Doping dependence of the gap anisotropy in La_{2-x}Ce_xCuO_4 studied by millimeter-wave spectroscopy

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We measure the penetration depth of optimally doped and underdoped La_{2-x}Ce_xCuO_4 in the millimeter frequency domain (4 - 7 cm^{-1}) and for temperatures 2 K < T < 300 K. The penetration depth as function of temperature reveals significant changes on electron doping. It shows quadratic temperature dependence in underdoped samples, but increases almost exponentially at optimal doping. Significant changes in the gap anisotropy (or even in the gap symmetry) may account for this transition.

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Being one of the keystones for theories of high-temperature superconductivity, the symmetry and the actual shape of the gap function in high- Tc’s is one of most attractive issues for experimental studies. At present the d-wave pairing symmetry in the hole doped materials seems to be well established.1,2,3 But so far there is no common consensus on the electron-doped cuprates. It was initially suggested that these materials reveal an s-wave symmetry, however, later measurements supported strongly a d-wave scenario.4,5,6

A number of recent reports indicate possible transition in the gap symmetry with doping both in hole4,7,8,9,10,11 and electron12,13,14 doped cuprates. Tunnelling data by Dag
can and Deutscher12 and by Sharoni et al.13 suggest a possible transition from pure d_{x^2-y^2} to d_{x^2-y^2} + id_{xy} or d_{x^2-y^2} + is symmetry while changing from the under- to the overdoped regime in YBa_{2}Cu_{3}O_{7-δ}. This transition could be due to surface effects, but possibly reflects a bulk property, namely the existence of a quantum critical point in these materials.12,14,15 The paper by Yeh et al.16 reports on changing of the pairing symmetry from pre- dominantly d_{x^2-y^2} in the under- and optimally doped YBa_{2}Cu_{3}O_{7-δ} single crystals to d_{x^2-y^2} + s in the overdoped Y_{1-x}Ca_{x}Ba_{2}Cu_{3}O_{7-δ} thin films. That is, there is no apparent breaking of the time-reversal symmetry.

The point contact spectroscopy data on electron doped Pr_{2-x}Ce_{x}CuO_{4} by Biswas et al.17 also indicate different pairing symmetries in samples with different doping: d-wave in the underdoped and s-wave in the overdoped case. The radio-frequency inductance measurements by Skinta et al.18 show a tiny, but measurable difference in the low temperature (< 3 K) behavior of the penetration depth between underdoped, optimally doped, and overdoped samples of Pr_{2-x}Ce_{x}CuO_{4} and La_{2-x}Ce_{x}CuO_{4}, indicating d-wave symmetry in the underdoped, and s-wave symmetry in the optimally doped and overdoped regimes.

Overall the majority of these studies is quite consistent: the underdoped samples tend to demonstrate pure d-wave symmetry, while the overdoped samples rather reveal d + id_{xy}, d + is or s-wave-like behavior. Optimal doping stays at the border of these two possibilities, falling more into the pure d-wave limit in the hole-doped compounds,14 and into the conventional s-wave-like behavior in the electron-doped ones.15

Here we present measurements of the superconducting penetration depth λ of optimally doped and underdoped electron superconductors La_{2-x}Ce_xCuO_4 by a quasi-optical method at millimeter wavelengths.20 We show that the temperature dependence of λ sensitively depends on the doping concentration.

High quality La_{2-x}Ce_xCuO_4 films with x = 0.106 (optimally doped) and x = 0.081 (underdoped), have been deposited by molecular-beam epitaxy,21,22 on transparent (001)-oriented SrLaAlO_4 substrates. The substrates were plane-parallel plates, approximately 10 x 10 mm in size with thickness of 0.335 mm for underdoped and of 0.472 mm for optimally doped films. The film thickness was 140 nm. The films had sharp resistive and inductive transitions at T_c = 30 K (optimally doped sample) and 25 K (underdoped sample) with ΔT_c < 1 K.

