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Universal Superconducting Ground State in Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4} and Nd\textsubscript{2}CuO\textsubscript{4}

Yoshiharu Krockenberger\textsuperscript{*}, Hideki Yamamoto, Masaya Mitsuhashi\textsuperscript{1}, and Michio Naito\textsuperscript{1}

\textsuperscript{1}Department of Applied Physics, Tokyo University of Agriculture and Technology, Kaganei, Tokyo 184-8588, Japan

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1. Introduction

The discovery of superconductivity in cuprates marked a breakthrough in solid state physics. Until superconductivity was found in electron doped cuprates\textsuperscript{1,11} the initial research efforts focused on hole doped cuprate systems. When electron doped cuprates are synthesized, an annealing process is necessary in order to induce superconductivity since the as-grown sample contains non-stoichiometric oxygen.\textsuperscript{2}

Moreover, angle resolved photoemission spectroscopy (ARPES) was found in electron doped cuprates\textsuperscript{1} the initial research breakthrough in solid state physics. Until superconductivity was discovered in cuprates, it marked a transition from insulating to metallic and superconducting behavior.\textsuperscript{3,4}

Causes severe modifications in the electronic structure, e.g., Ar or vacuum. The reduction process during the annealing process has been performed rather arbitrarily thus conditions during the reduction process are less stringent compared to dopant-free samples. Moreover, any additional atom species in a system increases the entropy during crystallization thus leading to a higher defect concentration level as compared to dopant-free sample. Since the annealing process is a diffusion driven process where oxygen atoms move along the CuO planes and along the grain boundaries of the crystal,\textsuperscript{17} many parameters have to be taken into account in order to optimize the annealing process. Thin film samples show a significantly larger surface-to-volume ratio compared to bulk powder or single crystal samples, thus they are more viable for timesaving tuning of the annealing parameters.\textsuperscript{18}

Here, we report on the superconducting states of optimally doped Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4} and dopant-free Nd\textsubscript{2}CuO\textsubscript{4} using thin film specimens.

2. Experimental Methods

High-quality single phase thin films of Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4} and Nd\textsubscript{2}CuO\textsubscript{4} have been grown by molecular beam epitaxy (MBE) on (001) SrTiO\textsubscript{3} substrates.\textsuperscript{19-21} The typical film thickness is 1000 ± 12 Å. X-ray diffraction patterns were taken by a Bruker AXS D8 Advanced four circle diffractometer. Transport properties were measured using a Quantum Design 14 T physical property measurement system (PPMS) cryostat. In Fig. 1, we plot the growth and annealing conditions for both, Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4} and Nd\textsubscript{2}CuO\textsubscript{4}. For the growth of Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4}, O\textsubscript{2} was used as an oxidizing agent, whereas rf-activated oxygen was used for the growth of Nd\textsubscript{2}CuO\textsubscript{4}. Within the present investigation, the differences between the oxidizing agents are minor though the theoretical oxidizing potentials of O\textsubscript{2} and O\textsuperscript{2-} are different. After the growth, Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4} has been annealed in situ before it is released to ambient atmosphere at ambient temperature. In the case of the dopant-free Nd\textsubscript{2}CuO\textsubscript{4}, the in situ annealing step is skipped and the sample is annealed ex situ by a two step annealing process.\textsuperscript{8} Standard four probe technique was used for resistivity measurements. Silver pads (50 nm), spaced 1–2 mm, were deposited onto the film surface (approximately 2.5 × 5 mm\textsuperscript{2}).

3. Results and Discussion

Before we take a closer look on the superconducting

\textsuperscript{8}E-mail address: yoshiharu.k@lab.ntt.co.jp
\textsuperscript{9}On leave from Nagaoka University of Technology.

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are \( \text{in situ} \) and for \( \text{NdO} \) induce superconductivity. Function of time for the synthesis of superconducting \( \text{NdO} \) substrates. From the RSM, in-plane lattice constants of \( \text{NdO} \) and \( \text{NdO} \) (black) and \( \text{NdO} \) (red) thin films. \( \text{NdO} \) grown by \( \text{O}_3 \) and \( \text{NdO} \) by \( \text{O}^+ \). For \( \text{NdO} \) annealing is performed \( \text{in situ} \) and for \( \text{NdO} \) a two-step annealing process is used in order to induce superconductivity.

