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Short Communication

Copper-deficiency in Ln$_{2-x}$Ce$_x$CuO$_4$ (Ln=Nd, Gd) crystals and oxygen disorder in Gd$_2$CuO$_4$ crystals

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(Reçu le 24 novembre 1989, accepté sous forme définitive le 16 janvier 1990)

Résumé. — La structure de sept monocristaux de Nd$_{2-x}$Ce$_x$CuO$_4$ (x=0 et x=0.18) et Gd$_2$CuO$_4$ est déterminée par diffraction des rayons X. Tous les cristaux ont la structure tétragone T' du Nd$_2$CuO$_4$ (groupe d'espace I$_4$/mmm, n° 139). Un défaut de cuivre de l'ordre de 3 à 6% est trouvé dans six cristaux alors que les deux sites de l'oxygène (dans les plans CuO$_2$ O(1) et entre les plans de terre rare O(2)) sont complètement occupés dans la limite d'erreur. Les ellipsoïdes de vibration des sites Nd, Cu et O(2) sont plus allongés parallèlement à l'axe c dans les cristaux recuit sous atmosphère inerte que dans les cristaux bruts de croissance. L'atome d'oxygène des plans CuO$_2$ (O(1)) dans Gd$_2$CuO$_4$ est trouvé décentré dans la direction de l'axe a de 0.18 (2) Å.

Abstract. — The structure of seven Nd$_{2-x}$Ce$_x$CuO$_4$ (x=0 and x=0.18) and Gd$_2$CuO$_4$ single crystals is determined by means of X-ray diffraction. All crystals have the Nd$_2$CuO$_4$ tetragonal T' structure, space group I$_4$/mmm (139). The copper site is found deficient (3 - 6%) in six crystals whereas both oxygen sites (within the CuO$_2$ planes O(1) and between rare earth layers O(2)) remain fully occupied within standard deviation. The vibration ellipsoids of Nd, Cu and O(2) appear to be more elongated in the c direction in Nd-based crystals reannealed in an inert atmosphere than in as-grown ones. The oxygen of the CuO$_2$ basal plane (O(1)) in Gd$_2$CuO$_4$ is found off-centered in the a direction by 0.18 (2) Å.

1. Introduction.

Superconductivity was recently discovered in the Ln$_{2-x}$Ce$_x$CuO$_4$ (Ln = Nd, Pr, Sm, Eu) and Ln$_{2-x}$Th$_x$CuO$_4$ (Ln = Nd, Pr) copper-oxide materials with a critical temperature up to 24 K for x=0.16 [1 - 3]. These compounds are not spontaneously superconducting but need to be annealed...
(900 °C) in an inert atmosphere (N₂, Ar) to achieve superconductivity. X-ray absorption near-edge structure measurements of the Ce L₃ edge [4, 5], Ce ionic-radius analysis [6, 7] and Ce X-ray photoemission measurements [8] indicate that the valence of Ce is greater than +3. These compounds can therefore be considered as electron-doped superconductors in agreement with Hall coefficient measurements [1, 9] which show that, in the normal state, the transport properties are essentially due to electrons. At least one parent compound of these materials, namely Nd₂CuO₄, exhibits magnetic order of the Cu moments at 245 K with an antiferromagnetic arrangement of spins in the CuO₂ planes [10, 11].

At room temperature, all electron-doped superconductors have the Nd₂CuO₄ tetragonal T' structure (space group I₄/mmm, Z=2) [12] which differs from the related high temperature tetragonal T structure of La₂CuO₄₋ₓ in that the two apical oxygen atoms are removed from the (0,0, z) position to the (0, 1/2, 1/4) position (Fig. 1). Hence the coordination numbers of Cu and Ln (Ln = Nd, Pr, Sm, Eu) become respectively 4 (square plane) and 8 instead of 6 (octahedral) and 9.

