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Structural distortion and superconductivity in $(\mathrm{Nd}_{1-x}\mathrm{Tb}_x)_{1.85}\mathrm{Ce}_{0.15}\mathrm{CuO}_4$

M. Braden
Forschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik, D-76021 Karlsruhe, Germany
and Laboratoire Léon Brillouin, CEA, CNRS, F-91191 Gif-sur-Yvette Cedex, France

P. Adelmann, P. Schweiss, and T. Woisczyk
Forschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik, D-76021 Karlsruhe, Germany

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The phase diagram of $(\mathrm{Nd}_{1-x}\mathrm{Tb}_x)_{1.85}\mathrm{Ce}_{0.15}\mathrm{CuO}_4$ has been studied by resistivity, magnetic susceptibility, x-ray, electron-, and neutron-diffraction experiments. For low-Tb concentrations the samples are superconducting; however, T_c diminishes rapidly with increasing x. For higher Tb concentrations all diffraction studies indicate the long-range lattice deformation characterized by the rotation of the CuO_4 squares around the c axis (i.e., the orthorhombic phase recently observed in $\mathrm{Gd}_2\mathrm{CuO}_4$); the structural consequences of the distortion are discussed.

Recently a structural distortion of the T' phase was observed in $\mathrm{Gd}_2\mathrm{CuO}_4$,[1] where the CuO_4 squares are rotated around the c axis by an angle of 5.2° at room temperature. The underlying structural phase transition appears to be dominated by the ionic radius of the R since $\mathrm{Nd}_{0.38}\mathrm{Tb}_{1.62}\mathrm{CuO}_4$, which possesses the same averaged ionic radius as $\mathrm{Gd}_2\mathrm{CuO}_4$, presents the identical distortion.[1]

It is well known that the T' phase compounds $R_2\mathrm{CuO}_4$ with $R=$Pr, Nd, Sm, and Eu become superconducting by doping with Ce or Th; however, attempts to render $\mathrm{Gd}_2\mathrm{CuO}_4$ superconducting failed.[2] The Gd compounds remain semiconducting and present antiferromagnetic order with a weak ferromagnetic component even for elevated Ce contents.[2,3] It seemed interesting to analyze whether the nonexistence of superconductivity (SC) in $\mathrm{Gd}_{2-x}\mathrm{Ce}_x\mathrm{CuO}_4$ and the appearance of the structural distortion are related. In this sense, the suppression of SC in the T' phase might resemble the effect of the low-temperature-tetragonal-type (LTT) structural distortion in the $\mathrm{La}_{2-x-y}R_yM_x\mathrm{CuO}_4$ ($M=$Sr, Ba) compounds of the T phase.[4,5]

In order to study both the structural distortion and SC in $(\mathrm{Nd}_{1-x}R_x)_{1.85}\mathrm{Ce}_{0.15}\mathrm{CuO}_4$ we were looking for a system which would allow us to vary the mean ionic radius on the R site close to an expected critical value of 1.09 Å. The possible candidates Eu, Sm, and Gd had to be excluded due to their bad properties for thermal neutron diffraction which, however, is necessary in order to analyze the small oxygen displacements. Therefore, we chose $(\mathrm{Nd}_{1-x}\mathrm{Tb}_x)_{1.85}\mathrm{Ce}_{0.15}\mathrm{CuO}_4$ (NTCCO) for our studies; superconducting and structural properties were studied by resistivity and susceptibility measurements and by neutron, x-ray, and electron diffraction.

The samples of NTCCO with $0.2\leqslant x\leqslant 0.65$ were prepared by the standard solid-state reaction,[2] the last reduction step was performed at ~900 °C. The reduction temperature had to be slightly adapted to the Tb concentrations as, for increasing Tb contents, the samples start to decompose at lower temperature. The samples were first characterized by x-ray diffraction indicating an impurity phase concentration of less than 2%. For a Ce concentration of 0.15 the Tb solubility limit was found near $x=0.7$; for the Ce-free compounds Tb up to $x=0.8$ could be introduced into the structure. Superconducting transition temperatures were measured by four contact resistivity and/or superconducting quantum interference device magnetometer measurements. Neutron diffraction experiments at the ORPHEE reactor were performed using the diffractometers G6.1 ($\lambda=4.04$ Å, high flux; between 11 and 550 K, G4.1 ($\lambda=2.43$ Å; $T=11$ and 295 K), and 3T.2 ($\lambda=1.22$ Å, high resolution, 20 counters; $T=11$ K). High-resolution structural analyses were performed for 11-K data obtained at 3T.2 ($5°<2\Theta<125°$), an example diffraction pattern being shown in Fig. 1. The Rietveld analyses with the program FULLPROF[6] yielded agreement factors, R_{wp}, near 5% for each data set. For Tb concentrations lower than 0.3 the ideal T' structure (space group $I4/mmm$) was refined, whereas, for higher Tb concentrations a better agreement with the data was achieved by describing the distorted structure according to $Acam$. In addition, the samples were analyzed on a Philips CM30 electron microscope.

