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$\leq T \leq$300 K. The penetration depth as a 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 of the gap function in high T_c's is one of the most attractive issues for experimental studies. At present *d*-wave pairing symmetry in hole-doped materials seems to be well established.[1,2] But so far there is no common consensus on electron-doped cuprates. It was initially suggested that these materials reveal an *s*-wave symmetry,[3–6] however, later measurements strongly supported a *d*-wave scenario.[7–11]

A number of recent reports indicate a possible transition in the gap symmetry with doping both in hole-[12–14] and electron-[18,19] doped cuprates. Tunneling data by Dagan and Deutscher[12] and by Sharoni *et al.*[14] 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 underdoped to the overdoped regime in $YBa_2Cu_3O_{7-\delta}$ as well as in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$. This transition could be due to surface effects, but possibly it reflects a bulk property, namely, the existence of a quantum critical point in these materials.[15–17] The paper by Yeh *et al.*[13] reports the changing of the paring symmetry from predominately $d_{x^2-y^2}$ in the underdoped and optimally doped $YBa_2Cu_3O_{7-\delta}$ single crystals to $d_{x^2-y^2}+s$ in the overdoped $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ thin films. That is, there is no apparent breaking of the time-reversal symmetry.

The point-contact spectroscopy data on electron-doped $Pr_{2-x}Ce_xCuO_4$ by Biswas *et al.*[19] also indicate different pairing symmetries in samples with different doping: *d*-wave in the underdoped case 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 among underdoped, optimally doped, and overdoped samples of $Pr_{2-x}Ce_xCuO_4$ and $La_{2-x}Ce_xCuO_4$, indicating *d*-wave symmetry in the underdoped regime 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,[13] and into the conventional *s*-wave-like behavior in the electron-doped ones.[18]

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 quasioptical method at millimeter wavelengths.[21] 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[22,23] on transparent (001)-oriented $SrLaAlO_4$ substrates. The substrates were plane-parallel plates, approximately 10×10 mm in size with thicknesses of 0.335 mm for underdoped and 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 $\Delta T_c<1$ 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 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 measurements. Although it is generally very difficult to evaluate the exact oxygen content in films, our *in situ* Cu 2*p* x-ray photoemission spectra on the film surfaces indicate that the Cu ions are mostly coordinated by four O ions in a square planar configuration (no apical oxygen). Similar studies are reported for $Nd_{2-x}Ce_xCuO_4$ films in Ref. 20.

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.[23]

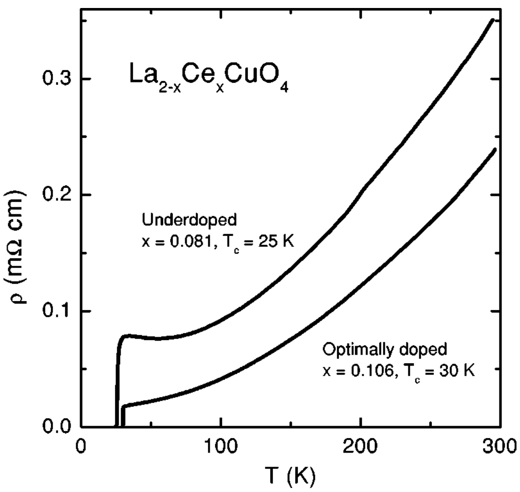

FIG. 1. Temperature dependence of dc resistivity for the optimally doped (bottom line) and the underdoped (upper line) $La_{2-x}Ce_xCuO_4$ samples.

The measurements have been performed with a quasioptical coherent source (backward-wave oscillator) spectrometer,[21] 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 $La_{2-x}Ce_xCuO_4$ films on the substrates. Using 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 ω the angular frequency of the incident radiation. The optical parameters of the bare substrate have been measured in a separate experiment. At 5 cm^{-1} the absorptive index of the substrate, k_{sub}, is below 0.01 at any temperature. The refractive index, n_{sub}, is equal to 4.06 ± 0.01 at room temperature and 4.03 ± 0.01 for $T \to 0$ K.

The as-measured transmission and phase-shift data are shown in Fig. 2. Since the $SrLaAlO_4$ 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_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 $La_{2-x}Ce_xCuO_4$.

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_{sub} and by the frequency of probing radiation. Since the thicknesses of the substrates were different, the phase level for the sample with the optimally doped film is higher than that for the sample with the underdoped film. The film contribution to the phase shift comes from both the real and the imaginary parts of the complex conductivity. Below T_c due to the Meissner effect, σ_2 increases significantly and diverges at $\omega \to 0$, which leads to a negative contribution to the phase shift.

