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On the Distribution of Monovalent Copper in $Cu_{0.6}Nb_6O_{14.6}F_{1.4}$ of $LiNb_6O_{15}F$ Structure Type

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A structure determination of $Cu_{0.6}Nb_6O_{14.6}F_{1.4}$ isostructural with $LiNb_6O_{15}F$, has been performed with single crystal X-ray data, to an R-value of 0.058. The compound is orthorhombic, space group *Pmma* (No. 51), the unit cell is $a=16.772(6)$, $b=3.876(1)$, and $c=8.973(2)$ Å with $Z=2$. The structure is an *average structure* where all Nb atoms are split and shifted out of the mirror plane perpendicular to the b-axis. Cu atoms partially occupy sites in the four-sided tunnels running parallel to the b-axis. Weak extra reflections in electron diffraction patterns indicate a doubling of the b-axis. These extra reflections were invisible on the X-ray films.

Several systems involving niobium or tantalum pentoxide in combination with copper(I) or copper(II) oxide and/or NbO_2F have been studied in this laboratory in order to provide more information on the coordination chemistry of Cu(I) and Cu(II) in compounds of transition metal oxides.[1-5] In a recent study of the copper-tantalum-oxygen system, the distribution of monovalent and divalent copper in the structure of $Cu_{0.8}Ta_3O_8$,[6] of the $LiNb_6O_{15}F$-type,[7] has been reported.

This article describes the result of a crystal structure investigation of a phase found in the Cu(I)–Nb(V)–O–F system and its relation to the structure of $Cu_{0.8}Ta_3O_8$. A detailed phase analysis of the Cu(I)–Nb(V)–O–F system has not been performed.

EXPERIMENTAL

Samples of the gross composition $CuNb_6O_{15}F$ were made from weighed mixtures of Cu_2O (Matheson Coleman and Bell min 96 %), Nb_2O_5 (Carl Roth min 99.9 %) and NbO_2F (prepared as in Ref. 8), in a dried, evacuated and sealed copper tube for 3 d at 975 K. The copper tube was chosen as container since it could withstand the attack of oxyfluorides, and it seemed to suppress the disproportionation of Cu_2O. The tube was enclosed in a dried and evacuated silica tube to protect it from oxidation. The resulting product consisted of rod-shaped crystals of red colour. X-Ray powder photographs were taken at room temperature with a Guinier-Hägg camera using $CuK\alpha_1$ radiation and KCl as an internal standard ($a_{KCl}=6.2930$ Å at 298 K).[9] The photographs indicated the presence of a major phase, here called A, of the $LiNb_6O_{15}F$ structure type,[7] and small amounts of Cu_2O. The powder pattern of A could be indexed on the basis of an orthorhombic unit cell, and least squares refinement[10] gave the unit cell listed in Table 1.

Weissenberg photographs along the b and c axes confirmed the Laue symmetry *mmm*, and a crystal with the dimensions $0.060\times0.150\times0.12$ mm^3 was used for the intensity data collection on a Philips PW1100 four-circle diffractometer equipped with a graphite monochromator. Intensities for 1077 independent reflections with

Table 1. Crystallographic data for $Cu_{0.6}Nb_6O_{14.6}F_{1.4}$.

Unit cell	a (Å)	16.772(6)
	b (Å)	3.876(1)
	c (Å)	8.973(2)
	V (Å^3)	583.32
Space group		*Pmma* (No. 51)
Unit cell content Z		2
Density (calc.)(g·cm^{-3})		4.84

0302-4377/84 $2.50

$\theta<35°$ within an octant of the reciprocal lattice were collected with the $\omega-2\theta$ scan technique (scan width=1.5 °, scan speed=0.015 °.s^{-1}). 556 reflections with $I<3\sigma(I)$ were used in the structure refinement. The intensities were corrected for Lp and absorption effects (μ=69.4 cm^{-1}). The scattering factors for unionized atoms were used,[11] and anomalous dispersion terms for niobium, copper and oxygen atoms were taken from Cromer and Waber.[12] All crystallographic computing was carried out in a combination of full matrix least squares and Fourier synthesis with the programs SHELX[13] and UPPALS.[14]

