Evidence of charge carrier interaction above T_c in the $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ superconductor

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Resistivity, thermopower, and magnetic susceptibility of the $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ *n*-type superconductor have been measured on samples with well-known charge carrier density. Superconductivity is achieved only for charge carrier densities greater than a threshold value. When this value is approached, mobility drops to less than a tenth of the value for nonsuperconducting samples, the effective mass increases from $8m_e$ to $25m_e$, and susceptibility falls to lower values. All these phenomena are apparent well above T_c, thus indicating a charge carrier interaction above T_c. [S0163-1829(98)01438-6]

I. INTRODUCTION

One of the striking features of the copper oxide superconductors is the remarkable dependence of their properties on the charge carrier density. For example, for the *p*-type oxide superconductors a ''universal relationship'' holds[1] relating the normalized critical temperature ($T_{c,N} \equiv T_c/T_{c,\max}$) to the carrier density: $T_{c,N}$ is zero until a critical charge density value is reached; it then rapidly approaches unity and after a wide plateau drops to zero[1] [we will show in the following that the *n*-doped $Nd_{2-x}Ce_xCuO_{4+\delta}$ high-temperature superconductor (HTSC) system follows this universal relationship too]. This behavior strongly suggests that the charge carrier density should be considered as the actual ''driving force'' of the transition between normal and superconducting states and that in turn it can be singled out as the pertinent thermodynamic variable to be explored for obtaining quantitative data about the transport properties in HTSC's. The determination of the charge carrier density could be a nontrivial problem in most HTSC systems where more than one band is present at the Fermi level and/or the defect structure is made intricate by the large number of chemical degrees of freedom. In this respect, the *n*-type $Nd_{2-x}Ce_xCuO_{4+\delta}$ HTSC may be considered as a model system because the number of chemical degrees of freedom is very low indeed and because, about band structure, x-ray-absorption spectroscopy (XAS) and electron-energy-loss spectroscopy (EELS) results strongly suggest that a unique band with a predominant Cu $d_{x^2-y^2}$ character is present at the Fermi level.[2–6] As a consequence, at a given Ce and oxygen content, the charge carrier density in the conduction band is uniquely determined by the defect equations[7]

$$Nd_{Nd}+Ce \rightarrow Ce^{\cdot}_{Nd}+Nd+e',$$

$$O_i'' \rightleftarrows 2e' + \tfrac{1}{2}O_2.$$

As direct proof of the validity of this argument, we can quote that XAS measurements and point defect calculations are in fairly nice agreement in estimating the charge carrier density in this system.[4,8]

In this paper a study of the magnetic and transport properties in the $Nd_{2-x}Ce_xCuO_{4+\delta}$ HTSC system is presented as a function of the charge carrier density: in particular, conductivity, thermoelectric power, and magnetic susceptibility results of the $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ superconducting composition will be discussed. All the investigated quantities display a bell-shaped trend with the charge carrier density, while the expected one should be monotonic. This is apparent at $T > T_c$, and it is the authors' opinion that it can be due to an interaction between charge carriers above T_c.

II. EXPERIMENT

$Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ samples have been prepared by solid state synthesis in air at 1070 °C for 200 h with intermediate grinding. Each material was found to be single phase, homogenous, well crystalline, and well sintered by x-ray powder diffraction and microscopic inspection (scanning electron microscopy, electron microprobe analysis, and optical microscopy). Further details have been reported elsewhere.[4,7]

$Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ samples for dc measurements have been cut into bars ($10\times4\times2$ mm^3, $l\times w\times h$), annealed for more than 50 h at 1173 K and $10^{-6}<P(O_2)<1$ atm in a gas flow apparatus and fast quenched to room temperature by dropping the whole annealing apparatus in a water and ice mixture, keeping the gas flowing during the quenching. The quenching rate, as measured by a thermocouple near the sample, was always greater than 50 °C/s down to 200 °C. This procedure gives samples with a known and reproducible carrier density *n*, defined as the number of electrons per copper atom (or unit cell). dc measurements have been performed in the $13<T$(K)<290 range in a Leybold-Rok cryostat, using the four-probe method, and a Solartron 1286 galvanostat.

$Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ samples for the thermoelectric power (TEP) have been cut into disks (13 mm in diameter and 3 mm thick), annealed with the same procedure described above, and their flat faces have been coated with platinum paint (Engelhard). Measurements have been performed at 300 K in a home-made apparatus;[9] a heating coil is used to produce a series of preset temperature differences ΔT, while keeping constant the average temperature of the cell. After having controlled the proportional behavior of the potential difference ΔE vs ΔT, the thermopower (α) is obtained as the mean value of $\Delta E/\Delta T$. A correction for Pt thermopower has been applied using the tabulated values from Cusak and Kendall.[10]

Susceptibility measurements were performed by a Metronique Ingenierie Atne superconducting quantum interference device (SQUID) susceptometer, working at $H=40$ G either in zero-field-cooling (ZFC) and field-cooling (FC) conditions in the temperature range 3.2–250 K. The samples were sintered in the shape of a cylinder ($h\cong 3$ mm, diameter$\cong 6$ mm). With this sample geometry and the applied field H parallel to the cylinder axis, the demagnetizing field and single-ion diamagnetic contribution are negligible. The density of each sample was determined by measuring the buoyancy of the solid body when immersed in a liquid of known density (ethyl acetate), using a Mettler ME-40290 density determination kit and a Mettler AE-163 balance. The density of each sample was averaged on at least four measurements. Knowing the density, it was possible to estimate the Meissner fraction of the superconducting samples, which resulted to be of the order of 15–20 %.

III. RESULTS

The conductivity behavior was fully discussed in a previous paper.[4] Here the analysis will be limited to the dependence on the annealing $P(O_2)$. The conductivity at 290 K for variously annealed samples of $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ is displayed in Fig. 1 (circles), as $\log_{10}(\sigma/\Omega^{-1}\ cm^{-1})$: here and in the following figures, the oxygen partial pressure is expressed as $\log_{10}[P(O_2)/atm]$. It can be pointed out that the trend of Fig. 1 is fulfilled at any temperature in the $T_c < T$ (K)<290 range: see, for example, the open symbols in the same figure referring to 200 K (squares) and 100 K (triangles). The actual oxygen content should decrease with decreasing oxygen partial pressure at fixed temperature. This in turn should give rise to additional electronic charge carriers, and the conductivity σ should increase monotonically. While the expected trend is apparent for ''nonsuperconducting'' samples (open symbols), a sharp decrease of σ is found for ''superconducting'' samples (solid symbols). Here and in the following, the term ''superconducting'' (''nonsuperconducting'') refers to samples that at some temperature display (do not display) a superconducting transition disregarding their actual state: as a matter of fact, samples with charge carrier density n lower than ≈ 0.07 electrons per copper atoms [i.e., annealed at $P(O_2)\geqslant 10^{-3}$ atm] are ''nonsuperconducting.'' As was stated previously, the n-doped $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ system follows the same universal relationship proposed by Zhang and Sato[1] for the p-doped superconductors. This is shown in Fig. 2 in which $T_{c,N}$ data are plotted as a function of the charge carrier content: data from the present work are plotted together with data for various p-doped cuprate superconductors, as taken from Ref. 1.

