2\text{O}_5$  was less (*i.e.* composition *A* in Fig. 1), the product was free from  $\text{CuNb}_{13}\text{O}_{33}$  but was instead mixed with copper(II) oxide and copper metal. Upon treatment with aqueous nitric acid ( $\text{HNO}_3\cdot 4\text{H}_2\text{O}$ ) the product yielded a Guinier photograph which showed no other lines than those of the  $\text{LiNb}_3\text{O}_8$  type pattern. A sample of composition  $\text{Cu}_{1.02}\text{Nb}_{2.98}\text{O}_8$  (*C* in Fig. 1) gave the same pattern plus two very weak lines from  $\text{Cu}_2\text{O}$ , which indicates that the true composition of the compound may be slightly off the line connecting the  $\text{CuNb}_2\text{O}_6$  and  $\text{CuNb}_3\text{O}_8$  points in the phase diagram. Above 800 °C decomposition to  $\text{CuNbO}_3$ <sup>1</sup> and  $\text{CuNb}_{13}\text{O}_{33}$  took place.

The copper content was determined in the following way. About 0.7 g of a sample *A* (Fig. 1), which had been carefully treated with nitric acid (1:4) in order to remove any copper oxide or copper metal present, was dissolved in 8 ml of concentrated hydrofluoric acid + 2 ml of nitric acid (1:1) and boiled. The solution was diluted with 20 ml of water and the acidity was adjusted to  $\text{pH} \approx 4$  by dropwise addition of ammonia (1:1). Potassium iodide was added, and the liberated iodine was titrated with 0.1 M sodium thiosulfate. Cu found: 13.42(1) %.

For determination of the niobium content about 0.4 g of a similar sample was dissolved in a hydrofluoric acid–nitric acid mixture as above. After evaporation to dryness 1 ml of concentrated sulfuric acid was added and the evaporation was repeated. The product was then slowly heated to 750 °C and weighed as copper(II) oxide + niobium(V) oxide. Nb found: 59.5(2) %.

Density measurements of a sample *A*, likewise treated with nitric acid, were made from observations of the loss of weight in diethyl phthalate. Found: 5.49(3)  $\text{g cm}^{-3}$ .

On a sample *A* treated with nitric acid magnetic susceptibility measurements in the temperature

interval 77 K–750 K were made according to the Faraday method with an apparatus constructed at our Institute.<sup>5</sup>  $\mu_{\text{eff}}$  found: 0.32.

The combined results of the chemical analyses and the density measurements, with estimated uncertainties, yield the following formula:  $\text{Cu}_{0.98 \pm 0.02}\text{Nb}_{2.97 \pm 0.03}\text{O}_8$ . Calculated analysis and property values for this composition are: Cu 13.36 %, Nb 59.19 %,  $D = 5.525 \text{ g/cm}^3$ ,  $\mu_{\text{eff}} = 0.78$  (estimated from a Bohr magneton number of 1.9 for Cu(II); Nb(IV) has been assumed absent). The compound will be denoted  $\text{CuNb}_3\text{O}_8$  in the following.

Due to lack of suitable single crystals the structural study had to be based on X-ray powder diffraction data.

## DATA COLLECTION

A powder diffraction photograph of sample *A* (*cf.* Fig. 1) was taken in a focusing camera of the Guinier–Hägg type with strictly monochromatized  $\text{CuK}\alpha_1$  radiation. Potassium chloride ( $a/\lambda = 4.08477$  at 25 °C)<sup>6,7</sup> was added as an internal theta-standard. In order to avoid backlayer profiles a single-coated film was used; this simplifies the profile analysis. Peak positions, step-scan intensities and integrated intensities were extracted from the photograph with an extended version of the film-scanner system described by Malmros and Werner.<sup>8</sup>

The film-scanner<sup>9</sup> records transmission data from a  $45 \mu\text{m} \times 2040 \mu\text{m}$  area on the photograph at each theta value. The longer dimension, in the direction along the powder lines is divided into 34 individually measured parts, the measuring window at the film-scanner being  $45 \mu\text{m} \times 60 \mu\text{m}$ . The advantages of applying this procedure have recently been discussed by Berg and Werner in a paper on the use of Guinier film data for structure analysis.<sup>10</sup>