Several neutron and X-ray powder diffraction structural studies have been performed on these compounds. The main results for the prototype material Nd₂₋ₓCeₓCuO₄ can be summarized as follow:

(i) the c parameter decreases from 12.17 Å to 12.06 Å when the Ce content is increased from x = 0 to x = 0.20, upper limit of the solubility range, while the a parameter remains quasi-constant at 3.945 Å [8, 13],

(ii) superlattice reflexions have been reported by Izumi et al. in agreement with electron diffraction results [14] while other groups did not mention such extra peaks [8, 12, 13, 15] and

(iii) oxygen-deficiency on both sites O(1) (within the CuO₂ planes (0, 1/2, 0)) and O(2) (0, 1/2, 1/4) have been encountered by Izumi et al. [14] and Takayama-Muromachi et al. [16] on superconducting Nd₁.₈₅Ce₀.₁₅CuO₄ and on Ce free sample. For non-reannealed (non-superconducting) Nd₁.₈₅Ce₀.₁₅CuO₄, only the O(2) site was found deficient. In the light of thermogravimetry analysis, these authors suggest, in their latest paper [16], that the occupation factor of O(2) may be

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Fig. 1. — Body centered tetragonal unit cells of the high temperature T-structure of La₂CuO₄ (left) and the T'—structure of Nd₂CuO₄ (right).
underestimated and, eventually, that oxygen defects are introduced at least into the O(1) site by reduction.

We have performed a detailed Nd$_{2-x}$Ce$_x$CuO$_4$ single crystal analysis, using X-ray diffraction, in order to obtain valuable structural information and to investigate possible structural changes between as-grown and reannealed samples. One Gd$_2$CuO$_4$ single crystal is also included in the present study.

2. Experimental.

Several Nd-based crystals were prepared using two different methods, growth from a flux (CuO) between 1150 °C and 1000 °C for the Ce free samples (N1, N2, N3, N4) and spontaneous crystallisation from the powders at 1200 °C for the Ce-containing samples (N5, N6). N3 was extracted from the shiny free surface of the preparation, N1 and N4 from the innermost layers of this surface and N2 from the flux at the bottom of the preparation. N4 and N6 were further annealed at 900 °C under flowing nitrogen for 12 hours. The Gd$_2$CuO$_4$ crystal (Gd) was obtained by spontaneous crystallisation at 1200 °C.

All the crystals were found tetragonal with systematic extinction conditions corresponding to a body centered unit cell in agreement with unpublished X-ray powder diffraction results. $\theta - 2\theta$ and $\omega$ scans performed on the (200), (020) and (006) reflexions of each sample revealed a high crystalline quality and no trace of twinning. The Ce content of N5 and N6 was estimated from the c parameter to lie between 0.17 and 0.19 (Tab. I). The data collection was performed on a half sphere of the reciprocal space up to 65° (Mo Kα). After absorption correction, the independent reflexions were obtained as an average of 8 equivalent reflexions. The whole set of independent reflexions were kept in the refinement including those with zero intensity.

Table I. — Lattice parameters (Å) and volume of unit cell (Å$^3$). The lattice constants are obtained from a reflexion centering routine (25 reflexions).

<table>
<thead>
<tr>
<th>Crystals</th>
<th>a</th>
<th>c</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>3.941(1)</td>
<td>12.174(3)</td>
<td>189.08(15)</td>
</tr>
<tr>
<td>N2</td>
<td>3.942(1)</td>
<td>12.175(3)</td>
<td>189.19(15)</td>
</tr>
<tr>
<td>N3</td>
<td>3.944(1)</td>
<td>12.176(3)</td>
<td>189.40(15)</td>
</tr>
<tr>
<td>N4</td>
<td>3.946(1)</td>
<td>12.159(3)</td>
<td>189.33(15)</td>
</tr>
<tr>
<td>N5</td>
<td>3.950(1)</td>
<td>12.073(3)</td>
<td>188.37(15)</td>
</tr>
<tr>
<td>N6</td>
<td>3.949(1)</td>
<td>12.065(3)</td>
<td>188.15(15)</td>
</tr>
<tr>
<td>Gd</td>
<td>3.893(1)</td>
<td>11.888(3)</td>
<td>180.17(15)</td>
</tr>
</tbody>
</table>

