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Preparation, Structural and Magnetic Properties of Electron–Doped Infinite–Layer HTSC $Sr_{1-x}Nd_xCuO_{2-\delta}$

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Abstract

We present our method of fabricating superconducting compounds of the infinite–layer structure $Sr_{1-x}Nd_xCuO_{2-\delta}$ with various doping concentrations. The samples undergo a high temperature–high pressure process and are then bulk superconductors without any further treatment. A slightly reducing atmosphere was necessary to get doped layer–phases. Refinement of the crystallographic data was done by a least squares method. The T_c^{onset} values are in the range of 36–41 K. The lower critical field $H_{c1}^{ab}(T=0)$ is extrapolated to 15 G, while magnetization cycles show extremely weak pinning behaviour. From photoemission data a considerably diminished Cu–O–hybridisation is found. The particular shape of partial Nd–valence band spectra for these compounds shows Nd to work as a trivalent dopant for divalent Sr.

1. Introduction

In 1991, Smith et al.[1] published the discovery of a new superconducting compound, which is composed of an infinite stacking of CuO_2–layers separated by doped alkaline–earth–layers only and is, like the isostructural, but not superconducting compound $Ca_{1-x}Sr_xCuO_{2-\delta}$, x=0.14 [2], called "all–layer phase" or "parent structure of all copper–oxide superconductors" [3]. A basic understanding of the physical properties of this electron–dopable system with T_c up to 40 K could lead the direction to find the mechanism of superconductivity in high temperature superconductors (HTSC). Hiroi et al.[4] found superconductivity in Sr–Cu–O systems with transition temperatures of about 80 K and 100 K. Furthermore, superconductivity is observed in these systems for Lanthanide dopants Ln=La[5,6], formally leading to electron doping, and also Ca is used as a dopant on Sr–sites leading to hole injection arising from Sr and Ca deficiency[7]. It was shown that the in–plane Cu–O bond length is the decisive parameter for determining if the plane can be reduced or oxidized[1,4].
Thin film preparation of $Sr_{1-x}Nd_xCuO_{2-\delta}$ is reported by Adachi et al.[8] and also by Sugii et al.[9]. We present our investigations on $Sr_{1-x}Nd_xCuO_{2-\delta}$ samples using various methods like X–ray analysis combined with methods of structural refinement, X–ray photoemission spectroscopy and photoemission with synchrotron radiation and measurement of the behaviour of the samples in magnetic fields. The way of preparation is described completely.

2. Experimental

Well homogenized citrate precursors were used as starting materials for the preparation of oxide compounds of the formula $Sr_{1-x}Nd_xCuO_{2-\delta}$, $0 \leq x \leq 0.16$. Appropriate amounts of $Cu(OH)_2 \cdot CuCO_3$ (purity $\geq$ 99.5%), $SrCO_3$ (99.9%) and Nd_2O_3 (99.9%) are added to a solution of nitric and citric acid containing about 30% excess of the citric acid with respect to the amount needed for the formation of citrates from the starting chemicals. HNO_3 is needed for dissolving Nd–oxides. After 1 hour of vigorously stirring and thereby homogenization of the solution on a molecular level, the dark blue liquid is ready to be dried slowly. After decomposition and removing the organics at temperatures of 600°C, the resulting fine, black powders are sintered using high temperatures by also applying high mechanical, uniaxial pressure in a modified belt apparatus. Typical parameters of this step are $p=4\times10^9$ Pa and T=1400°C with dwelling times up to

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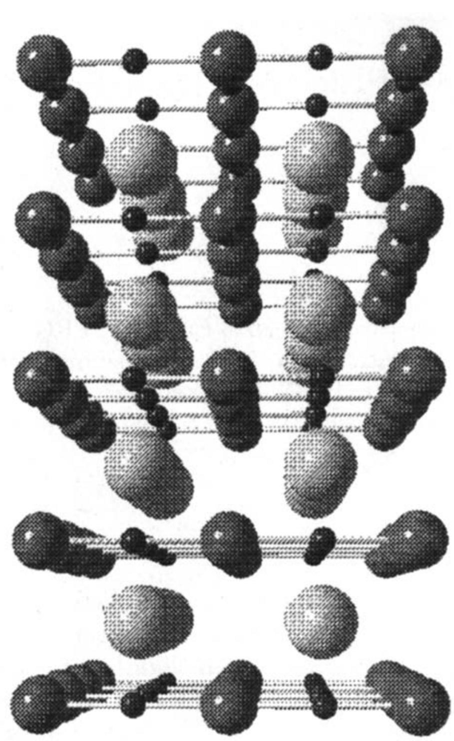

Figure 1: Infinite–layer structure (several unit cells) of $Sr_{1-x}Nd_xCuO_{2-\delta}$

2 hours and a second annealing step around 1100°C. Finally, the samples are quenched to room temperature before releasing the applied pressure. Platinum is used as a crucible material because of its high melting point and stability and also due to its reducing power during preparation which is essential for inducing superconductivity. No further annealing step is needed. The samples are cylindrical and have dimensions of about 2mm in diameter and 1.5mm in height.