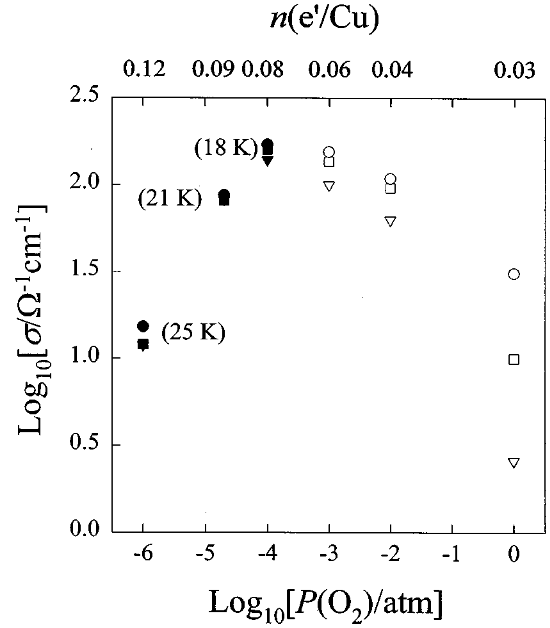

FIG. 1. Conductivity (σ) at 290 K (circles), 200 K (squares), and 100 K (triangles) for $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ samples annealed at 900 °C under various oxygen partial pressures. Here and in the following figures, open and solid circles, unless expressly indicated, refer to samples that are nonsuperconductors and superconductors, respectively, at low T; for the latter samples, the T_c value is given in brackets.

According to $\sigma=[e']q\mu$ ($q\equiv$electron charge and $[e']$ $\equiv$carrier density defined as the number of electrons per unit

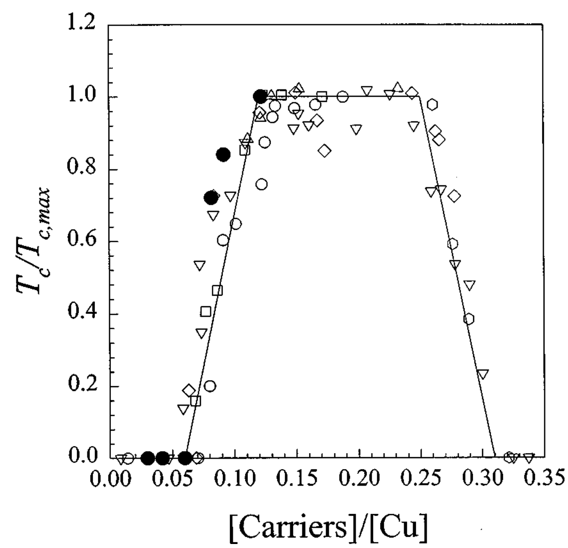

FIG. 2. ''Universal relationship'' between $T_{c,N}$ and charge carrier content, expressed as the number of charge carriers per copper atom. The meaning of the symbols is as follows: solid circles, present work; open circles, $YBa_2Cu_3O_{7-\delta}$ (Ref. 11); open squares, $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Refs. 12 and 13); open up triangles, $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (Ref. 14); open down triangles, $La_{2-x}Sr_xCuO_{4+\delta}$ (Ref. 15); open hexagons, $Tl_2Ba_2CuO_{6+\delta}$ (Ref. 16); open diamonds, $TlBa_2CaCu_2O_{7-\delta}$ (Refs. 17 and 18), as quoted by Ref. 1. The solid line is a guide to the eye (Ref. 1).

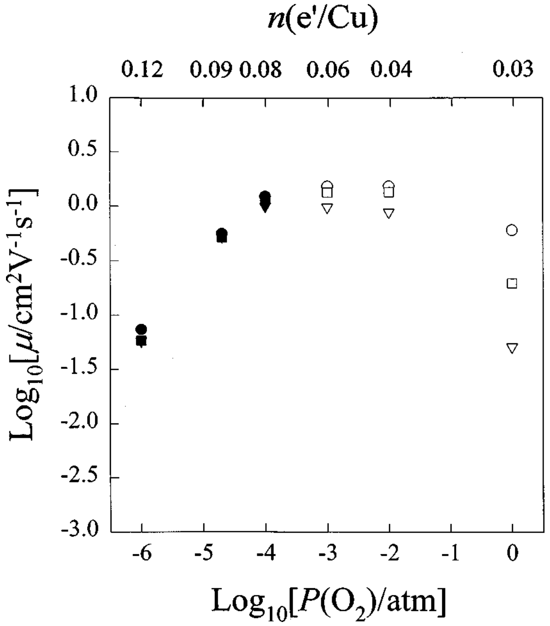

FIG. 3. Carrier mobility (μ) as a function of the annealing oxygen partial pressure for $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ samples, as in Fig. 1.