The  $2\theta$  range used,  $11.810^\circ < 2\theta < 87.186^\circ$ , was covered in steps of  $0.03179^\circ$ , each corresponding to  $45 \mu\text{m}$  on the photograph. Although it was possible to index most of the peaks by the least-squares refined monoclinic unit cell given in Table 1, not only the lines from the internal standard, KCl, but also a few, very weak lines arising from copper and copper(I) oxide in the sample were identified. Therefore all the intensities within the ten  $2\theta$  intervals listed in Table 2 were excluded from the calculations. This is not likely to affect the results appreciably, but rather demonstrates the applica-

Table 2. Least-squares profile refinement of Guinier-Hägg powder film data of  $\text{CuNb}_3\text{O}_8$ .

| Excluded<br>2 $\theta$ -regions (°) | Intensity contributions from<br>Substance ( <i>hkl</i> ) | 2 $\theta_{\text{calc}}$ (°) |
|-------------------------------------|--|------------------------------|
| 28.000–28.510                       | KCl (200)  | 28.340                       |
| 36.167–37.667                       | $\text{Cu}_2\text{O}$ (111)                              | 36.417                       |
| 40.200–40.720                       | KCl (220)  | 40.510                       |
| 41.980–42.700                       | $\text{Cu}_2\text{O}$ (200)                              | 42.296                       |
| 43.045–43.545                       | Cu (111)   | 43.295                       |
| 49.940–                             | KCl (222)  | 50.176                       |
| –51.060                             | Cu (200)   | 50.431                       |
| 58.440–58.800                       | KCl (400)  | 58.630                       |
| 61.091–61.591                       | $\text{Cu}_2\text{O}$ (220)                              | 61.341                       |
| 66.080–66.600                       | KCl (420)  | 66.378                       |
| 73.170–                             | $\text{Cu}_2\text{O}$ (311)                              | 73.523                       |
| –                                   | KCl (422)  | 73.690                       |
| –74.410                             | Cu (220)   | 74.128                       |

bility of the profile analysis technique even to samples containing certain amounts of extraneous phases.

## PROFILE REFINEMENT ANALYSIS

From the relatively few resolved lines in the powder pattern and the great number of positional parameters, 36, it was obvious that it would not be possible to refine the structure solely from integrated peaks. On the other hand, the Rietveld-type of profile refinement procedure originally developed for neutron diffraction<sup>11</sup> and rewritten for Guinier-Hägg diffraction data<sup>12,13</sup> makes it possible to take full account of the overlaps in the pattern. Therefore, we decided to make a profile-fitting least-squares refinement of the compound, starting with the positional parameters given by Lundberg for  $\text{LiNb}_3\text{O}_8$ <sup>2</sup> and assuming  $\text{CuNb}_3\text{O}_8$  stoichiometry.

Taking into account the results from the phase analysis and from the chemical analysis which show that a slight deficiency in the copper content cannot be ruled out, a copper occupancy parameter was added to the variables in the least-squares refinement. Because of the strong correlations between the occupancy parameter and the temperature factors only two temperature factors, *viz.* one for the metal atoms and one for the oxygen atoms, were refined in the subsequent calculations. The variables refined included 36 positional parameters, one copper occupancy parameter, the two tempera-

ture factors mentioned above, one scale factor, one asymmetry and three half-width parameters, *i.e.* a total of 44 variables. In the last refinement cycles the asymmetry and half-width parameters were held fixed.

The refinement was considered complete when all shifts were less than the estimated standard deviations of the corresponding parameters. The largest shifts were obtained for O(6) where the shifts in the *x* and *z* coordinates were approximately 90 % of the e.s.d.'s in the last refinement cycle. The shifts in the remaining parameters were all less than 2/3 of the e.s.d.'s.

Two reliability indices  $R_p$  and  $R_F$  defined in the following way:

$$R_p = \frac{\sum_i |y_i(\text{obs}) - y_i(\text{calc})|}{\sum_i |y_i(\text{obs})|}$$

where  $y_i$  = step scan intensities, and

$$R_F = \frac{\sum_k |\sqrt{I_k(\text{obs})} - \sqrt{I_k(\text{calc})}|}{\sum_k \sqrt{I_k(\text{obs})}}$$

where  $I_k$  = the integrated intensity for reflexion *k*, illustrate the accuracy of the refinement. The final values were  $R_p = 0.215$  and  $R_F = 0.127$ . The positional parameters obtained are listed in Table 3. A list of 399 structure factors is available from the authors.