3.Results and Discussion

Phase purity was checked by X-ray powder diffractometry ($\Theta - 2\Theta$-geometry (Siemens D5000) and Huber Guinier diffractometer). Only minor secondary phases were detected, but could not yet be identified. The samples show phase purity to an amount of $\geq$ 90%. To get more precise structural parameters a Rietveld refinement was applied (DBW Version 3.2 of the program[10]) using space group P4/mmm[2]. The symmetry was lowered to P4mm to allow independent movements for O– and Sr–atoms in z–direction ($z_O \neq 0$, $z_{Sr} \neq 1/2$) in order to examine the flatness of the Cu–O– or Sr–layers, respectively. However, in this case the quality of fit became worse. Lattice parameters were refined using 22 lines in a range of $20° \leq 2\Theta \leq 92°$ (Cu $K\alpha_1$). For a superconducting sample of composition $Sr_{1-x}Nd_xCuO_{2-\delta}$, x=0.15, according to the stoichiometry of starting powders, we find a=3.9427Åand c=3.3922Åin good agreement with the data from Smith et al.[1]. Thus the Cu–O–bond length is nearly exactly the same as is in $Nd_{2-x}Ce_xCuO_{4-\delta}$ [11]. We compared samples prepared from the same starting powders but sintered in different crucible materials. The sample mentioned above from a Pt–crucible was superconducting (T_c^{onset}=40 K), whereas those from Au-crucibles showed no superconductivity down to 4.2 K. Independent of starting stoichiometry and Nd–doping level, the lattice parameters a=3.9207Å, c=3.4226Åof these samples show according to the data of Smith et al.[1] the formation of $Sr_{1-x}Nd_xCuO_{2-\delta}$ with x around 0.0 to 0.02, although an infinite–layer structure was built up. Obviously, a slightly reducing atmosphere is necessary to grow the Nd–doped structure which is the case when using Pt–crucibles. This was also observed by Er et al.[5] in the system $Sr_{1-x}La_xCuO_{2-\delta}$. The question, why excess O can prohibit the formation of the high pressure phase of the $Sr_{1-x}Nd_xCuO_{2-\delta}$ – and $Sr_{1-x}La_xCuO_{2-\delta}$ –solid solutions is still open.
Proper and reliable estimation of occupancy and temperature factors from Rietveld refinement was not possible due to the unknown impurities. From the above data a unit cell volume of 52.7314Å^3 is derived and a bulk crystal density of D_{X-Ray}=6.033 g/cm^3 (formula weight of $Sr_{1-x}Nd_xCuO_{2-\delta}$ (x=0.15)=191.6578 g/mol, one formula unit per unit cell).

Resonant photoemission with synchrotron radiation at DESY/HASYLAB was used for investigations of the valence bands (Cu–resonance at $\hbar\omega$=74 eV) and recording the partial Nd–spectra of $Sr_{1-x}Nd_xCuO_{2-\delta}$ in order to get information about the charge carriers that are introduced into the system by Nd–doping (Nd^{3+}) on Sr–sites (Sr^{2+}). The valence band spectra are shown in figure 2. We find narrow valence bands as a consequence of diminished hybridization if compared to the relatively broad bands in $Nd_2CuO_{4-\delta}$.
From CuO_4–cluster calculations we obtain the main difference in electronic parameters of the Cu–O–layers to be a 0.4 eV lower Cu–O–hybridization for the infinite-layer–compound[12], whereas the Coulomb correlation is the same as for the other n–type HTSC. The partial Nd–spectra (see figure 3) for the T′–phase and $Sr_{1-x}Nd_xCuO_{2-\delta}$ show the Nd4f–valence bands with localized 4f^2 final states typical for trivalent Nd[13] as well as a main contribution at lower binding energies originating from hybridization with O2p–states. As a result, we find that, like in T′–structures[14,15], the rare–earth–layers between the Cu–O–sheets act as charge carrier reservoirs.

