Superconductivity phase diagrams of electron doped cuprates $R_{2-x}Ce_xCuO_4$ ($R = \text{La, Pr, Nd, Sm, and Eu}$)

Y. Krockenberger, J. Kurian, A. Winkler, A. Tsukada, M. Naito and L. Alff

1Institute of Materials Science, TU Darmstadt, Petersenstr. 23, 64287 Darmstadt, Germany
2NTT Basic Research Laboratories, 3-1 Wakamiya, Atsugi-shi, Kanagawa 243-0198, Japan
3Department of Applied Physics, Tokyo University of Agriculture and Technology (TUAT), Japan

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The superconductivity phase diagrams of electron doped cuprates of the form $R_{2-x}Ce_xCuO_4$ (with $R = \text{La, Pr, Nd, Sm, and Eu}$) have been determined for cerium compositions $0 < x < 0.36$ in a consistent series of epitaxial thin films grown by reactive molecular beam epitaxy (MBE). The use of epitaxial thin films allows the growth of materials away from thermodynamical equilibrium expanding the accessible phase space beyond the availability of bulk material. The superconducting phase space systematically increases with the rare earth ionic size. The doping concentration where the maximal transition temperature occurs in La$_{2-x}$Ce$_x$CuO$_4$ is considerably shifted to lower doping ($x \approx 0.09$) compared to La$_{2-x}$Sr$_x$CuO$_4$ ($x \approx 0.15$). At the same time, the width of the superconducting region is broadened.

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The phase diagram of cuprate superconductors is a key ingredient to understand the still unresolved mechanism of high-temperature superconductivity. A particular interesting question is the comparison of the phase diagrams for hole and electron doping. A theory of high-temperature superconductivity has to explain the occurring differences and similarities when a copper-oxide plane is doped by holes or electrons. While for the hole doped case there is already an overwhelming amount of experimental data available, the electron doped side of the phase diagram still needs experimental clarification.

Electron doped cuprates are widely identified with the two materials Nd$_{2-x}$Ce$_x$CuO$_4$ and Pr$_{2-x}$Ce$_x$CuO$_4$. In contrast to the hole doped cuprates where in compounds of the form R$_{2-x}$Sr$_x$CuO$_4$ only for $R = \text{La}$ superconductivity shows up, for the electron doped side of the phase diagram a whole family of superconductors of the form R$_{2-x}$Ce$_x$CuO$_4$ ($LN = \text{La, Pr, Nd, Sm, and Eu}$) exists. It is solely due to historical reasons that most investigations of electron-doped cuprates have been made for Nd$_{2-x}$Ce$_x$CuO$_4$ and Pr$_{2-x}$Ce$_x$CuO$_4$. These two materials have an almost identical ionic radius and show, therefore, also a very similar phase diagram. This has led to the common belief that this properties of a specific electron doping phase diagram (in particular a narrow superconducting region) is intrinsic to electron doped cuprates in general. In addition, for Nd$_{2-x}$Ce$_x$CuO$_4$ (and to a lesser extent for Pr$_{2-x}$Ce$_x$CuO$_4$) the magnetism of Nd$^{3+}$ (and Pr$^{3+}$) masks in some experiments the intrinsic properties of the superconductor like the temperature dependence of the London penetration depth. Moreover, the difficulties in bulk sample preparation makes the determination of exact phase diagrams a much debated topic.

Using reactive MBE and pulsed laser deposition (PLD) recently superconducting epitaxial thin films of La$_{2-x}$Ce$_x$CuO$_4$ have been successfully grown. For bulk material up to now only the mixed compound LaPr$_{1-x}$Ce$_x$CuO$_4$ could be synthesized, and is now intensively studied. Here we present a new consistent and detailed study of the complete electron doped family R$_{2-x}$Ce$_x$CuO$_4$ (with $R = \text{La, Pr, Nd, Sm, Eu, and Gd}$) based on MBE-grown epitaxial thin films. The key results are that the width of the superconducting phase space increases systematically with the ionic size of the rare earth element LN, and that the doping level of maximal superconductivity with highest critical temperature, $T_C$, is not fixed (to $x \approx 0.15$), but shifts to significantly lower doping.