volume) and to the pertinent quasichemical point defect equilibria,[7] as the charge density is known, we can extract from the conductivity the mobility term μ; i.e., we can extract information on the nature of the charge carriers. The data displayed in Fig. 3, as $\log_{10}(\mu/\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1})$, for $T=290$ K are then obtained. The sharp decrease in conductivity of superconducting samples is entirely accounted for by a decrease in mobility. At lower temperatures, the same trend of mobility is obtained, except for the sample annealed at $P(O_2)=1$ atm, which presents a sharp increase of mobility which can be ascribed to an Anderson localization of charge carriers.[4]

A further insight into this behavior can be obtained by looking at the thermoelectric power data. The TEP data are plotted as α vs annealing $P(O_2)$ in Fig. 4. Increasing the carrier concentration n [i.e., lowering the annealing $P(O_2)$], α increases, reaches a limit value around $n\approx 0.07$ [annealing $P(O_2)\approx 10^{-3}$ atm], and then remains roughly constant: the trend of α vs annealing $P(O_2)$ is therefore nicely related to the same trend of σ. According to Ref. 19, all models proposed in the literature for the Seebeck coefficient are valid only in the limit of high temperature, as they can be reconnected to the original Mott's formulation, which gives correct results for $T\gg\theta_D$. Therefore, in order to explain this anomalous behavior, measurements in a higher-temperature range ($773<T<1073$ K) are required. The samples have been equilibrated for more than 10 h at various temperatures and $P(O_2)=2\times10^{-5}$ and 0.2 atm (air) before the measurements. TEP data for this temperature range are reported in Fig. 5 as αn vs T. Using the approach by Khlopkin *et al.*,[20] αn is proportional to m^*T where n is the charge carrier density here expressed as number of charge carriers per unit cell and m^* is the effective mass. Only slight deviations from linearity are found for the T and $P(O_2)$ ranges, giving rise upon quenching to nonsuperconducting samples (air, upper curve in Fig. 5). The effective mass is constant and is roughly equal to $8m_e$. As direct proof of the validity of our

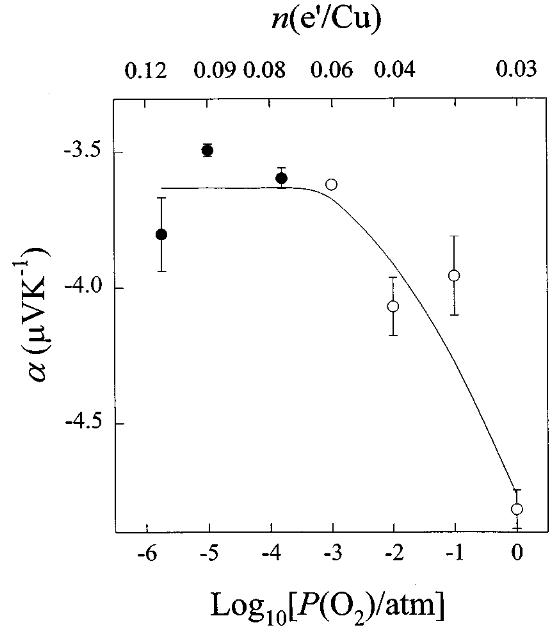

FIG. 4. Thermoelectric power (α) at 300 K for $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ samples annealed at different oxygen partial pressures. The line is a guide to the eye. The error bars refer to standard deviations on a set of (at least) three measurements.

approach, the inset in Fig. 5 shows the same plot in a wider T range. The data points are well interpolated by a straight line passing through the origin.

At low oxygen partial pressure [$P(O_2)=2\times10^{-5}$ atm, lower curve in Fig. 5], the deviation from linearity is dramatic. Using the slopes as a measure of m^* in the spirit of the approach of Khlopkin *et al.*, the effective mass changes from $9m_e$ at 773 K to $25m_e$ at $T=1173$ K. Samples quenched from $T=1173$ K and $P(O_2)=2\times10^{-5}$ atm are superconductors with $T_c=21$ K. For all the other external conditions of Fig. 5, no superconductivity is found. The onset of superconductivity is clearly associated with more than a dou-