An analytical electron microscope study was undertaken in order to determine the copper/niobium ratio in thin crystals of the *A* phase and to check the possible occurrence of superstructure reflections. In the first case, an X-ray microanalysis was performed on a Philips EM 301 electron microscope operated at 80 kV and equipped with a LINK SYSTEMS 860 ANALYSER attachment. Specimens were prepared by crushing crystals in an agate mortar, dispersing them in *n*-butanol and collecting them on carbon films supported by aluminium grids. The ratio method was applied on the Cu*Ka* and Nb*La* lines for the quantitative analysis. Standard profiles for Cu and Nb (foils) were used. Electron diffraction patterns were recorded on a Siemens "ELMISKOP 102" electron microscope, equipped with a double-tilt stage.

STRUCTURE INVESTIGATIONS AND RESULTS

The only systematic absent reflections were for *hk*0 with $h=2n+1$, which suggests the space groups *Pmma* (No. 51), *P*2$_1$*ma* (No. 26) or *Pm*2*a* (No. 28). A refinement was first carried out with all niobium atom sites restricted to the mirror planes perpendicular to the shortest axis (*b*-axis) in the space group *Pmma* (No. 51), starting from the coordinates reported for $LiNb_6O_{15}F$.[7] A three-dimensional Fourier synthesis gave approximate coordinates for the copper atoms. Further refinements with anisotropic Nb atoms and isotropic non-niobium atoms led to an *R*-value of 0.068. The temperature factors for the copper atoms were, however, high. The occupancy factors of the copper atom sites, which had been assumed to be unity for both positions, were refined in the same way as in Ref. 6, and decreased considerably in magnitude, and the thermal parameters were lowered as well.

All niobium atoms acquired large amplitudes in the direction of the *b*-axis indicating that they were not located exactly on the apparent mirror plane perpendicular to *b*, but the Weissenberg photographs showed neither extra reflections nor streaks on the films, even if strongly exposed. During the refinement of the structure of *H*-$LiTa_3O_8$[15] and $Cu_{0.8}Ta_3O_8$,[6] preliminary studies of electron diffraction patterns revealed superstructure reflections which the X-ray photographs did not show. In the present case, electron diffraction patterns taken for the zone [0 0 1] were carefully examined, and revealed weak superstructure reflections that required a doubling of the *b* and *a* axes.

At this stage, split positions across the apparent mirror plane were introduced for all niobium atoms, and were refined with isotropic temperature factors. This resulted in considerable shifts, ~0.15 Å along the *b*-direction, for all four niobiums. Although this did not improve the *R*-value significantly it led to lower temperature factors and lower standard deviations of all refined parameters. The positions of the non-niobium atoms did not change by more than $0.2\cdot\sigma$. The resulting temperature factors for the niobium atoms were approximately one sixth of the amplitudes along the *b*-axis obtained with anisotropic, unsplit atoms.

The weighting function used was $1/\sigma^2(F_{obs})$, minimizing $\Sigma\omega\Delta^2$ with $\Delta=||F_{obs}|-|F_{cal}||$. The final weight analysis showed no significant trends in the average of $\omega\Delta^2$ for intervals of $|F_{obs}|$ and $\sin\theta$, with all normalized $\omega\Delta^2$ values falling within the range 0.81–1.29. The observed structure factors of the six 0*k*0 reflections were much smaller than the calculated values. This was considered to be due to extinction and they were deleted in the final least squares refinements. The final *R*-value was 0.058. No significant changes in the parameters resulted. All non-metal atoms were treated as oxygen atoms. Table 2a shows the final positional, thermal and occupancy parameters and the interatomic distances are listed in Table 3. Table 2b gives the positional and thermal parameters for a model with unsplit Nb atoms.