We conclude that the most meaningful comparison of the superconductivity phase diagrams of hole and electron doped cuprates, that can be done given this material's situation, should be made using La-based cuprates. However, one still has to keep in mind that La$_{2-x}$Sr$_x$CuO$_4$ has the so-called $T$-structure (K$_2$NiF$_4$ structure) containing apical oxygen, while La$_{2-x}$Ce$_x$CuO$_4$ with $x \gtrsim 0.05$ has the so-called $T'$-structure (Nd$_2$CuO$_4$ structure) where the Cu ion is only fourfold coordinated, i.e., the apical oxygen ions are missing. The structural difference translates into different ionic radii of the Cu$^{2+}$ ions: 0.73 Å in the $T$-structure, and 0.57 Å in the $T'$-structure (reduction of more than 20%). It is still one of the most exciting future challenges in high-$T_C$ research to find a system, where a direct comparison of hole and electron doping can be made in a wide range of doping. All our films were grown by reactive MBE using simultaneous electron-beam evaporation from elemental sources on (001) SrTiO$_3$ substrates. The stoichiometry was controlled by electron-impact emission spectroscopy (EIES). A typical growth scenario of electron doped superconducting thin films is shown in Fig.

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*e-mail: yoshiharu.krockenberger@aist.go.jp
†Electronic address: alff@oxide.tu-darmstadt.de
disorder cannot be ruled out. For all samples Ce-doping as a measure of disorder, for our study a correlation be-
affect the material [17, 18]. Another important issue for elec-
strong reduction. In the case of bulk material synthesis,
oxygen without any measurable decomposition due to too
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shown in Fig. 1 have been determined experimentally by
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stands issue [14, 15, 16, 17]. We have adopted a consis-
doped cuprates is a crucial and so far not fully under-
to homogeneous and precipitate free epitaxial thin films.

Films are grown at a substrate temperature of about
700°C in an ozone pressure of about 2 \times 10^{-6} \text{ Torr}. During
growth the sample has to be in the region of divalent copper (correspondingly the rare earth elements are 3+, and Ce 4+). Growth rates are approximately 3 Å/s leading to homogeneous and precipitate free epitaxial thin films.

It is well known that the oxygen contents of electron
doped cuprates is a crucial and so far not fully under-
stood issue [14, 15, 16, 17]. We have adopted a consis-
ten sample treatment in order to exclude as far as possible
different oxygen contents in our samples: all samples were annealed in vacuum at temperatures close to the stability line of each compound. The stability lines shown in Fig. 1 have been determined experimentally by observing in real time the reflection high-energy electron diffraction (RHEED) signal which indicates starting decomposition. This procedure adopted in the present investigation enables the comprehensive removal of excess oxygen without any measurable decomposition due to too strong reduction. In the case of bulk material synthesis, the reduction process may either lead to non-complete removal of excess oxygen, or to partial decomposition of the material [17, 18]. Another important issue for electron doped cuprates is the presence of disorder that can affect \( T_C \) seriously. Taking room-temperature resistivity as a measure of disorder, for our study a correlation between disorder and ionic radii of the lanthanide ions can be excluded, since all compounds \( R_{2-x}Ce_xCuO_4 \) (with \( R = \text{La, Fr, Nd, and Sm} \)) have at optimal doping very similar resistivity, except for Eu where the possible role of disorder cannot be ruled out. For all samples Ce-doping reduces linearly the c-axis parameter, because the ionic radius of Ce\(^{4+} \) is 0.97 Å which is smaller than the radius of the rare earth elements. The typical thickness of the films in the present study was \( \sim 1000 \text{ Å} \).

\( La_{2-x}Ce_xCuO_4 \): It would be of course a breakthrough in the research on electron-doped cuprates to make available bulk material of \( La_{2-x}Ce_xCuO_4 \) in the \( Nd_2CuO_4 \) structure. For thin film growth in ultra high vacuum far from thermodynamic equilibrium, epitaxial growth of \( T' \)-\( La_{2-x}Ce_xCuO_4 \) is possible at a substrate temperature of 700°C and in a partial ozone pressure of \( 2 \times 10^{-6} \text{ Torr} \). As has been shown before, the structural phase transition into the \( T' \)-phase occurs for \( x \lesssim 0.05 \) [8]. However, a further reduction of growth temperature by 100°C allows the growth of \( T' \)-phase \( La_{2-x}Ce_xCuO_4 \) even down to \( x = 0 \) - but at the cost of crystalline quality. It is even possible to stabilize the \( T' \)-phase with improved crystallinity by substitution of smaller trivalent ions like Tb, Y etc. [19].

