Journal of Alloys and Compounds, 194 (1993) L5–L7
JALCOM 556

Letter

Evidence for interstitial oxygen and possible role of reduction in $Nd_{2-x}Ce_xCuO_{4+y}$

P. W. Klamut
Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 937, 50-950 Wrocław (Poland)

(Received October 19, 1992)

1. Introduction

The discovery of superconductivity in the $Ln_{2-x}M_xCuO_4$ (Ln ≡ Sm, Nd, Pr, Eu; M ≡ Ce, Th) system [1] revealed that two steps must be performed to induce superconductivity in the parent semiconductor Ln_2CuO_4. First, partial replacement of the 3+ rare earth (RE) element (Ln) by the 4+ ion (M), resulting in electron doping, is required. Then, for the material with Ce content in the narrow range $x=0.14$–0.17, superconductivity can be achieved by subtle reduction of the oxygen content. The role of this reducing step, as well as the choice of the oxygen positions in the crystal structure whose partial depletion is required, still seems to be a controversial subject in the literature. As far as the oxygen content value in this material is concerned, many authors report that it is less than four for reduced samples and equal to four for as-grown samples. The oxygen vacancy positions are reported to be located at both 0(1) and 0(2) sites [2] or at 0(1) sites only [3]. The possibility of oxygen depletion from 0(2) sites has also been suggested on theoretical grounds [4]. On the other hand, there are reports based on thermogravimetric measurements [5] and iodometric titration data [6] suggesting the oxygen content to be more than four, *i.e.* the presence of interstitial oxygen in the crystal structure of as-grown and even reduced samples. Our recent measurements of the thermal conductivity [7] of $Nd_{1.85}Ce_{0.15}CuO_{4+y}$ ceramics made before and after the reduction step suggested that partial oxygen depletion drives the sample to a more 'ordered' state, *i.e.* fewer structural defects are present than in the as-grown material. This supports the idea of removing oxygen from interstitial positions rather than from 0(1) or 0(2) sites in the structure. Double iodometric titration performed on this sample confirmed this interpretation: the oxygen content for already reduced, superconducting (at 24 K) $Nd_{1.85}Ce_{0.15}CuO_{4+y}$ was found to be 4.03 [7]. The value of the oxygen depletion leading to optimal superconducting properties (the highest T_c) is another data widespread in the literature. The values reported range from 0.04 [8] to 0 [9].

The above-mentioned inconsistencies in the experimental results reported so far have led us to study in more detail the oxygen content of as-grown and reduced $Nd_{2-x}Ce_xCuO_{4+y}$ samples with various Ce contents. The results are reported in this paper.

2. Sample synthesis

The $Nd_{2-x}Ce_xCuO_{4+y}$ ($x=0$, 0.1, 0.14, 0.15, 0.16) polycrystalline samples were prepared by the solid state reaction technique. Dried, stoichiometric quantities of the starting materials Nd_2O_3, CeO_2 and CuO were milled for 1 h, pressed into pellets and fired at 950 °C for 24 h. The product was ground, pelleted and refired at 1070 °C for 69 h, then furnace cooled to room temperature. Finally, three rectangular bars, all the same size, were cut from every sample. Two of them were subsequently reduced by annealing in a quartz tube under dynamic vacuum conditions (of the order of 10^{-6} Torr) at 875 °C for 3 and 6 h respectively.

The reduction procedure of 6 h vacuum annealing at 875 °C was chosen experimentally as the one leading to the highest T_c for the $x=0.15$ sample.

The X-ray powder diffraction pattern indicated the tetragonal Nd_2CuO_4-type structure with no impurity phases visible. No change in the crystal structure before and after the reduction step was detected within the accuracy of experiment.

The temperature dependences of the a.c. susceptibility were measured for the reduced samples using a Lake Shore Cryotronics, Inc. Model 7000 a.c. susceptometer.

3. Results and discussion

Figure 1 presents the oxygen content *vs.* the Ce concentration measured by double iodometric titration for three series of samples: unreduced and reduced in vacuum at 875 °C for 3 and 6 h respectively. The as-grown material reveals an excess of oxygen for all Ce contents. The excess value changes slightly with Ce concentration, with a broad maximum at about $x=0.1$. For the 6 h reduced samples the sudden decrease in oxygen content at low Ce concentrations indicates the