Experiments with lowering the symmetry gave no improvements and no further studies with shifted niobiums were performed, since the major objective of this investigation was to study the distribution of copper atoms in the compound. The value for the occupancy factors of the copper atoms obtained from the final refinement suggested a Cu/Nb ratio of 0.10±0.01, corresponding to the formula $Cu^{I}_{0.6}Nb^{V}_{6}O_{14.6}F_{1.4}$ and assuming, that no copper(II) was present. The values for the Cu/Nb ratio obtained from the microanalysis of several crystal fragments range from 0.06±0.01 to 0.17±0.01. The red colour of this compound suggests a single oxidation state of copper and agrees with the colour of other monovalent Cu compounds investigated at this laboratory.[3,5] It is possible that the phase has a homogeneity range as suggested by the microanalysis results. Then it is likely that the O/F ratio also varies, thus keeping copper monovalent. The value of 0.10±0.01 obtained from the least-squares refinement falls within the interval observed by means of due X-ray microanalysis.

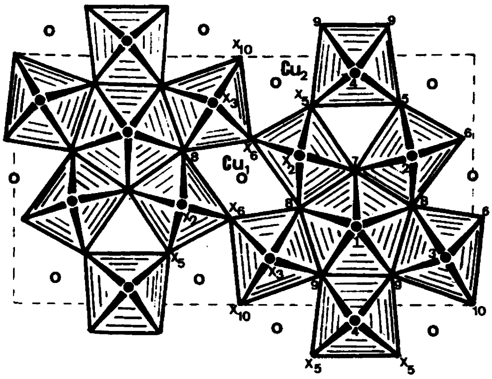

Fig. 1. The structure of $Cu_{0.6}Nb_6O_{14.6}F_{1.4}$ projected along the *b*-axis. The copper positions are also indicated. For the numbering of atoms, refer to Table 2. The anions in the copper coordination sphere are indicated by X.

DESCRIPTION AND DISCUSSION

The structure of $Cu_{0.6}Nb_6O_{14.6}F_{1.4}$ is of the same type as that of $LiNb_6O_{15}F$,[7] $H-LiTa_3O_8$,[15] and $Cu_{0.8}Ta_3O_8$.[6] It contains pentagonal columns with seven-coordinated niobium atoms in NbX_7 pentagonal bipyramids sharing edges with five NbX_6 octahedra (Fig. 1). These building units are linked *via* cornersharing, and the network gives rise to diamond-shaped and triangular tunnels running parallel to the *b*-axis and to square "windows" having their four-fold axes parallel to the *ac*-plane.

The mean value of the metal-anion distances within the pentagonal bipyramid is 2.01 Å. This agrees well with 2.03 Å in $Cu_{0.8}Ta_3O_8$[6] as do the corresponding distances in the three different octahedra, with mean values of 1.964, 1.983 and 1.960 Å. In $LiNb_6O_{15}F$[7] all niobium atoms are situated on a mirror plane perpendicular to the

Table 2a. Positional, thermal and occupancy parameters for $Cu_{0.6}Nb_6O_{14.6}F_{1.4}$ (Space group *Pmma*). R=0.058 Standard deviations are given in parentheses.

Atom	Position	*x*	*y*	*z*	$U/Å^2$	Occupancy factor
Nb(1)	4(*k*)	¼	0.04223(10)	0.6873(3)	0.0053(6)	½
Nb(2)	8(*l*)	0.13099(8)	0.0396(8)	0.3973(2)	0.0084(5)	½
Nb(3)	8(*l*)	0.05955(9)	0.0382(8)	0.8143(3)	0.0065(5)	½
Nb(4)	4(*k*)	¼	0.0367(2)	0.0571(4)	0.0084(6)	½
Cu(1)	2(*d*)	0	½	½	0.032(4)	0.28(3)
Cu(2)	4(*j*)	0.093(1)	½	0.093(3)	0.025(4)	0.14(4)
O(1)	2(*f*)	¼	½	0.689(2)	0.008(3)	1
O(2)	4(*j*)	0.129(1)	½	0.405(2)	0.035(4)	1
O(3)	4(*j*)	0.059(1)	½	0.820(1)	0.033(4)	1
O(4)	2(*f*)	¼	½	0.046(3)	0.035(6)	1
O(5)	4(*i*)	0.165(1)	0	0.195(2)	0.029(4)	1
O(6)	4(*i*)	0.021(1)	0	0.338(2)	0.023(3)	1
O(7)	2(*e*)	¼	0	0.457(2)	0.008(3)	1
O(8)	4(*i*)	0.131(1)	0	0.619(2)	0.014(3)	1
O(9)	4(*i*)	0.175(1)	0	0.876(2)	0.013(3)	1
O(10)	2(*a*)	0	0	0	0.015(4)	1