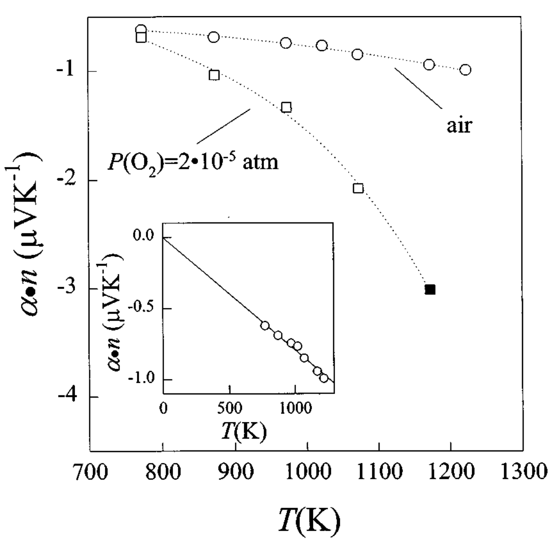

FIG. 5. αn for $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ samples in equilibrium with air (circles) and $P(O_2)=2\times10^{-5}$ atm (squares), as a function of T. The dotted lines are guides to the eye. In the inset the air αn vs T plot is shown in a wider T range.

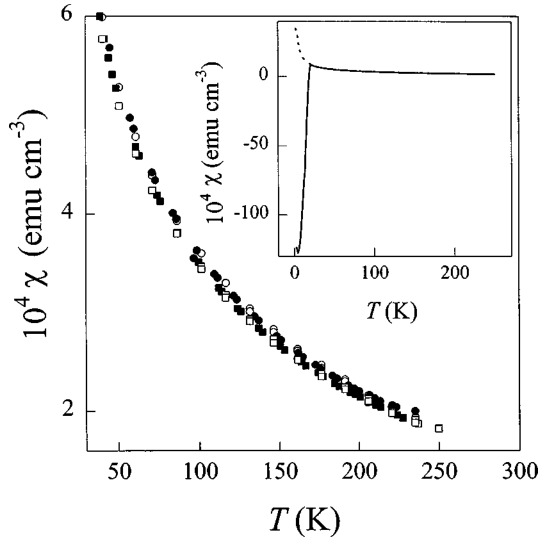

FIG. 6. Magnetic susceptibility of $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ samples annealed at 900 °C and $P(O_2)=10^{-6}$ atm (squares) and 1 atm (circles). Open and solid symbols refer to zero-field-cooled and field-cooled measurements, respectively. In the inset the same plot is shown in a wider T range (only the zero-field-cooled measurements are shown); the solid and dotted lines refer to samples annealed at $P(O_2)=1.8\times10^{-6}$ and 1 atm, respectively.

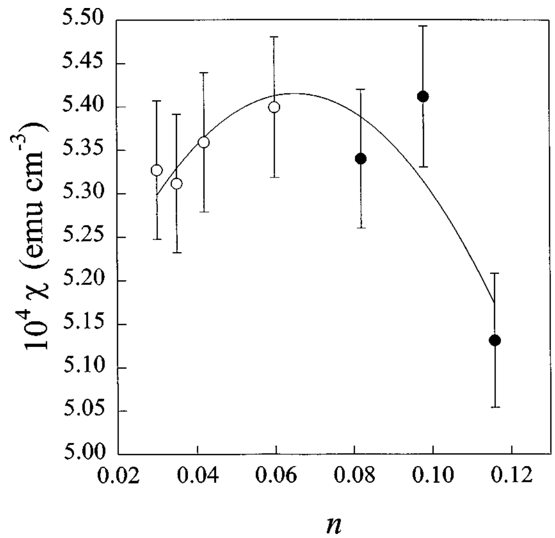

FIG. 7. Magnetic susceptibility at 50 K for $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ samples annealed under different $P(O_2)$ and, therefore, having different charge carrier densities. Open and solid symbols refer to nonsuperconducting and superconducting samples, respectively: the line is a guide to the eye; the error bars refer to a mean error (≈3%) that, according to our experience, is associated with the measurement.

bling of the effective mass value *at a temperature well above* T_c.