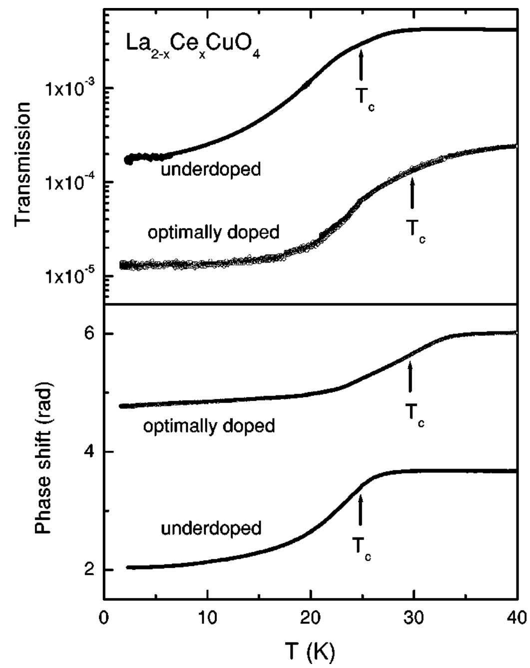

FIG. 2. Temperature dependence of the millimeter-wave (5 cm^{-1}) intensity transmission (top panel) and of the corresponding phase shift (bottom panel) for optimally doped ($x = 0.106$, $T_c = 30$ K) and underdoped ($x = 0.081$, $T_c = 25$ K) $La_{2-x}Ce_xCuO_4$ films on $SrLaAlO_4$ substrates.

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.

Figure 3 shows the penetration depth of the optimally doped and the underdoped $La_{2-x}Ce_xCuO_4$ 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 $[1-(T/T_c)^2]$ behavior, typical for high-temperature superconductors.[24] The results for the optimally doped sample look quite different; now a BCS-like[25] $[1-(T/T_c)^4]$ dependence (fully gapped superconductor) fits the experimental data. We note that the high-temperature ($T > 0.9T_c$) tails in $\lambda^2(0)/\lambda^2(T)$ are due to the influence of the normally conducting electrons: σ_2 is not exactly zero above T_c at high frequencies.

The low-temperature variation of λ is shown in Fig. 4 as a 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

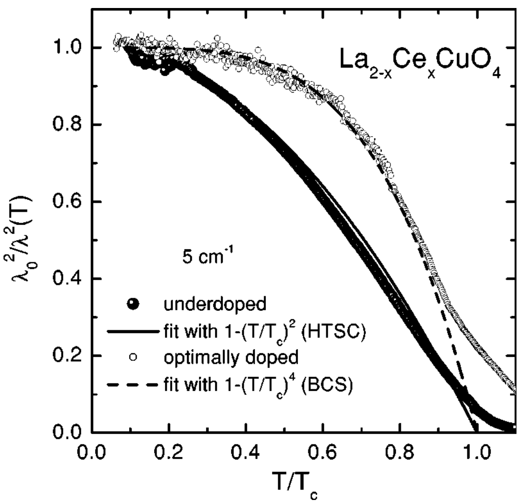

FIG. 3. Temperature dependence of the penetration depth in optimally doped ($x=0.106$, $T_c=30$ K) and underdoped ($x=0.081$, $T_c=25$ K) $La_{2-x}Ce_xCuO_4$ at 5 cm^{-1}. Points are experimental data, and lines indicate fits using $1-(T/T_c)^2$ (solid line) and $1-(T/T_c)^4$ (dashed line).

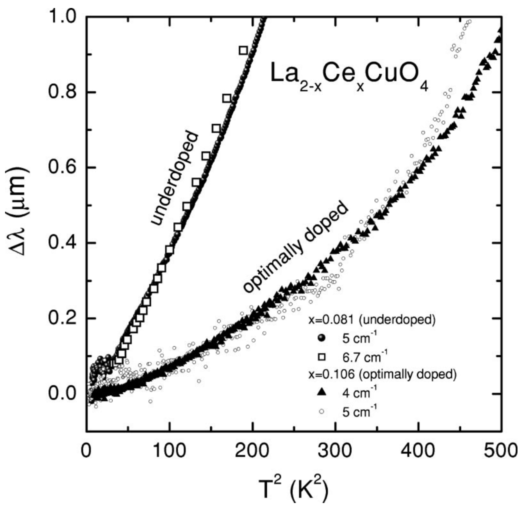

FIG. 4. Temperature variation of the penetration depth in $La_{2-x}Ce_xCuO_4$ at low temperatures vs T^2. The experimental data for $\nu=5$ cm^{-1} are replotted from Fig. 3, and two additional data sets at 4 and 6.7 cm^{-1} are added for the optimally doped and the underdoped samples, respectively.

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 samples and 0.38 ± 0.03 μm in the underdoped samples. Both values are in good agreement with data of Skinta *et al.*[18] Minor differences can be explained by slightly different doping levels of the samples marked as "underdoped" and "optimally doped" in Ref. 18 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[26] 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[26] seem to be good candidates for the gap symmetry in optimally doped $La_{2-x}Ce_xCuO_4$.

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. 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 just anisotropic s-wave symmetry.

It is important to note that the influence of the quasiparticle scattering on the high-frequency (millimeter-wave) penetration depth data has to be clarified before making final conclusions on gap symmetry or the 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.*[27] 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 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 difference between the as-measured and the corrected penetration depth data is so minor because of very low residual losses in the investigated films. The details of the recalculation procedure together with the determination of the scattering rate in $La_{2-x}Ce_xCuO_4$ 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 $La_{2-x}Ce_xCuO_4$. $\lambda(T)$ behaves quadratically in the underdoped, but it is close to exponential in the optimally doped regime. A change in the gap anisotropy (or symmetry) is a plausible explanation for these dramatic differences.

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