Table 2b. Positional and thermal parameters for a model with unsplit Nb atoms. R=0.068. Anisotropic thermal parameters are given in the form:
$\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})$. Standard deviations are given in parentheses.

Atom	Position	x	y	z	U or U_{11}	$U_{22}^{\downarrow}$ [a]	U_{33}	U_{12}	U_{13}	U_{23}
Nb(1)	2(*e*)	¼	0	0.6873(4)	0.0059(7)	0.042(3)	0.005(9)	0	0	0
Nb(2)	4(*i*)	0.13092(9)	0	0.3973(3)	0.0085(6)	0.039(2)	0.008(7)	0	−0.0012(1)	0
Nb(3)	4(*i*)	0.05957(9)	0	0.8144(3)	0.0068(5)	0.036(2)	0.008(6)	0	0.0008(9)	0
Nb(4)	2(*e*)	¼	0	0.0573(4)	0.0088(7)	0.036(3)	0.009(8)	0	0	0
Cu(1)	2(*d*)	0	½	½	0.033(4)					
Cu(2)	4(*j*)	0.092(1)	½	0.092(3)	0.025(4)					
O(1)	2(*f*)	¼	½	0.688(3)	0.008(3)					
O(2)	4(*j*)	0.130(1)	½	0.403(2)	0.036(5)					
O(3)	4(*j*)	0.059(1)	½	0.821(2)	0.033(4)					
O(4)	2(*f*)	¼	½	0.047(4)	0.036(6)					
O(5)	4(*i*)	0.165(1)	0	0.195(3)	0.036(5)					
O(6)	4(*i*)	0.031(1)	0	0.337(3)	0.031(4)					
O(7)	2(*e*)	¼	0	0.459(3)	0.013(4)					
O(8)	4(*i*)	0.131(1)	0	0.619(2)	0.019(3)					
O(9)	4(*i*)	0.174(1)	0	0.876(2)	0.018(3)					
O(10)	2(*a*)	0	0	0	0.018(4)					

[a] Large amplitudes in the direction of the b-axis are indicated by an arrow (↓).

Table 3. Some interatomic distances in $Cu_{0.6}Nb_6O_{14.6}F_{1.4}$.

Metal–metal distances in Å within the pentagonal column	
Nb(1)–Nb(2)	3.280(3) 3.296(3)
–Nb(3)	3.392(2) 3.406(2)
–Nb(4)	3.319(4) 3.333(4)
Niobium–anion distances in Å within the pentagonal bipyramid	
Nb(1)–2X(1)	1.774(4) 2.103(4)
–X(7)	2.072(20)
–2X(8)	2.092(11)
–2X(9)	2.119(14)
Niobium–anion distances in Å within the octahedra	
Nb(2)–2X(2)	1.787(3) 2.093(3)
–X(5)	1.910(17)
–X(6)	1.925(14)
–X(7)	2.073(5)
–X(8)	1.996(15)
Nb(3)–2X(3)	1.791(3) 2.087(3)
–X(6)	1.931(16)
–X(8)	2.131(14)
–X(9)	2.010(12)
–X(10)	1.948(2)
Nb(4)–2X(4)	1.799(5) 2.083(5)
–2X(5)	1.897(16)
–2X(9)	2.067(13)
Copper–anion distances in Å	
Cu(1)–2X(2)	2.322(16)
–4X(6)	2.446(10)
–2X(3)	3.037(17)
Cu(2)–2X(5)	2.462(15)
–X(3)	2.516(21)
–2X(10)	2.625(12)
–X(4)	2.665(18)

