Structural instability under pressure in the HTSL (Nd, Gd, Ce)$_2$CuO$_4$

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The partial substitution of Nd by Gd and Ce on the structural properties of Nd$_2$CuO$_4$ n-type superconductor was studied by using X – ray diffraction measurements. The maximum value of critical transition temperature T$_c$ was obtained in Gd doped (Nd$_{2-x-y}$Ce$_x$ Gd$_y$)CuO$_4$ for x=0.15 Ce. The structural distortion of the T'-phase was investigated by X-ray diffraction measurements function of temperature for samples with high Gd content. Under normal-pressure, for small anomalies of the lattice parameter c, especially the deviation of the c/a-relationship, a more continuously structural transition was evidenced as a function of Gd concentration and temperature. The influence of pressure and Gd concentration on the lattice parameters and unit cell volume was also studied at room temperature in the optimal doped sample (x=0.15 Ce). In this case a higher pressure stabilizes the smallest undistorted phase.

1. Introduction

Considering that the superconductivity is created by carrier doping of the insulating parent compound Ln$_2$CuO$_4$ (Ln=Nd,Pr,Sm,Eu), some new superconductors were prepared and investigated [1].

The n-type superconducting oxide Nd$_{2-x}$Ce$_x$CuO$_{4+d}$ shows the maximum critical transition temperature T$_c$ = 24 K for optimum doping x=0.15 [2]. The replacement of Nd^{3+} by Ce^{4+} can reduce the copper valence, resulting an n-type conduction. In this compound cerium and copper are both multivalent ions and for optimum doping the cerium valence is about 3.84 and the copper valence is below 1.84 [3]

After the substitution of Nd by Gd, superconductivity is destroyed. Superconductivity occurs for Nd substitution of y ≤ 0.6 Gd in the optimal Cerium-doped system (Nd$_{1-y}$Gd$_y$)$_{1.85}$Ce$_{0.15}$CuO$_4$ [4]. For a doping level of y=0.65 the superconductivity is suppressed [4] and an anti-ferromagnetic order of the Cu-spins at a Néel-temperature of ~270 K appears. In addition to this, a weak ferromagnetism was evidenced [5].

In 1992 P. Adelmann et al [6] found a structural distortion for a small Gd content in the Cerium-free system (Nd,Gd)$_2$CuO$_4$, which degraded the increasing instability. Such a structural distortion has been evidenced by M. Braden and P. Adelmann in the (Nd,Tb)$_{1.85}$Ce$_{0.15}$CuO$_4$ system [7].

The transition from the structural normal phase (I4/mmm) to the distorted phase (Acam) was evidenced above y=0.65 Gd substitution level in (Nd$_{1-y}$ Gd$_y$)$_{1.85}$Ce$_{0.15}$ CuO$_4$. The structural phase transition temperature T$_{I-A}$ from undistorted phase to the distorted phase depends on the Gd concentration [8]. The Gd doping dependencies of the unit cell height c(y) and unit cell volume V(y) show that the slope of linear dependence changes around y=0.7.

This is the critical concentration for the transition between structural normal phase and a distorted phase [9]. The Gd concentration for transition in distorted phase and in the normal state is close to y=0.65.

The effect of pressure on the crystal structure of the n-type superconductors is complex, because the compression of different lattice parameters under pressure is not uniform and different bond length do not respond to the pressure in a similar manner [10,11]. The partial substitution of Nd by Gd favours the distortion in the (Nd,Gd)$_{2-x}$Ce$_x$CuO$_4$ system.

In this paper we report the effect of pressures on the structural parameters and unit cell volume of optimal electron doped (Nd$_{1-y}$Gd$_y$)$_{1.85}$Ce$_{0.15}$CuO$_4$ system.

2. Experimental

Samples of chemical formula (Nd$_{1-y}$Gd$_y$)$_{2-x}$Ce$_x$CuO$_4$ (where $0 \leq x \leq 2$; $0 \leq y \leq 1$) were prepared by conventional solid – state reaction method. Appropriate amounts of Nd$_2$O$_3$, CeO$_2$, Gd$_2$O$_3$ and CuO were mixed and sintered at 900 ^{o}C for 10h and at 1100 ^{o}C for 16 h, in a flowing oxygen gas. The sintered material was powdered, pressed into pellets and sintered at 1150 ^{o}C for 48 h in flowing oxygen, followed by quenching at room temperature.

The X – ray powder diffraction (XRD) measurements were carried out by a Siemens D-5000 diffractometer with Cu-K$_\alpha$ radiation. The lattice constants were obtained from the powder diffraction data. The normal phase shows a high tetragonal symmetry with a ≅ b and the space group I4/mmm.

Data were collected by step scanning with steps of 0.02 ^{0} 2θ. Phase purity was checked by using Crystallographic Search Match program.