In Fig. 2 we show the obtained phase diagram for \( La_{2-x}Ce_xCuO_4 \). The two major observations are (i) the strongly broadened superconductivity region ranging from \( x \approx 0.05 \) to \( x \approx 0.22 \), and (ii) the maximal \( T_C \) of 32K occuring at \( x \approx 0.09 \). Sawa et al. [8] claim a complete shift (i.e., no broadening) of the superconductivity region based on thin films grown by PLD if samples have high dopant homogeneity. However, the broader superconducting region as confirmed in this paper is clearly not due to any inhomogeneities of the samples. First, the sample size is too small (3 mm by 5 mm) to expect compositional inhomogeneities in the given MBE setup. For example, three different samples attached to the heater and grown in the same run give exactly the same \( T_C \). Second, the resistivity values of the MBE grown films are well below those of the PLD thin films [7, 8]. Third, the critical temperature in the MBE grown thin films (see Fig. 2) is higher than compared to PLD samples [8]. Fourth, the superconducting transition width in resistivity and magnetometry is even sharper for higher doping where the extended superconducting region is observed in this study. The room temperature resistivity values
of La$_{2-x}$Ce$_x$CuO$_4$ films lies between 0.22–2.0 mΩcm for optimal- and undoped samples, respectively.

$Pr_{2-x}$Ce$_x$CuO$_4$ and Nd$_{2-x}$Ce$_x$CuO$_4$: The corresponding superconductivity phase diagrams of MBE grown films are included in Fig. 2 for a direct comparison. The superconducting region expands from $x \approx 0.10$ to $x \approx 0.24$, and the maximal $T_C$ of 26 K occurs for $x \approx 0.145$. Note also, that UHV-annealing times and growth temperatures differ slightly for different $x$. In this study, we have always used the parameters yielding the highest $T_C$ for a given doping concentration $x$. The simple trend is, that for the highest crystallinity (as indicated in a standard x-ray diffraction pattern by the intensity of the (006) reflection of the epitaxial thin film), also the highest $T_C$ is obtained. The phase diagram based on thin film data fully agrees with the huge amount of published data for bulk material of $Pr_{2-x}$Ce$_x$CuO$_4$ and Nd$_{2-x}$Ce$_x$CuO$_4$.

The room temperature resistivity of optimal doped samples of Pr$_{2-x}$Ce$_x$CuO$_4$ and Nd$_{2-x}$Ce$_x$CuO$_4$ films were 0.26 and 0.23 mΩcm, respectively, whereas for undoped samples the respective values were 5.6 and 8.9 mΩcm.

Sm$_{2-x}$Ce$_x$CuO$_4$: The ionic radius of eight-fold coordinated Sm$^{3+}$ is 1.079 Å. From Fig. 3 one sees that the maximal $T_C$ of 19 K is obtained for $x = 0.150$, in consistency with earlier bulk data. The room-temperature and low-temperature resistivity values show also minima around $x \approx 0.15$. The resistivity range at room temperature for Sm$_{2-x}$Ce$_x$CuO$_4$ thin films lies between 0.2 mΩcm and 100 mΩcm for optimal doped and undoped samples, respectively. Superconductivity occurs in the range of approximately $x \approx 0.13$ to $x \approx 0.20$. Bulk superconductivity in Sm$_{2-x}$Ce$_x$CuO$_4$ has been reported by several authors.

Eu$_{2-x}$Ce$_x$CuO$_4$: The right hand side neighbor of Sm in the periodic table is Eu. Shortly after electron doped cuprates had been discovered, Markert et al. reported on superconductivity in Eu$_{2-x}$Ce$_x$CuO$_4$, however, so far no results on thin films have been reported. The ionic radius of eight-fold coordinated Eu$^{3+}$ is 1.066 Å. The superconducting region is very limited between 0.14 < $x$ < 0.19. Maximal $T_C$ of 12 K occurs at $x = 0.16$. The phase diagram is shown in Fig. 3. The resistivity range at room temperature for Eu$_{2-x}$Ce$_x$CuO$_4$ thin films lies between 0.6 mΩcm and 140 mΩcm for optimal doped and undoped samples, respectively.

The combined results of our thin-film study of R$_{2-x}$Ce$_x$CuO$_4$ (with $R =$ La, Pr, Nd, Sm, Eu, and Gd) show that the superconductivity phase diagrams depend systematically on the rare earth ionic radius of the compound. Superconductivity can only be observed above a threshold ionic size of about 1.053 Å of Gd$^{3+}$ (or tolerance factor > 0.85 [23]). The superconducting phase region expands significantly with LN$^{3+}$ ionic radii, i.e., for $LN = La$ the superconducting region spans from $x = 0.05$ to $x = 0.22$ whereas $LN = Eu$, it is from $x = 0.14$ to $x = 0.19$. Correspondingly, it is also observed that the maximal $T_C$ increases with ionic radii (for $LN = La - 31 K$ and $LN = Eu - 12 K$) and it occurs at consider-

Figure 3: (Color online) Superconductivity phase diagrams of Sm$_{2-x}$Ce$_x$CuO$_4$ and Eu$_{2-x}$Ce$_x$CuO$_4$.