3. Results and discussion.

The first refinement was carried out, using atomic structure factors, with the structural results of Rietveld analysis as starting parameters [14, 16], isotropic thermal parameters and occupations factors constrained to their ideal values. The temperature factors for all sites were then allowed to be anisotropic with symmetry constraints $U_{11} = U_{22}$ for Nd(Ce), Cu and O(2) sites and $U_{ij} = 0$ ($i \neq j$) for all atoms. Eventually the occupancies of Cu, O(1) and O(2) were successively refined.
3.1 Copper deficiency. — For six crystals (N1, N2, N3, N5, N6 and Gd), a significant copper-deficiency was found which led to a decrease of the R-factor. In Table III are reported the results of the $R_1/R_2$ ratio (respectively without and with a variation of the Cu occupancy) compared with the minimum value it should exhibit to be statistically significant $R_{k,n-m,0.005}$ [17]. In all cases, the $R_1/R_2$ ratio is higher than $R$. Furthermore it is to be noted that:

(i) the standard deviations on the occupation factors of Cu are at least four times lower than the deviation from the ideal value and

(ii) the decrease of the R-factor is all the more important than the deficiency is significant.

This copper-deficiency could result from a preparation temperature of crystals higher than the maximum stability temperature of CuO ($\approx 1050 \, ^\circ C$). Above this temperature Cu$_2$O rather than CuO is the stable form of copper oxide which leads to a fugacity of copper. Indeed a reddish hue, characteristic of Cu$_2$O, is observed in the flux after crystal growth. In addition N1, N2, N3 and N4 prepared at lower temperature than N5, N6 and Gd and with CuO in excess exhibit a smaller deficiency. Such a defect has already been encountered in YBa$_2$Cu$_3$O$_{7-y}$ crystals [18] but affects only the Cu(1) site (chain site) because of lower preparation temperature. In the present case, however, the CuO$_2$ planes are concerned and this should affect both superconducting and magnetic properties of Nd$_{2-x}$Ce$_x$CuO$_4$ crystals. In fact Tarascon et al. reported that they could not obtain zero resistance down to 2.5 K in the basal plane of superconducting Nd$_{2-x}$Ce$_x$CuO$_4$ ($x = 0.14$ and $x = 0.16$) crystals while it is currently achieved at 20 K in polycrystalline ceramics [19]. However we point out that this deficiency is not systematic since it is not observed in N4. It seems to be closely related to the preparation method and may vary from crystal to crystal as a function of local surrounding during growth.

We now come to the problem of oxygen content. Keeping in mind the copper defect reported above, it is reasonable to think that it should induce a related oxygen deficiency at least on the O(1) site. However no significant deviation from the ideal value was found except for the O(1) site of N2 (Tab. II). Our results do not allow to draw any definite conclusion.

<table>
<thead>
<tr>
<th>Nd (Ce, Gd)</th>
<th>N2</th>
<th>N5</th>
<th>N6</th>
<th>Gd</th>
</tr>
</thead>
<tbody>
<tr>
<td>z</td>
<td>0.35117(4)</td>
<td>0.35260(4)</td>
<td>0.35269(4)</td>
<td>0.34942(5)</td>
</tr>
<tr>
<td>Beq.</td>
<td>0.44(2)</td>
<td>0.47(2)</td>
<td>0.53(2)</td>
<td>0.47(2)</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td>0.39(4)</td>
<td>0.35(4)</td>
<td>0.43(5)</td>
</tr>
<tr>
<td>Beq.</td>
<td></td>
<td>2a (0, 0, 0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.046(5) *</td>
</tr>
<tr>
<td>y</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
</tr>
<tr>
<td>z</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Beq.</td>
<td>0.9(2)</td>
<td>0.9(2)</td>
<td>0.9(3)</td>
<td>0.9(2)</td>
</tr>
<tr>
<td>O (2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>y</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>z</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beq.</td>
<td>0.7(1)</td>
<td>0.8(1)</td>
<td>0.7(1)</td>
<td>0.65(15)</td>
</tr>
</tbody>
</table>

(*) The off-centering of O(1) in Gd is discussed in section 3.4.
The possibility of interstitial oxygen at the apex position O3 (0, 0, z) was also investigated. Indeed some electronic density was found at this site resulting in a slight decrease of the R factor and in large standard deviations over the multiplicity g, the position z and the temperature factor B. However the additional oxygen content (about the same for all crystals: doped or undoped, reannealed or not) was found to be approximately 0.25 (12) which is unrealistic. Moreover the refined O3 position (z ≈ 0.2) would lead to much too short Nd-O3 and O2-O3 distances. This result, although highly unprobable, may indicate complex structural features associated with oxygen disorder which can hardly be solved with X-ray diffraction. Single crystal neutron diffraction is needed to answer this question.