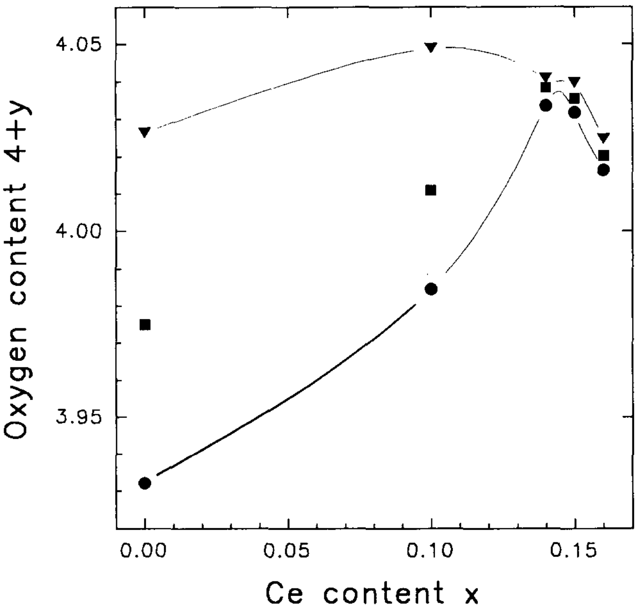

Fig. 1. Oxygen content *vs.* Ce stoichiometry for $Nd_{2-x}Ce_xCuO_{4+y}$: triangles, as-grown samples; circles, 6 h, 875 °C reduced samples; squares, 3 h, 875 °C reduced samples.

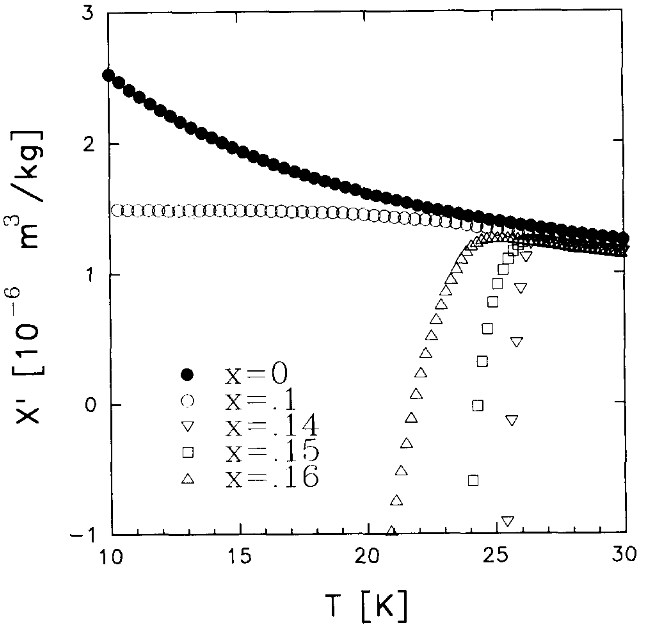

Fig. 2. Real component of a.c. susceptibility as a function of temperature for 6 h, 875 °C reduced $Nd_{2-x}Ce_xCuO_{4+y}$.

introduction of oxygen defects into the structure for $x=0$ ($\delta \approx 0.09$) and $x=0.1$ ($\delta \approx 0.07$). However, with increasing Ce concentration the oxygen depletion (from the value characteristic for as-grown material) becomes considerably smaller and finally a nearly constant value of $\delta \approx 0.01$ for $x=0.14$, 0.15 and 0.16 was detected. Because in this range of x the oxygen content already falls for the unreduced material, a well-defined maximum in the case of the reduced samples is detected. It is an interesting coincidence that its peak value of 4.03 appears for the Ce concentration at which the maximum T_c for the $Nd_{2-x}Ce_xCuO_{4+y}$ system is achieved. The 3 h reduced samples have an intermediate oxygen content, with a similar but more gradual maximum (squares in Fig. 1).

The measurements of the a.c. susceptibility for the 6 h reduced samples are presented in Fig. 2. The difference the χ' (T) dependences for $x=0$ and 0.1 may originate from the small amount of superconducting phase in the $x=0.1$ sample. The T_c onset for this phase, identified as the temperature at which these two curve ends follow each other, is the value of critical temperature onset for the $x=0.14$ sample.

To interpret these results, we will distinguish between two different parts of Fig. 1: (1) low Ce content ($0<x<0.14$), where the amount of released oxygen changes with the Ce concentration; (2) $x>0.14$, where the oxygen depletion is approximately constant. A possible interpretation of these different behaviours consistent with the χ' (T) data is that in the low range of x the material is not single phase, *i.e.* a phase separation to at least two phases takes place [10, 11]. One of them, a superconducting phase with a Ce concentration ≈ 0.15 and a small oxygen deficiency $\delta \approx 0.01$, coexists with a phase or phases without Ce or with lower Ce content and higher δ. By changing the Ce concentration in the sample, we can change the volume ratio between these phases and thus the total amount of oxygen released during the reduction procedure (see left part of Fig. 1). We note that several metastable phases can be realized in this range of x for given kinetics of the solid state reaction [11]. For $x>0.14$, in the already single-phase region, the oxygen depletion remains approximately constant for different Ce contents. The decrease in total oxygen content may originate in a shortening of the c axis by Ce doping [5] and thus a diminishment of the space available for interstitial ions in the structure.