For the pressure experiments we used the measuring desk F2/1 at the synchrotron radiation laboratory in *Hamburg* (*HASYLAB*) at the "*Deutsches Synchroton (DESY)*", Germany, with energy dispersive polychromatical X-ray light. The measurement desk F2/1 is driven by a 2-axis-goniometer, a germanium-detector and a multi-stamp-device *MAX-80*. In this experiment the pressure was approximately 5.5 GPa at room-temperature and only dispersive x-ray-radiation energy was used [12].

The multi-stamp-device *MAX-80* (with six *Wolframcarbid* stamps) is the essential components of the high pressure-cell. A mixture of 75% amorphous boric and 25% *Epoxidresin* and more roughly existing components serves for high pressure measurements. In order to avoid the x-ray absorption we used build-in components from *Bornitrit* as they consist of relatively light atoms. Hollow-cylinders were moulded and into them the samples as pressure-regulation-standard *NaCl* were used.

The pressure is generated by a hydraulic 250t-press. The low stamp is pressed against the stationary with the same strength. By increasing the pressure the material of the *Bor-Epoxid-insertion* penetrates into the gaps of the stamps. The arrangement of through the gaps allows a maximum 30° inflection-angle of the synchrotron radiation.

The press-forces are set and monitored by means of an electronic pressure-regulation over a hydraulic-pump. The precision of the pressforces can be regulated until on 1/2 tons.

The $(Nd_{1-y}Gd_y)_{1.85}Ce_{0.15}CuO_4$ samples with y = 1.0, 0.95, 0.90 and 0.85 which showing distorted phase at room temperature, were analyzed under pressure.

3. Results and discussion

The transition from the structural normal phase (I4/mmm) to the distortion phase (Acam) was evidenced above y=0.65 Gd substitution level in $(Nd_{1-y} Gd_y)_{1.85} Ce_{0.15} CuO_4$. The structural phase transition temperature T_{I-A} from undistorted phase to the distorted phase changes with the Gd concentration [8,9]
The scaled XRD spectra of the samples with distorted phase do not show any foreign phase. Thus, no additional reflexes as a function of pressure or changes of the peak positions appear.

Fig. 1 shows the volume of unit cell and the lattice constants as a function of pressure for $(Nd_{0.10}Gd_{0.90})_{1.85}Ce_{0.15}CuO_4$ sample.

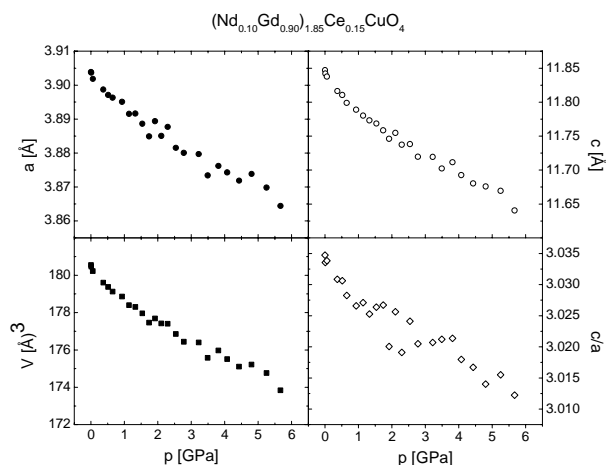*Fig. 1. Lattice parameter a and c, volume and the c/a as a function of pressure for $(Nd_{0.10}Gd_{0.90})_{1.85}Ce_{0.15}CuO_4$ sample.*

The lattice parameters *a* and c and the unit cell volume V decrease by increasing the pressure. As seen in Fig. 1, the pressure dependence of c/a shows a more significant dispersion of data in the range 2GPa-4GPa. This is the crossover from distorted to undistorted structural phase.

In order to recognize a possible deviation of the linear course of the lattice parameter c or the lattice parameter relation c/a, the corresponding data were normalized to their values under normal pressure. Figs. 2 and 3 shows these normalized values for different y stoechiometries.
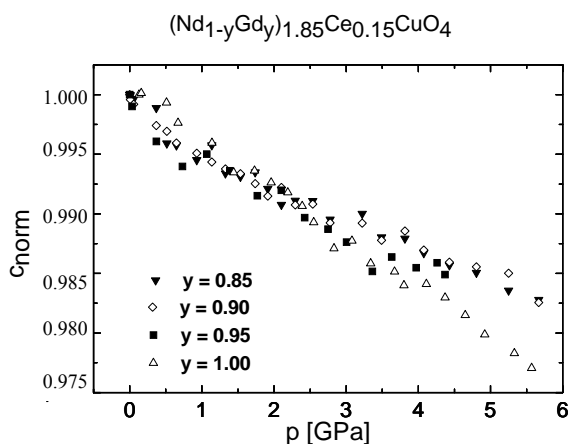