## COPPER OCCUPANCY AND CHEMICAL COMPOSITION

The formal thermal parameters ( $\beta$ -values) obtained for the metal and oxygen atoms were  $-1.71(7)$  and  $-2.9(2) \text{ \AA}^2$ , respectively. It has been found in a number of profile refinements of Guinier-Hägg powder diffraction data that due to strong correlations between scale factor, occupancy parameters, temperature factors and absorption effects, negative thermal parameters are usually obtained.<sup>13</sup> Therefore, no physical significance can be given to the thermal parameters. On the other hand, individual temperature factors which are refined to values far above the average level usually indicate errors in the structural model. The difficulties are strongly enhanced, however, when occupancy parameters are refined. The value of the copper "occupancy" parameter obtained in the present refinement was 0.75(2).

Table 3. Atomic coordinates. Estimated standard deviations in parentheses. A =  $\text{CuNb}_3\text{O}_8$ . Guinier-Hägg powder diffraction data. B =  $\text{LiNb}_3\text{O}_8$ . X-ray single crystal data (Lundberg (1971)). Space group  $P2_1/a$ . All atoms in position 4(c).

| Atom  | x          | y         | z           | Study |
|-------|------------|-----------|-------------|-------|
| Nb(1) | 0.1690(4)  | 0.268(2)  | 0.0070(9)   | A     |
| Nb(1) | 0.16852(5) | 0.2696(3) | 0.00831(10) | B     |
| Nb(2) | 0.0788(5)  | 0.754(2)  | 0.2485(8)   | A     |
| Nb(2) | 0.07508(5) | 0.7549(3) | 0.24924(11) | B     |
| Nb(3) | 0.1638(4)  | 0.257(2)  | 0.5107(8)   | A     |
| Nb(3) | 0.16458(5) | 0.2576(3) | 0.51674(10) | B     |
| Cu    | 0.4252(8)  | 0.274(3)  | 0.273(2)    | A     |
| Li    | 0.420(2)   | 0.267(8)  | 0.260(3)    | B     |
| O(1)  | 0.280(3)   | 0.421(8)  | 0.061(7)    | A     |
| O(1)  | 0.2817(5)  | 0.433(2)  | 0.0846(11)  | B     |
| O(2)  | 0.141(3)   | 0.390(8)  | 0.739(7)    | A     |
| O(2)  | 0.1558(5)  | 0.400(2)  | 0.7354(10)  | B     |
| O(3)  | 0.198(3)   | 0.587(8)  | 0.401(6)    | A     |
| O(3)  | 0.2157(5)  | 0.589(2)  | 0.4148(11)  | B     |
| O(4)  | 0.040(3)   | 0.129(8)  | 0.872(5)    | A     |
| O(4)  | 0.0389(5)  | 0.108(2)  | 0.8551(11)  | B     |
| O(5)  | 0.105(4)   | 0.947(8)  | 0.492(7)    | A     |
| O(5)  | 0.0989(5)  | 0.940(2)  | 0.5005(10)  | B     |
| O(6)  | 0.048(4)   | 0.432(8)  | 0.341(6)    | A     |
| O(6)  | 0.0485(5)  | 0.439(2)  | 0.3528(10)  | B     |
| O(7)  | 0.085(3)   | 0.552(9)  | 0.028(6)    | A     |
| O(7)  | 0.1006(5)  | 0.580(2)  | 0.0375(11)  | B     |
| O(8)  | 0.154(4)   | 0.093(7)  | 0.243(7)    | A     |
| O(8)  | 0.1551(5)  | 0.086(2)  | 0.2225(11)  | B     |

In order to check the significance of the refinement all positional parameters for the oxygen atoms were held fixed at the values listed in Table 3, and individual occupancy parameters were refined for all four metal atoms. When all shifts in the 23 parameters refined were less than 10% of the standard deviation no significant changes between input and output values of the parameters could be detected. This indicates that all "niobium" positions are fully occupied by metal atoms. The magnetic

measurements indicate the presence of Nb(IV) and/or Cu(II). It is unlikely, however, that Nb(IV) should be present in any appreciable amount in this particular compound due to its very strong reducing properties. Nor is there any evidence from the phase analysis that Nb(IV) should be present in intermediary phases found in the region of the Cu–Nb–O system under investigation. The analyses given above imply, however, that copper substitutes for a minor proportion of the niobium atoms.