![Fig. 1](image_url) Fig. 1. (Color online) Temperature and oxygen partial pressure as a function of time for the synthesis of superconducting \( \text{NdO} \) (black) and \( \text{NdO} \) (red) thin films. \( \text{NdO} \) was grown by \( \text{O}_3 \) and \( \text{NdO} \) by \( \text{O}^+ \). For \( \text{NdO} \) the annealing is performed \( \text{in situ} \) and for \( \text{NdO} \) a two-step annealing process is used in order to induce superconductivity.

![Fig. 2](image_url) Fig. 2. (Color online) Reciprocal space maps of \( \text{NdO} \) (a) and \( \text{NdO} \) (b) grown on (001) \( \text{SrTiO}_3 \) substrates after the annealing process.

Properties of both samples, we briefly describe the crystallographic relationship between substrate and film as well as the crystalline quality in order to provide confidence in our high quality single phase thin films. Figure 2 shows the reciprocal space maps (RSM) of \( \text{NdO} \) [Fig. 2(a)] and \( \text{NdO} \) [Fig. 2(b)]. In both cases, the films are grown fully relaxed onto the (001) \( \text{SrTiO}_3 \) substrates. From the RSM, in-plane lattice constants of 3.954 Å for \( \text{NdO} \) and 3.940 Å for \( \text{NdO} \) are estimated. Conversely, doping into the \( \text{CuO}_2 \) plane takes place in \( \text{NdO} \) since the Cu–O bond length increased despite the substitution of \( \text{Nd}^{3+} \left( r^{\text{III}} = 1.109 \text{Å} \right) \) by \( \text{Ce}^{4+} \left( r^{\text{IV}} = 0.97 \text{Å} \right) \). The c-axis lengths shrink upon the substitution from 12.126 to 12.082 Å for \( \text{NdO} \) and \( \text{NdO} \), respectively. The shrinkage of the c-axis upon cerium substitution is easily seen by comparing the \( \theta \)–2\( \theta \) X-ray diffraction patterns in Figs. 3(a) and 3(b). Our superior sample quality is further supported by the appearance of a sharp (0014) reflection in contrast to samples prepared by other methods, such as pulsed laser deposition technique.

In Figs. 4(a) and 4(b), the resistivity as a function of temperature is plotted. For \( \text{NdO} \), the superconducting transition appears at 24 K whereas it is 25 K for \( \text{NdO} \) at \( \mu_0 H = 0 \) T. We would like to mention that for the \( \text{NdO} \) [Fig. 4(b)] sample a sharp resistivity drop appears at 27 K; however, the resistivity is still finite between 25 and 27 K. This is also consistent with our magnetization measurements, where the Meissner signal appears at 25 K. Moreover, the absolute resistivity value at 40 K is significantly higher for \( \text{NdO} \) than for \( \text{NdO} \). At present, we may not be able to provide a conclusive answer on the differences of the absolute resistivity values. A high resistivity value might be attributed to an inhomogeneous oxygen distribution in \( \text{NdO} \), i.e., excessively and/or insufficiently reduced portions of the samples coexist.

Film partitions in proximity to or at the surface therefore might be reduced in excess (even regular oxygen sites are evacuated) and partitions close to the substrate interface might be close to the stoichiometric amount. Microscopic oxygen inhomogeneities may also appear at corner and edges of the grains. A monotonous
Fig. 4. (Color online) Resistivity vs temperature of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ (a) and Nd$_2$CuO$_4$ (b) thin films grown on (001) SrTiO$_3$ substrates after the annealing process for magnetic fields $B = 0, 1, 2, 4, 6, 8, 10, 12,$ and $14$ T.

variation of the net oxygen concentration towards the film-substrate interface therefore monotonously increases the $c$-axis length. Thus, the coexistence of unequally reduced grains (diameter $\approx 200–300$ nm) is supported by a broader (109) diffraction spot in RSM [Fig. 3(b)] than that of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ [Fig. 3(a)]. For increasing magnetic field inductions, the superconducting transition is shifted to lower temperatures, due to the pair-breaking character of the magnetic field. At $B = 6$ T, zero resistivity is not observed at 1.8 K for both samples, albeit a drastic drop of the resistivity value appears. For $B = 8$ T, both samples do not show any signs of superconductivity. Therefore, we conclude that the upper critical magnetic field is nearly identically about $\mu_0 H_{c2} \approx 6$ T, even though both samples significantly deviate each other since one is a so-called “optimally-doped” and the other is a dopant-free $T'$-cuprate superconductor. The upper critical magnetic field provides an estimation of the superconducting coherence length $\xi_{GL} \approx 7$ nm. For magnetic fields larger than 8 T, the resistivity behavior is found to be quite different between the samples. While an upturn of the resistivity is found for Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ below 12 K, the dopant-free Nd$_2$CuO$_4$ cuprate shows metallic behavior over the entire temperature range. The resistivity upturn might be associated to a localization effect caused by apical oxygen ions$^{31}$ although further investigations are necessary to clarify its origin.$^{32}$