In Fig. 6 the susceptibility per unit volume of two typical samples with $n=0.03$ [annealed at $P(O_2)=1$ atm] and 0.116 [annealed at $P(O_2)=1.8\times10^{-6}$ atm] is shown. The critical temperatures T_c obtained from susceptibility well agree with the evaluations previously obtained from conductivity. As a further confirmation that there seems to be a precise value of n (number of carriers per copper atom) at which the magnetic and transport properties change in behavior, in Fig. 7 the susceptibility at a fixed temperature (50 K) is shown as a function of n. It is apparent that the susceptibility χ has a maximum around 0.06 and drops to significantly lower values for n greater than 0.07. Although the behavior shown in Fig. 7 could be also indicative of different crystal field (CF) contributions for each sample (see, for instance, Ref. 21), the good agreement between magnetic and transport results make us confident that the effect is genuinely due to the approach toward the critical value $n\cong0.07$ of the charge carrier density.

IV. DISCUSSION AND CONCLUSIONS

Evidence of two types of charge carriers in this system has been reported previously.[22] This evidence is achieved by comparison of the transport properties of samples on the ascending and descending parts of the T_c vs n plot. A similar comparison is not possible for the results of the present work, because all samples belong to the ascending part of the plot.

It is important to note that all the transport results described above cannot be explained by grain boundary or grain size phenomena, nor by the formation of weak links between grains. In fact, the samples have all been chemically synthesized and then sintered in the same conditions (1070 °C and air atmosphere) and the grain boundaries and size are determined by the sintering processes. The annealing step of each sample was performed at much lower temperature (900 °C). At this temperature, the grain boundary and size do not change anymore, as demonstrated by microscopic inspection. If grain boundary and size or weak link contributions existed, they should give origin to systematic errors, for example, to a constant additive term to the resistivity of each sample. This cannot change the meaning of the results reported above. Moreover, the transport property trend is followed by susceptibility as well. As grain boundary effects on susceptibility are negligible, this provides confirmation that the results discussed in this paper correspond to a bulk phenomenon.

The experimental results show that increasing the charge carrier density, the mobility of charge carriers initially remains roughly constant, but presents a sudden decrease at a threshold value, which well agrees with the critical value for superconductivity: the mobility of charge carriers is much lower in $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ samples, which give rise to superconductivity with respect to nonsuperconducting samples. The mobility drop corresponds to an increase of the effective mass from $9m_e$ to $25m_e$, as measured by the slope of the αn vs T plot and to a similar drop of susceptibility. It is important to note that all these phenomena are apparent at temperatures well above T_c; i.e., they refer to the normal-state properties of this system. This is not trivial, as the complete comprehension of the normal-state properties of superconductors is a prerequisite for the understanding of the phenomenon of superconductivity.

It is the authors' opinion that the previously discussed experimental evidence can be symptomatic of a charge carrier interaction in the normal state. Naively, this can be understood by considering that charge carriers fill the upper Mott-Hubbard band. The dispersion relation in the k space of this band is determined by the short-range $3d$ electron-electron interaction. The effective mass of the charge carriers is in turn determined by the curvature of this band, and therefore, by the $3d$ electron-electron interaction. Therefore, this suggests that the above increase of the effective mass is probably due to an interaction of the charge carriers themselves. It should be noted that any *quantitative* correlation between transport and susceptibility results must be inferred starting from a detailed model for the interaction between charge carriers, and such a model is still absent. Further experimental work (muon scattering and heat capacity measurements) is planned by the present group aiming at clarifying the nature of the charge carrier interaction.

As a final comment, it could be noticed that the same universal relationship relating $T_{c,N}$ to n that holds for p-type superconductors is followed also by the n-type $Nd_{2-x}Ce_xCuO_{4+\delta}$. This may suggest that the present results on mobility found in this system may be relevant also for the p-type superconductors. As a matter of fact, the available literature data[23,24] show an opposite behavior, i.e., that in p-type superconductors the mobility in the normal state *increases* with increasing charge carrier density. It should be noted, however, that the appearance of superconductivity is accompanied in p-type superconductors by other phenomena, for example, structural phase transitions. These phenomena make difficult any direct comparison with the present results.

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