Table III. — Refinement results and Cu occupancy.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Number of ref.</th>
<th>(R_1/R_2)</th>
<th>(R_{0.005})</th>
<th>R factor</th>
<th>Cu occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>125</td>
<td>1.048</td>
<td>1.033</td>
<td>2.28</td>
<td>0.964(9)</td>
</tr>
<tr>
<td>N2</td>
<td>126</td>
<td>1.055</td>
<td>1.033</td>
<td>1.80</td>
<td>0.964(8)</td>
</tr>
<tr>
<td>N3</td>
<td>128</td>
<td>1.053</td>
<td>1.033</td>
<td>2.08</td>
<td>0.961(8)</td>
</tr>
<tr>
<td>N4</td>
<td>124</td>
<td>1.000</td>
<td>1.033</td>
<td>2.18</td>
<td>1.008(12)</td>
</tr>
<tr>
<td>N5</td>
<td>129</td>
<td>1.073</td>
<td>1.033</td>
<td>1.79</td>
<td>0.937(9)</td>
</tr>
<tr>
<td>N6</td>
<td>122</td>
<td>1.079</td>
<td>1.033</td>
<td>1.91</td>
<td>0.937(12)</td>
</tr>
<tr>
<td>Gd</td>
<td>125</td>
<td>1.047</td>
<td>1.033</td>
<td>2.15</td>
<td>0.944(12)</td>
</tr>
</tbody>
</table>

3.2 Effective valence of cerium in Nd-based crystals. — Knowing the average distances between atoms in one compound, it is possible to compute the ionic radius of each element and therefore its valence state for a certain coordination number. From our structural results we may evaluate the mean valence state of cerium in \(\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4\) (\(x = 0.18 \pm 1\)). In table IV is reported the average distance between the rare earth ion and its eight surrounding oxygens for each crystal. For Ce-free sample this distance is 2.501 (1) Å in good agreement with the theoretical value, 2.499 Å, computed from the following ionic radii:

\[
R (\text{Nd}^{3+}, \text{VIII}) = 1.109 \text{ Å},
\]

\[
R (\text{O}^{2-}, \text{IV}) = 1.38 \text{ Å for O(2)}
\]

and

\[
R (\text{O}^{2-}, \text{VI}) = 1.40 \text{ Å for O(1)}.
\]

In Ce-containing crystals (N5 and N6), we find 2.4945(10) Å which leads to a mean ionic radius, 1.1045(10) Å, and eventually to a mean valence state of cerium, 3.61(7), computed from:

\[
R (\text{Ce}^{3+}, \text{VIII}) = 1.143 \text{ Å}
\]

and

\[
R (\text{Ce}^{4+}, \text{VIII}) = 0.97 \text{ Å}.
\]

The error bar takes into account both the standard deviation on distances and the uncertainty on Ce content \((x = 0.18 \pm 1)\). This result is similar to that found by Hor et al., 3.59, from the variation of the volume of the unit cell [8] but much lower than that computed by Huang et al. from the decrease of the c parameter, 3.84 and would lead to a total extra-electron concentration of \(1.17(13) \times 10^{+21} \text{ cm}^{-3}\) in the absence of any other chemical difference between \(\text{Nd}_2\text{CuO}_4\) and \(\text{Nd}_{1.82}\text{Ce}_{0.18}\text{CuO}_4\).
3.3 ANISOTROPY. — In all Nd-based crystals the O(1) site exhibit strongly anisotropic temperature factors ($U_{22} < U_{11}, U_{33}$) due to Cu attraction along the b direction (Tab. V). For other sites, we must distinguish between as-grown (N1, N2, N3 and N5) and reannealed crystals (N4 and N6). In the first case, the Cu and O(2) thermal parameters are found isotropic within standard deviation while the Nd site exhibit smaller temperature factor in the c direction. For the latter crystals however, the Nd, Cu and O(2) sites have larger thermal parameter in the c direction than within the basal plane.