Finally, we make a comment on the origin of electron carriers in Nd$_2$CuO$_4$. In both Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ and Nd$_2$CuO$_4$, the as-grown samples are insulating and superconductivity appears after a reduction treatment. In the case of Ce-substituted Pr$_{1.85}$Ce$_{0.15}$CuO$_4$, Richard et al.$^{33}$ demonstrated that the reduction process does not alter the carrier concentration. Such a scenario can be projected to the case of cerium-free Nd$_2$CuO$_4$ samples, thus, scenarios where oxygen vacancies provide electron carriers to the CuO$_2$ planes might be ruled out. The difference between Nd$_2$CuO$_4$ and Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ is simply a modified thermodynamic stability region of the annealing procedure. At present, site-resolved oxygen occupancy measurement data of superconducting Nd$_2$CuO$_4$ thin films do not exist. However, it is safe to exclude the possibility of an O1 deficiency in the CuO$_2$ plane, which results in non-superconducting or insulating samples. An O2 deficiency in the Nd$_2$O$_3$ fluorite layer also appears unlikely since the Nd–O bond is significantly stronger compared to the Cu–O bond. Hence, there are no experimental data suggesting a modification of the O2 occupancy upon annealing.$^{33,34}$ At the very moment, the sole mechanism rendering a non-superconducting Nd$_2$CuO$_4$ into a superconducting Nd$_2$CuO$_4$ sample upon annealing is the evacuation of apical sites although further investigation on site specific oxygen occupancies are vital for a sound comprehension of the superconductivity influencing factors in $T'$-cuprates.

4. Conclusions

We have prepared high quality single phase thin films of Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ and Nd$_2$CuO$_4$ by MBE. For Nd$_2$CuO$_4$ films, an ex situ annealing process was used in order to induce superconductivity. As-grown Nd$_2$CuO$_4$ samples are insulating antiferromagnets and an appropriate annealing process induces superconductivity. However, the magnetic ground state of superconducting Nd$_2$CuO$_4$ is subject to further investigations. We found that the superconducting properties are very similar for the “optimally-doped” and dopant-free $T'$-cuprates. We conclude that the ground state of $T'$-cuprates is a superconductor irrespective of the cerium substitution level.

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Yoshiharu Krockenberger received his diploma in physics from the Technical University of Munich in 2002 and his Ph. D. degree in physics from the Darmstadt University of Technology in 2006. His principal research areas are superconductivity, strongly correlated electron systems and thin film growth. He has been working at NTT Laboratories, NTT Corporation since 2010. In the meantime, he was a research scientist at RIKEN, Advanced Scientific Institutes, in the cross-correlated materials research group of Professor Y. Tokura (2006–2010).

Hideki Yamamoto received B.S., M.S., and Ph. D. degrees in Chemistry from the University of Tokyo in 1990, 1992, and 1995, respectively. His principal research areas are superconductivity, thin film growth, and surface science. He has been working at NTT Laboratories, NTT Corporation since 1995. He was a visiting scholar of Geballe Laboratory for Advanced Materials, Stanford University (2004–2005). Currently, he is the Group Leader of the Thin-Film Materials Research Group, NTT Basic Research laboratories.

Masaya Mitsuhashi received B.S. degree in electrical engineering from Nagaoka University of Technology (NUT) in 2011. During his undergraduate course, he worked in NTT Laboratories, NTT Corporation as an internship student. He is at a graduate course in NUT and is working on a power generator using electrets at Extreme Energy-Density Research Institute.

Michio Naito is a professor of Department of Applied Physics, Tokyo University of Agriculture and Technology. He received his B.S., M.S., and Ph. D. degrees in applied physics from the University of Tokyo in 1976, 1978, and 1981, respectively. His scientific research interests include physics, material science and applications of high- and medium- Tc superconductors.