The requirements to prepare high-quality La_{2-x}Ce_xCuO_4 films are stringent cation stoichiometry adjustment and careful removal of the apical oxygen without phase decomposition. With regard to the latter issue, we kept films at 600 °C for 10 min in the oxygen pressure less than 10^{-8 } Torr just after the film growth. By this reduction recipe, the superconducting properties were optimized. No phase decomposition was detected in the reflection high-energy electron diffraction (RHEED) measurements. Although it is generally very difficult to evaluate the exact oxygen content in films, our in-situ Cu 2p x-ray photoemission spectra on the film surfaces indicate that the Cu ions are mostly coordinated by four

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The refractive index, temperature and of the substrate, k a separate experiment. At 5 cm\textsuperscript{-1} intensity transmission (top panel) and of the corresponding phase shift (bottom panel) for optimally doped (x = 0.106, T\textsubscript{c} = 30 K) and underdoped (x = 0.081, T\textsubscript{c} = 25 K) La\textsubscript{2-x}Ce\textsubscript{x}CuO\textsubscript{4} films on SrLaAlO\textsubscript{4} substrates.

have very low losses in the millimeter-to-submillimeter frequency range, the transmission level of the substrate-film "sandwich" is determined predominantly by the film properties. In the normally-conducting state (above T\textsubscript{c}) the transmission is mainly controlled by the real part of the complex conductivity, while in the superconducting state both components of the complex conductivity contribute to the transmission, the imaginary part dominating at the lowest temperatures. The overall difference in the transmission levels between the two samples studied is due to difference of carrier concentrations in optimally doped and underdoped La\textsubscript{2-x}Ce\textsubscript{x}CuO\textsubscript{4}.

The main contribution to the absolute values of the phase shift comes from the substrate. The major term of the phase shift is proportional to the substrate thickness multiplied by its refractive index n\textsubscript{sub} and by the frequency of probing radiation. Since the thickness of the substrates were different, the phase level for the sample with optimally doped film is higher than for the sample with the underdoped film. The film contribution to the phase shift comes from both, the real and the imaginary part of the complex conductivity. Below T\textsubscript{c} due to the Meissner effect, \sigma_2 increases significantly and diverges at

O ions in a square planar configuration (no apical oxygen). Similar studies are reported for Nd\textsubscript{2-x}Ce\textsubscript{x}CuO\textsubscript{4} films in Ref. 23.

The temperature dependence of dc resistivity of both films, as measured by the standard four probe method with evaporated Ag electrodes, is shown in Fig. 1. The overall shape of the \rho(T) curves is quadratic rather than linear. The underdoped sample reveals a slight upturn in \rho(T) at low temperatures (\lesssim 70 K). This is an indication of localization effects, and is quite typical for this compound in the underdoped regime.\textsuperscript{22}

The measurements have been performed with a quasi-optical coherent source (backward-wave oscillator) spectrometer\textsuperscript{24} working in the millimeter to submillimeter wavelength domain. The Mach-Zehnder interferometer arrangement allows measuring both, the intensity and the phase shift of the wave transmitted through the La\textsubscript{2-x}Ce\textsubscript{x}CuO\textsubscript{4} films on the substrates. Using the Fresnel optical formulas for the complex transmission coefficient of the substrate-film system, both components of the in-plane dynamic conductivity (\sigma_1 + i\sigma_2) of the films have been directly calculated from these measurements. The penetration depth has been determined as \lambda = c/(4\pi\omega\sigma_2)^{1/2}, where c is the light velocity and \omega the angular frequency of the incident radiation. The optical parameters of the bare substrate have been measured in a separate experiment. At 5 cm\textsuperscript{-1} the absorptive index of the substrate, k\textsubscript{sub}, is below 0.01 at any temperature. The refractive index, n\textsubscript{sub}, is equal to 4.06 \pm 0.01 at room temperature and 4.03 \pm 0.01 for T \rightarrow 0 K.

The as-measured transmission and phase shift data are shown in Fig. 2. Since the SrLaAlO\textsubscript{4} substrates
$\omega \rightarrow 0$, that leads to the negative contribution to the phase shift.

Let us recall that while processing the penetration depth data we used the complete Fresnel formulas, which automatically involve all contributions from the film complex conductivity to the transmission and phase shift, and take multiple reflections within the substrate into account.

Fig. 3 shows the penetration depth of the optimally doped and the underdoped La$_{2-x}$Ce$_x$CuO$_4$ samples measured at 5 cm$^{-1}$. For better comparison with model calculations, the penetration depth data are plotted as $\lambda^2(0) / \lambda^2(T)$ versus $T/T_c$, where $\lambda(0)$ is the zero-temperature limit of the penetration depth. A substantially different behavior of $\lambda(T)$ for samples with different doping is clearly seen at all temperatures below $T_c$. In the underdoped regime the experimental curve can be well fitted by a $[1 - (T/T_c)^2]^x$ behavior, typical for high-temperature superconductors. The results for the optimally doped sample look quite different, now a BCS-like $[1 - (T/T_c)^4]$ dependence (fully gapped superconductor) fits the experimental data. We note that the high-temperature $(T > 0.9 T_c)$ tails in $\lambda^2(0) / \lambda^2(T)$ are due to influence of the normally conducting electrons: $\sigma_2$ is not exactly zero above $T_c$ at high frequencies.