Another difference between as-grown and reannealed crystals is readily seen from table I: N4 and N6 have a lower c parameter than N1, N2 or N3 and N5 respectively.

Table V. — Anisotropic temperature factors for N2,N5 and N6 (Å² x 10⁴).
\[
\begin{array}{ccc}
\text{Crystal} & U_{11} & U_{22} \\
\hline
N2 Nd & 60(3) & U_{11} \\
N5 Nd & 63(3) & U_{11} \\
N6 Nd & 63(3) & U_{11} \\
N2 Cu & 48(6) & U_{11} \\
N5 Cu & 43(6) & U_{11} \\
N6 Cu & 41(7) & U_{11} \\
N2 O(1) & 124(34) & 68(31) \\
N5 O(1) & 121(29) & 71(26) \\
N6 O(1) & 129(39) & 64(30) \\
N2 O(2) & 95(22) & U_{11} \\
N5 O(2) & 98(17) & U_{11} \\
N6 O(2) & 74(23) & U_{11} \\
\end{array}
\]

3.4 OFF-CENTERING OF O(1) IN Gd₂CuO₄. — The refinement of Gd was carried out in the same manner as for the other crystals. Isotropic thermal parameters for the Nd, Cu and O(2) sites were found very similar to those of the as-grown Nd-based samples. In contrast, the temperature factor of O(1) was much higher ($B_{eq} = 1.7(4)$) indicating a possible off-centering of the atom. Anisotropic refinement showed that this disorder was confined to the a direction ($U_{11} = 435(80) \times$
$10^{-4} \text{Å}^2$, $U_{22} = 70(23) \times 10^{-4} \text{Å}^2$ and $U_{33} = 145(40) \times 10^{-4} \text{Å}^2$. The $x$ parameter of the atom was therefore allowed to vary and reached rapidly its convergence value, 0.046(5), that is an absolute off-centering, 0.18(2) Å. A significant decrease of the $R$ factor was obtained giving a $R_1/R_2$ ratio, 1.093, higher than the minimum statistical value, 1.033. In this configuration, the temperature factor of the off-centered atom is nearly divided by two ($B_{eq} = 0.9(2)$).

Another feature in Gd$_2$CuO$_4$ arises from the experimental value of the mean distance between the Gd cation and its surrounding oxygens, 2.461(1) Å, which is significantly lower than the theoretical one, 2.443 Å, computed from:

$$R(\text{Gd}^{3+}, \text{VIII}) = 1.053 \text{Å}.$$

4. Summary.

The main feature reported in this work is the occurrence of copper defects within the CuO$_2$ plane resulting from a preparation temperature higher than the stability temperature of CuO. This result obtained on single crystals is in agreement with the difficulty in obtaining zero resistance in the basal plane of Nd$_{2-x}$Ce$_x$CuO$_4$ ($x = 0.14, 0.16$) [19]. In contrast, no significant oxygen deficiency could be detected except in one crystal extracted from the inner part of the preparation. Further single crystal neutron diffraction analysis is required to investigate this problem more accurately.

The mean valence state of cerium in Nd$_{1.82}$Ce$_{0.18}$CuO$_4$, evaluated from the mean rare earth-oxygen distance, is found significantly higher than +3, 3.61(7), thus confirming the results obtained by means of X-ray absorption and X-ray photoemission measurements [4, 5, 8]. Detailed investigations of the magnetic and transport properties of Nd$_{2-x}$Ce$_x$CuO$_4$ are in progress as well as single crystal neutron diffraction studies.

Eventually the O(1) site in Gd$_2$CuO$_4$ appeared to be off-centered in the $a$ direction (0.18(2) Å) which can perhaps be related to the lack of superconductivity in Gd$_{2-x}$Ce$_x$CuO$_4$.

Acknowledgements.

The authors thank J. Godard for his help in growing the crystals and for making available a high temperature furnace.

References