Figure 4: (Color online) Direct comparison of La-based cuprates with respect to electron and hole doping: Superconductivity phase diagrams of La$_{2-x}$Ce$_x$CuO$_4$ (thin film data) and La$_{2-x}$Sr$_x$CuO$_4$ (bulk data [2, 26]).

ably lower doping (i.e., for $LN = La$ at $x = 0.09$ whereas $LN = Eu$ at $x = 0.16$). In other words, with increasing ionic radius, not only the superconducting phase region expands, but also the maximal $T_C$ increases, and the doping level where it is observed is shifted towards lower doping. The end-point is set by La$_{2-x}$Ce$_x$CuO$_4$ which hits at low doping ($x \lesssim 0.05$) the instability line where the structural transition from $T' \rightarrow$ into $T$-structure occurs. The breakdown of superconductivity in La$_{2-x}$Ce$_x$CuO$_4$ around $x \approx 0.05$ therefore is clearly due to this structural phase transition. As underdoped samples below $x \approx 0.05$ are not systematically available, the experimental evaluation of the phase competition between superconductivity and antiferromagnetism is elusive. The important issue is clearly how to compare electron and hole doped compounds experimentally. Based on our results, it is suggestive that this comparison should be made in the system La$_{2-x}$X$_x$CuO$_4$ with $X =$ Sr and Ce. The caveat here is, that one is still dealing with a different crystal structure.

The key result of this paper is summarized in Fig. 3. Here, we compare directly La$_{2-x}$Ce$_x$CuO$_4$ and La$_{2-x}$Sr$_x$CuO$_4$. The La$_{2-x}$Sr$_x$CuO$_4$ data are taken from
literature and have been obtained from bulk materials (i.e., no effects of substrate strain are considered that can increase $T_C$). The comparison of hole and electron doped cuprates made in Fig. 1 is the most direct possible with available data. The width of the superconducting phase region is very similar for hole and electron doping. The electron doped side of the phase diagram even extends to slightly lower doping. The absolute value of $T_C$ is about 10 K (or 33%) higher in the hole doped case. Surprisingly, the doping where the maximal $T_C$ occurs at the electron doped side is shifted to below $x = 0.1$ for $La_{2-x}Ce_xCuO_4$, which is a reduction by about one third compared to hole doping. There is no such thing as a distinguished intrinsic or general valid for electron doped cuprates. In most Hubbard model calculations (see for example recent variational cluster perturbation theory in the $t - t' - t'' - U$ Hubbard model [27] and also recent quantum Monte Carlo simulations [28]), the phase competition between d-wave superconductivity and antiferromagnetism comes out like experimentally observed for the unspecific phase diagram of Nd$_{2-x}$Ce$_x$CuO$_4$ and Pr$_{2-x}$Ce$_x$CuO$_4$, i.e., for electron doping the antiferromagnetic phase persists to higher doping before superconductivity sets in, and the superconducting region is narrower compared to the hole doping case. With respect to the superconducting part of the phase diagram, our experimental results here show that these properties are not intrinsic or general valid for electron doped cuprates. From our thin film experiments, we cannot establish the antiferromagnetic region of the phase diagram. It is well possible that in a certain doping range, both order parameters coexist [29, 30]. It remains a theoretical task to understand the presented superconductivity phase diagrams of electron doped cuprates. Note that the phase diagram of the electron doped infinite layer compound Sr$_{1-x}$La$_x$CuO$_2$ where copper is four-fold coordinated as is the case in the $T'$-structure, shows maximal superconductivity also around $x \approx 0.1$ [31].

In summary, we have shown by a consistent study of MBE-grown cuprate thin films, that the superconductivity phase diagrams of the electron doped cuprates depend strongly on the rare earth ionic radius. The most suited compound for a comparison of hole and electron doped cuprates so far is $La_{2-x}Ce_xCuO_4$. The extended superconductivity range and the occurrence of maximal $T_c$ at considerably reduced doping indicates even slightly higher superconductivity phase stability for the electron doped side of the phase diagram.

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