The positional coordinates obtained for the copper atoms should be regarded as average values for randomly distributed Cu(I) and Cu(II) atoms, since there are no indications of a superstructure in the X-ray data. From general Fourier analysis arguments follows that this average copper position must give rise to an increased value of the  $\beta$  parameter and/or a value of the occupancy parameter less than the sum of the real occupancies for the Cu(I) and Cu(II) atoms. This is also in agreement with the fact that the refined formal occupancy parameter for the average copper position is as low as 0.75(2), whereas the copper occupancy determined from chemical analysis and density measurements is 0.98(2).

From the arguments given above the following composition of the compound is deduced:  $\text{Cu}_{0.95}\text{-(Cu}_{0.03}\text{Nb}_{2.97})\text{O}_8$ . As shown in the formula some copper may have replaced niobium. For the copper at the positions corresponding to lithium in  $\text{LiNb}_3\text{O}_8$ , the occupancy factor is around 0.95 – well above the one derived from the profile analysis. As explained above, however, this lower value merely signals the presence of two different species with slightly different atomic coordinates and with a slightly different surrounding of oxygens. The formula of the compound " $\text{CuNb}_3\text{O}_8$ " should therefore read  $\text{Cu}_{0.81}^{2+}\text{Cu}_{0.14}^{2+}(\text{Cu}_{0.03}^{2+}\text{Nb}_{2.97}^{5+})\text{O}_8$ .

## DISCUSSION OF THE STRUCTURE

A comparison of the atomic coordinates of " $\text{CuNb}_3\text{O}_8$ " with those of  $\text{LiNb}_3\text{O}_8$  reveals some obvious differences (cf. Table 3). Thus the x-coordinates of Nb(2), O(2), O(3) and O(7) and the z-coordinates of Nb(3) differ by five to eight standard deviations. The formal positional coordinates of copper in the "Li position" differ by about seven standard deviations in x and z. The greater differences in the latter case are to be

Table 4. Comparison of some interatomic distances in  $\text{CuNb}_3\text{O}_8$  and  $\text{LiNb}_3\text{O}_8$ . Standard deviations are given within parentheses.

|                              | $\text{CuNb}_3\text{O}_8$ | $\text{LiNb}_3\text{O}_8$ |
|------------------------------|---------------------------|---------------------------|
| Metal – oxygen distances (Å) |                           |                           |
| Nb(1) – O(1)                 | 1.81(5)                   | 1.844(8)                  |
| – O(7)                       | 1.98(5)                   | 1.922(8)                  |
| – O(2)                       | 2.03(5)                   | 2.091(7)                  |
| – O(1)                       | 2.05(5)                   | 1.844(8)                  |
| – O(4)                       | 2.06(5)                   | 2.129(7)                  |
| – O(8)                       | 2.06(5)                   | 1.913(7)                  |
| Mean value                   | 2.00                      | 1.993                     |
| Nb(2) – O(4)                 | 1.87(5)                   | 1.818(7)                  |
| – O(6)                       | 1.90(5)                   | 1.866(8)                  |
| – O(7)                       | 1.98(4)                   | 1.945(8)                  |
| – O(5)                       | 2.01(5)                   | 2.027(7)                  |
| – O(3)                       | 2.03(5)                   | 2.290(8)                  |
| – O(8)                       | 2.08(4)                   | 2.107(8)                  |
| Mean value                   | 1.98                      | 2.009                     |
| Nb(3) – O(5)                 | 1.79(5)                   | 1.872(8)                  |
| – O(2)                       | 1.97(5)                   | 1.823(7)                  |
| – O(3)                       | 2.01(4)                   | 1.943(8)                  |
| – O(6)                       | 2.06(5)                   | 2.043(7)                  |
| – O(8)                       | 2.14(5)                   | 2.320(7)                  |
| – O(3)                       | 2.20(5)                   | 2.077(8)                  |
| Mean value                   | 2.03                      | 2.013                     |
| Cu(Li) – O(6)                | 2.08(5)                   | 2.16(3)                   |
| – O(5)                       | 2.15(5)                   | 2.08(2)                   |
| – O(2)                       | 2.20(5)                   | 2.20(4)                   |
| – O(4)                       | 2.25(5)                   | 2.08(4)                   |
| – O(1)                       | 2.43(5)                   | 2.27(3)                   |
| – O(7)                       | 2.49(4)                   | 2.34(3)                   |
| Mean value                   | 2.27                      | 2.19                      |
| Metal – metal distances      |                           |                           |
| Nb(1) – Cu(Li)               | 3.31(2)                   | 3.25(4)                   |
| – Cu(Li)                     | 3.36(2)                   | 3.25(4)                   |
| Nb(2) – Nb(3)                | 3.23(2)                   | 3.239(2)                  |
| – Nb(3)                      | 3.24(2)                   | 3.260(2)                  |
| – Cu(Li)                     | 3.40(2)                   | > 3.60                    |
| Nb(3) – Cu(Li)               | 3.44(2)                   | 3.43(4)                   |
| – Cu(Li)                     | 3.56(2)                   | 3.53(4)                   |
| – Cu(Li)                     | 3.58(2)                   | > 3.60                    |