b-axis, while in the present compound the corresponding atoms are shifted out of this plane. Such a shift is also reported for Ta(4) in *H*–$LiTa_3O_8$,[15] with a magnitude of 0.15 Å, and is of the same magnitude as observed in the present compound, where the range is 0.14–0.16 Å. In $Cu_{0.8}Ta_3O_8$[6] and Nb_2WO_8[16] the corresponding intervals are 0.07–0.18 and 0.11–0.27 Å, respectively. In the latter compound a superstructure with double *c*-axis was evident from the X-ray data.[16]

It is a well-known fact[17] that pentavalent niobium and tantalum frequently occur off-center in octahedral coordination. This often results in ferro- or antiferroelectric behaviour in ternary oxides containing these elements.[18] In the structures of *H*–$LiTa_3O_8$,[15] $Cu_{0.8}Ta_3O_8$[6] and Nb_2WO_8,[16] which are all of the $LiNb_6O_{15}F$ type, the heavy metal atoms are displaced in an ordered fashion out of the common plane at $y=0$, and form a puckered sheet. This is obviously the case also in the present compound. However, this displacement seems to be more or less disordered as no displacement pattern compatible with the unit cell and apparent symmetry could be found. The X-ray data give no information about the nature of disorder to be associated with the splitting. If the weak superstructure reflection visible in the electron diffraction patterns were caused by displacements of the Nb atoms, the shifts should be extremely small since no extra spots were visible on the X-ray photographs. It seems more likely that the O- and perhaps also the Cu-atoms are responsible for this superstructure reflections.

According to difference Fourier maps with the calculated contribution of the niobium and oxygen atoms subtracted, the only two maxima found correspond to atomic sites of copper in the four-sided tunnels running parallel to the *b*-axis. The ratio of these two maxima (peak 2/peak 1) is ~0.6, and this implies that the two different crystallographic sites contain different amounts of copper. None of these sites is fully occupied (Table 2), and it is interesting to note, that the X-ray microanalysis suggests a variation in the Cu/Nb ratio for different crystals.

The Cu–X bond distances are shown in Table 3. The coordination of copper atoms based upon interatomic distances is not easy to define in this particular compound, as the small Cu atoms are located in rather large holes. As seen from Table 3, there is a gradual increase in near-neighbour distances. Shannon and Prewitt[19] pointed out that several groups of ions exhibit irregular coordination, and among them are ions with d^{10} configuration. Cu(1) has two nearest X(2) anions at a distance of 2.32 Å. The linear X(2)–

Cu−X(2) bond is required by symmetry. The next closest ions are four X(6) at a 2.45 Å distances, completing a distorted octahedron. This type of coordination of monovalent copper was also found in $Cu_xV_2O_5$ (x=0.85).[20]

In a recent study on the distribution of mono- and divalent copper in this structure type, it has been found that copper(II) atoms located in "window" interstices occur in a square four-coordination, whereas the Cu(I) atoms in the same structure are found at nearly the same crystallographic sites as the monovalent copper in the present study, and accordingly have very similar coordination.[6] The other copper atom, Cu(2), is surrounded by six nearest anions. Its coordination polyhedron can be described as approximately octahedral. The shortest Cu−X bond distances in this compound are longer than expected and suggest weak interaction between copper(I) and the neighbouring anions. This is characteristic of many ionic-type compounds. In Ag_2TeO_3[21] for example the Ag(I)−O distances range from 2.368−2.87 Å. On the other hand, short bonds have been observed in $Cu^{I}_{0.6}NbO_{2.6}F_{0.4}$[5] with Cu−X bond length of 1.84 Å, which is similar to 1.85 Å in Cu_2O.[22]

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