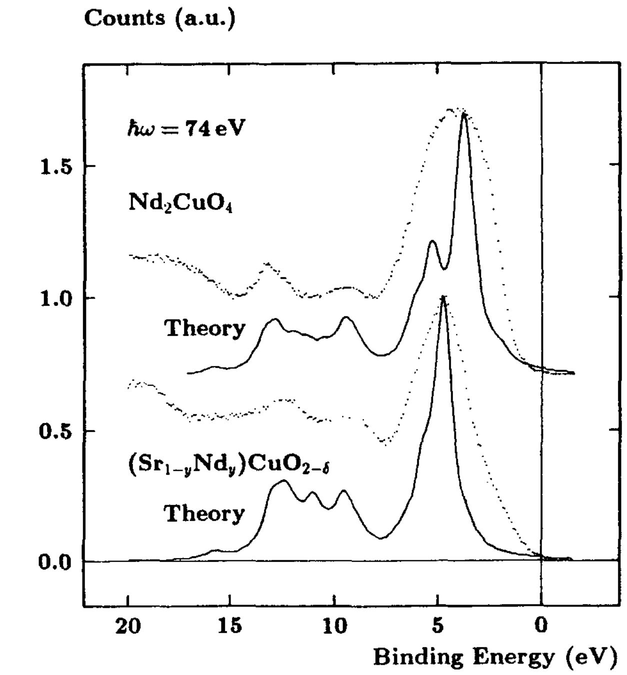

Figure 2: Valencebandspectra of $Sr_{1-x}Nd_xCuO_{2-\delta}$, x=0.15, and $Nd_2CuO_{4-\delta}$ in the Cu–resonance at $\hbar\omega$=74 eV as well as partial Cu–valence bands (full line) from CuO_4–Cluster calculations

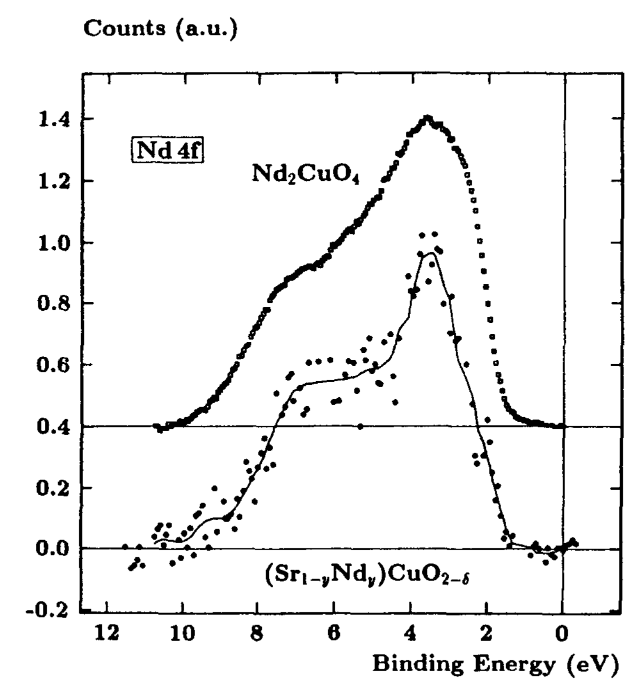

Figure 3: Partial Nd-valence band spectra for $Sr_{1-x}Nd_x$-$CuO_{2-\delta}$, x=0.15, and $Nd_2CuO_{4-\delta}$

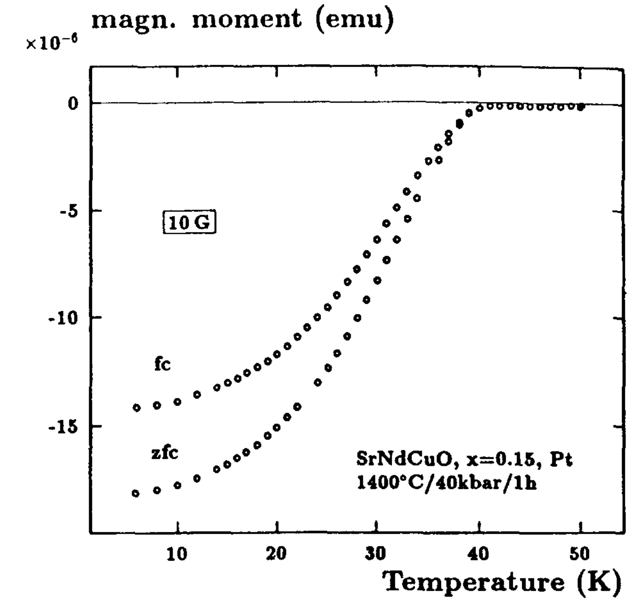

Figure 4: Fc– and zfc–transition to superconductivity for $Sr_{0.85}Nd_{0.15}CuO_{2-\delta}$