Fig. 2. The normalised unit cell height (c_{norm}) as a function of pressure for different stoechiometries y of distorted phase samples.
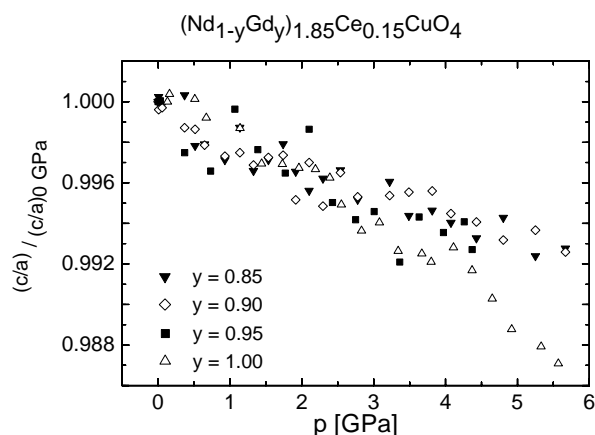
$(Nd_{1-y}Gd_y)_{1.85}Ce_{0.15}CuO_4$

Fig. 3. The normalised (c/a) ratio under pressure to (c/a) ratio in the absence of pressure as a function of pressure for different stoechiometries y of distorted phase samples.

As shown in Fig. 2, the sample with y = 1.00 can easily be identified due to its distinct dependence of (c/a) / (c/a)$_0$ ratio with pressure. For such values of the pressure all the samples are in the distorted phase. Thus, it is difficult to obtain from the plot given in Fig. 2 a reasonable value for the crossover pressure p$_{I-A}$.

Fig. 4 shows the pressure dependence of unit cell volume V. The unit cell volume shows the lowest dispersion data as a function of pressure and how it is to obtain the transition pressure p$_{I-A}$. The change of the slope of linear dependence suggests the transition from distorted to undistorted phase by increasing the pressure. The value for p$_{I-A}$ is obtained at the crossover of the two linear dependences of V(p) in distorted and undistorted phases. The crossover pressure p$_{I-A}$ increases by increasing the level of Gd concentration (y).
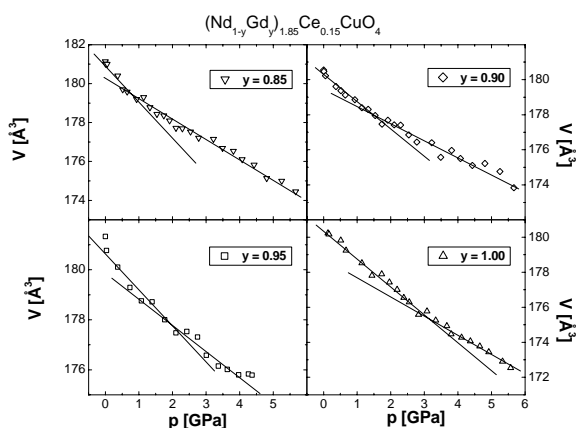
It can be concluded that the structural distortion of the T'-phase in high Gd doped samples is reduced by increasing pressure. This effect coincides with the reduction of the c-axis parameter followed by a higher compressibility.

In order to characterize the change of crossover critical pressure function of gadolinium doping level in initially distorted samples, a diagram phase p$_{I-A}$ = f(y) is desirable.

A linear connection between the critical pressure p$_{I-A}$ and the Gd-doping y can be distinctly seen in Fig. 5. This line is the border between the undistorted and distorted phases. By increasing the Gd level (y) to unity (y=1), the critical pressure increase up to 3GPa.
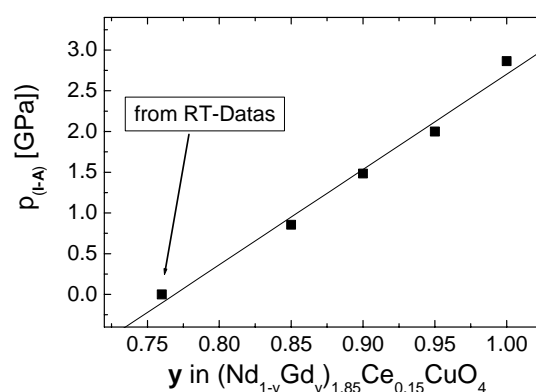

Fig. 5 Structural phase diagram for the pressure controlled distortion in $(Nd_{1-y}Gd_y)_{1.85}Ce_{0.15}CuO_4$ system.

4. Conclusions

X-ray diffraction measurements under pressure is a good method to evidence the structural phase transition induced by Gd in $(Nd_{1-y}Gd_y)_{1.85}Ce_{0.15}CuO_4$ system.

The Gd doping dependencies of the unit cell parameters and unit cell volume V(y) under different pressure for our samples, show a critical pressure p$_{I-A}$ for the transition from distorted to undistorted phase.

The critical pressure from distorted to undistorted phase is obtained at the crossover of the two linear dependences of V(p) in distorted and undistorted phases.

The structural phase transition pressure p$_{I-A}$ linearly increases by increasing Gd-concentrations above y=0.75.

The phase diagram p$_{I-A}$=f(y), shows that the structural distortion is controlled by the Gd ions concentration under different pressures. Higher pressure stabilizes the smalles undistorted phase.

Fig. 4. The pressure dependence of unit cell volume V for samples with different Gd concetration.

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