The low-temperature variation of $\lambda$ is shown in Fig. 4 as function of $T^2$. Measurements at two additional frequencies (4 and 6.7 cm$^{-1}$) are also presented in this figure. In this representation the data of the underdoped sample follow rather well a straight line, while the data for the optimally doped sample demonstrate a much more gradual (although not really exponential) temperature dependence. No measurable frequency dependence of our findings is detected.

The absolute values of the penetration depth at the lowest temperatures are found to be equal to 0.22 ± 0.02 μm in the optimally doped, and 0.38 ± 0.03 μm in the underdoped samples. Both values are in good agreement with data by Skinta et al. Minor differences can be explained by slightly different doping levels of the samples marked as "underdoped" and "optimally doped" in Ref. 15 and in the present study.

The quadratic temperature dependence of the penetration depth in the underdoped sample provides strong experimental evidence of nodes in the gap function and, likely, the $d_{x^2-y^2}$-wave paring symmetry. The results in the optimally doped sample indicate a more isotropic gap function: $d + is$ or $s$-wave symmetry seems to be good candidates for the gap symmetry in optimally doped La$_{2-x}$Ce$_x$CuO$_4$.

Since penetration depth measurements are not phase sensitive, it is impossible to decide from these measurements alone, whether a transition of the gap symmetry exists or not. However, our results provide experimental evidence that the superconducting gap in the underdoped regime is significantly more anisotropic than in the optimally doped regime. As an alternative to a transition between two superconducting states characterized by different gap symmetries, one can imagine a gradual change in the gap anisotropy with $d + is$, or even with

**FIG. 3:** Temperature dependence of the penetration depth in optimally doped ($x = 0.106, T_c = 30$ K) and underdoped ($x = 0.081, T_c = 25$ K) La$_{2-x}$Ce$_x$CuO$_4$ at 5 cm$^{-1}$. Points - experimental data, lines indicate fits using $1 - (T/T_c)^2$ (solid) and $1 - (T/T_c)^4$ (dashed).

**FIG. 4:** Temperature variation of the penetration depth in La$_{2-x}$Ce$_x$CuO$_4$ at low temperatures vs. $T^2$. The experimental data for $\nu = 5$ cm$^{-1}$ are replotted from Fig. 3 two additional data sets at 4 and 6.7 cm$^{-1}$ are added for the optimally doped and the underdoped samples, respectively.
just anisotropic s-wave, symmetry.

It is important to note that the influence of the quasi-particle scattering on the high-frequency (millimeter-wave) penetration depth data has to be clarified before making final conclusions on gap symmetry or gap anisotropy transition. Strictly speaking, only the zero-frequency penetration depth is associated with the superconducting condensate, while the penetration depth at a finite frequency is partly influenced by the normal-conducting carriers.

A way to correctly and model-independently exclude the normal-conducting contribution to the high-frequency λ has been recently proposed by Dordevic et al.28 It requires measurements of the complex conductivity over a wide frequency range. Such measurements have been undertaken by us at T = 5 K using the backward-wave-oscillator technique for frequencies from 4 to 40 cm⁻¹, and the standard infrared reflectivity measurements (40 - 4000 cm⁻¹) with a Fourier-transform spectrometer.28

Applying the analysis given in Ref. 27 we have found the corrected zero-temperature values of the penetration depth: 0.23 µm for the optimally doped and 0.4 µm for the underdoped samples. The minor difference between the as-measured and the corrected penetration depth data is due to very low residual losses in the investigated films. The details of the recalculation procedure together with the determination of the scattering rate in La₂₋ₓCeₓCuO₄ will be given elsewhere.29

In conclusion, we observed significant changes in the temperature dependence of the millimeter-wave penetration depth in optimally doped and underdoped La₂₋ₓCeₓCuO₄. λ(T) behaves quadratic in the underdoped, but is close to exponential in the optimally doped regime. Change in the gap anisotropy (or symmetry) is a plausible explanation for these dramatic differences.

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