Superconducting parameters were examined using a commercial SQUID (SHE Corp., Model MPMS2). The samples were mounted on sample holders such that demagnetization factors can be neglected. In figure 4 the transition to superconductivity in an applied external field of 10 G is plotted as a function of temperature for field–cooled– (fc) and zero–field–cooled (zfc) measurements. A T_c^{onset} of about 40 K is observed. The curves reveal a very broad transition and saturation is reached only at very low temperatures. We attribute this behaviour to a very small particle size of the short reacted samples. The superconducting volume fraction of about 25% as deduced from the field–cooling measurements proves bulk superconductivity.

We measured the magnetic moment M of some samples as a function of field H and temperature T in the range of 0 mT to 12 mT and 4.5 to 30 K, respectively, in order to get the value of the lower critical field H_{c1}^{ab}. Evaluation of the data was done determining the onset of the deviation of M(H) from linear behaviour. In the temperature range from 4.5 K to 29 K the parabolic fits for the lower critical field

$$H_{c1}^{ab}(T) = H_{c1}^{ab}(T = 0\,K) \cdot \left(1 - \frac{T^2}{T_c^2}\right)$$

extrapolate to T_c=31 K and $\mu_0 H_{c1}^{ab}(0\,K)$ about 1.5 mT

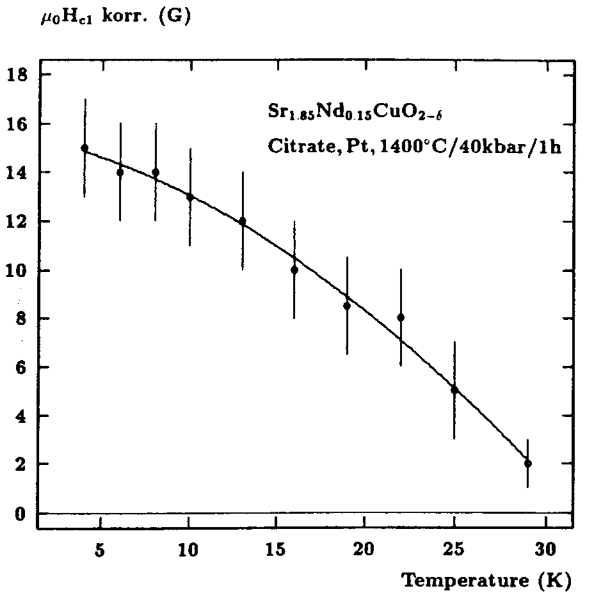

Figure 5: Temperature dependence of the lower critical field of $Sr_{0.85}Nd_{0.15}CuO_{2-\delta}$

(see figure 5). This value is very small as compared to e.g. $\mu_0 H_{c1}^{ab}$ of $Nd_{2-x}Ce_xCuO_{4-\delta}$ of about 13.5 mT[16]. Cycling the sample in varying magnetic fields well above H_{c1}^{ab} we find nearly reversible behaviour which we explain by a very large penetration depth along the c–axis of these weakly coupled layer structures.

4. Conclusions

In summary, superconducting samples of the infinite-layer structure $Sr_{1-x}Nd_xCuO_{2-\delta}$ were prepared by a high pressure method. Superconducting transition temperatures (onset) reached about 41 K and the estimated Meißner fractions about 25%. The material shows very weak pinning behaviour. Electrons are thought to be the charge carriers in $Sr_{1-x}Nd_xCuO_{2-\delta}$ because of a) a formal doping of e^- by introducing Nd^{3+} on divalent Sr–sites, b) the need of a reducing atmosphere for inducing superconductivity: oxygen vacancies in the Cu–O–layers could lead to the observed diminished Cu–O–hybridization, c) Cu–O–bond lengths are identical to T′–structures $Nd_{2-x}Ce_xCuO_{4-\delta}$, and d) Er et al.[6] found for the very similar compound $Sr_{1-x}La_xCuO_{2-\delta}$ also prepared in reducing surrounding, negative values for thermoelectric power S, quite similar to the n–doped T′–system $Nd_{2-x}Ce_xCuO_{4-\delta}$.

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