Measurements of the Hall constant for as-grown and reduced samples [12] demonstrate that a small oxygen depletion δ causes a much higher (more than 2δ) change in the carrier density. Thus a question arises about the mechanism of electron doping which can be activated by removing such small quantities of oxygen ions. The oxygen contents reported in this paper suggest that oxygen removal from interstitial positions only is needed to induce superconductivity in this material. Moreover, already reduced samples with the highest T_c still possess an oxygen content greater than four (see Fig. 1). Recently, Matsuda *et al.* [13] proposed a mechanism in which excess oxygen in as-grown samples stabilizes the magnetic correlations. In the model, removal of these oxygen atoms causes a diminishment of the magnetic correlation and thus of the superconductivity at low temperature. The model leads to the highest critical temperature in the case of the completely ordered structure, *i.e.* with the oxygen index equal to four, which is in disagreement with our data. Here it is worth noting the X-ray single-crystal diffraction study done by Kajitani *et al.* [14]. Investigating the role of oxygen reduction, the authors report a shortening of the Nd/Ce–O(1) and Nd/Ce–Cu distances while the Nd/Ce–O(2) distance remains unchanged. Quite plausible positions for interstitial oxygen atoms in the crystal structure are empty apical positions above and below copper ions. Accordingly, removal of the oxygen from these sites may lead to the reported decrease in interatomic distances and thus allow electron transfer from the Nd/Ce layer to the Cu–O plane. In this model the main role of the reduction procedure is not to introduce electrons by oxygen removal itself, but rather to assure the proper conditions for electron transfer from the Nd/Ce layer acting here as a charge reservoir for the Cu–O plane. At the same level of oxygen content (not necessarily equal to four) the transfer conditions may be optimal for superconductivity.

In summary, we have shown that as-grown samples of $Nd_{2-x}Ce_xCuO_{4+y}$ have an oxygen content greater than four at all investigated Ce concentrations ($0<x<0.16$). The maximum in oxygen content (4.03) for already reduced and superconducting samples was found at $x\approx 0.15$. For lower Ce concentrations the phase separation model seems to explain quite well both the oxygen content and a.c. susceptibility data. The proposed mechanism of deoxygenation, necessary to transform the material into a bulk superconductor, is the partial removal of interstitial oxygen atoms and thus activation of the Nd/Ce layer acting as a charge reservoir for the Cu–O plane.

Acknowledgments

The author wishes to thank A. Nakonieczna for the thorough oxygen content analysis. This work was partially supported by the State Council for Scientific Research under Grant No. 204149101.

References

1 Y. Tokura, H. Takagi and S. Uchida, *Nature, 377* (1989) 345.
2 F. J. Izumi, Y. Matsui, H. Takagi, S. Uchida, Y. Tokura and H. Asano, *Physica C, 158* (1989) 433.
3 J. C. Phillips, *Phys. Rev. B, 41* (1990) 850.
4 T. Williams, Y. Maeno, J. Mongelschots, A. Reller and G. Bednorz, *Physica C, 161* (1989) 331.
5 E. Wang, J.-M. Tarascon, L. H. Greene and G. W. Hull, *Phys. Rev. B, 41* (1990) 6582.
6 T. C. Huang, E. Moran, A. J. Nazzal, J. B. Torrance and P. W. Wang, *Jpn. J. Appl. Phys., 28* (1989) L1760.
7 A. Jeżowski and P. W. Klamut, *J. Less-Common Met., 169* (1991) L17.
8 E. Moran, A. J. Nazzal, T. C. Huang and J. B. Torrance, *Physica C, 160* (1989) 30.
9 H. Kwei, S.-W. Cheong, Z. Fisk, F. H. Garzon, J. A. Goldstone and J. D. Thompson, *Phys. Rev. B, 40* (1989) 9370.
10 N. C. Baird and J. K. Burdett, *Physica C, 168* (1990) 637.
11 P. Lightfoot, D. R. Richards, B. Dabrowski, D. G. Hinks, S. Pei, D. T. Marx, A. W. Mitchell, Y. Zheng and J. D. Jorgensen, *Physica C, 168* (1990) 627.
12 N. A. Fortune, K. Murata, M. Ishibashi, Y. Yokoyama and Y. Nishikara, *Phys. Rev. B, 43* (1991) 12930.
13 M. Matsuda, Y. Endoch, K. Yamada, H. Kojima, J. Tanaka, R. J. Birgenau, M. A. Kastner and G. Shirane, *Phys. Rev. B, 45* (1992) 12548.
14 T. Kajitani, K. Hiraga, S. Hosoya, T. Fukuda, K. Oh-Jshi, M. Kikutchi, Y. Syono, S. Tomigoshi, M. Takahashi and Y. Muto, *Physica C, 169* (1990) 227.