expected due to the fact that the metal position is averaged between those of copper(I) and copper(II). Consequently the oxygen polyhedron around copper is markedly different from the octahedron in

$\text{LiNb}_3\text{O}_8$ . Thus it is found that the averaged position of the copper atoms is at the center of a very distorted tetrahedron with copper–oxygen distances ranging from 2.08 to 2.25 Å. There are two other oxygen atoms at 2.43 and 2.49 Å from the copper atom which complete a distorted octahedron of oxygens. They are *not* opposite to each other with respect to the copper atom. Five oxygen–oxygen distances in the tetrahedron range between 2.93 and 3.55 Å, while the sixth is appreciably longer, *viz.* 4.29 Å.

There are, however, striking similarities between the copper and the lithium compound. The octahedral environment of the niobium atoms is nearly the same in both compounds. The niobium – oxygen distances in the three types of  $\text{NbO}_6$  octahedra exhibit an even smaller range of variation than in  $\text{LiNb}_3\text{O}_8$ . The average values are very nearly the same (*cf.* Table 4). Regarding the oxygen – oxygen distances in the copper compound the shortest (2.34 Å) is found for the atoms forming the common edge between the  $\text{NbO}_6$  octahedra, which otherwise exhibit normal oxygen – oxygen distances.

The structure of “ $\text{CuNb}_3\text{O}_8$ ” is built of  $\text{NbO}_6$  octahedra (a few of which may contain copper(II) instead of niobium(V)) and of  $\text{CuO}_4$  tetrahedra

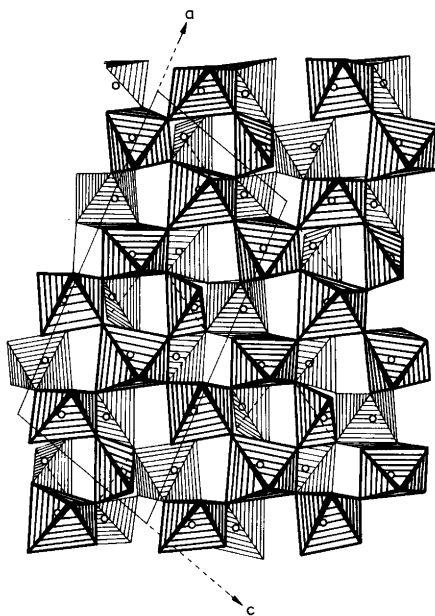


Fig. 2. The structure of  $\text{CuNb}_3\text{O}_8$  projected on the *ac*-plane.

containing copper(I) or copper(II) atoms. Some of the octahedra (those containing Nb(2) and Nb(3) atoms) share edges in such a way that zig-zag strings of octahedra are formed exactly as in  $\text{LiNb}_3\text{O}_8$ . The remaining octahedra [containing Nb(1) atoms] are connected by corners to  $\text{CuO}_4$  tetrahedra in such a manner that zig-zag strings are formed which consist of alternating octahedra and tetrahedra. The two types of strings, which are mutually connected by corners, run in the *b*-axis direction (cf. Fig. 2).

As a final remark we would like to point out that the structure type of  $\text{LiNb}_3\text{O}_8$  seems to possess a high degree of adaptability as it does allow the presence of Cu(I) and Cu(II) at the lithium positions involving a deformation of the surrounding oxygen polyhedra, without any appreciable changes in the niobium-oxygen framework.

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