Figure 2 shows the lattice constants of NTCCO as a function of the Tb concentration at 295 and 11 K. Whereas at

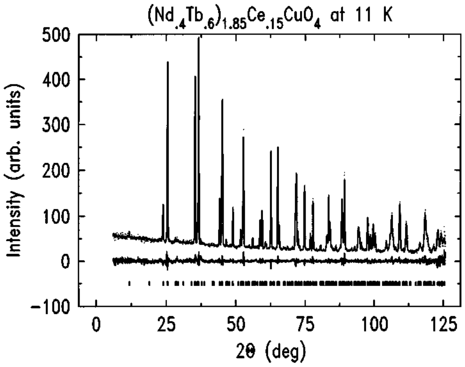

FIG. 1. High-resolution powder-diffraction pattern (3T.2, $\lambda=1.22$ Å) obtained for $(\mathrm{Na}_{0.4}\mathrm{Tb}_{0.6})_{1.85}\mathrm{Ce}_{0.15}\mathrm{CuO}_4$ at 11 K. Points represent data; lines, calculated (Rietveld) fit. Difference plot is centered at intensity=0. Vertical bars denote the positions of reflections.

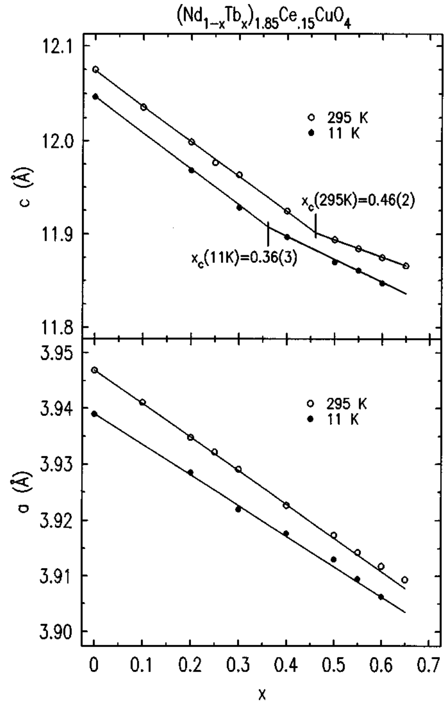

FIG. 2. Dependencies of the lattice parameters in $(Nd_{1-x}Tb_x)_{1.85}Ce_{0.15}CuO_4$ on the Tb concentration x at 295 K (x-ray diffraction) and at 11 K (neutron diffraction). The 11-K $x=0$ data point was obtained by applying the thermal expansion reported in[23] to the 295-K parameters.

both temperatures a linear dependence is observed for the a parameter, the c parameter plot represents clear kinks indicating a modified crystal structure for Tb concentrations higher than $x_c(295\ \mathrm{K})=0.46(2)$ and $x_c(11\ \mathrm{K})=0.36(3)$. A similar kink seen in the dependence of the published R_2CuO_4 c parameters on the R ionic radius[7,8] indicates a general strain order-parameter coupling. For high-Tb concentrations we additionally observe superstructure peaks which can be indexed in a $\sqrt{2}a\times\sqrt{2}a\times c$ lattice in respect to the high-temperature $I4/mmm$ structure; for example the (212) reflection is shown in Fig. 3. Rietveld refinements with the patterns obtained with $\lambda=2.43$ and 1.22 Å confirm that the superstructure in the NTCCO samples is identical to the one observed in Gd_2CuO_4 (Ref. 1) with space group $Acam$ (standard setting $Cmca$), i.e., the superstructure is characterized by the rotation of the CuO_4 squares. (In the following this transition will be called rotation transition in contrast to the tilt transitions in the T phase where the axes of rotation lie within the CuO_2 plane.) As discussed in Ref. 1, the simplest structural distortion due to a CuO_4 rotation corresponds to the space group $Acam$. More complex structures correspond to different stacking sequences of the distorted CuO_2 planes leading to at least a doubling of the c parameter, a situation not supported by the diffraction pattern. The space group $I4_1/acd$ which is reported for the similarly distorted Sr_2IrO_4 and Sr_2RhO_4 structures,[9] is incompatible with the positions of the superstructure reflections.

The main characteristic of the transition is the rotation of the CuO_4 squares around c (see Fig. 4 and Fig. 1 in Ref. 1), which is the order parameter. The $T=11$ K values scale roughly linearly with $(x-x_c)$. Attempts to refine a distortion of the rotated CuO_4 square gave no improvement compared to the rigid one; therefore, the plane oxygen [O(1)] position was constrained to $(0.25+d,0.25-d,0)$. The upper limit for the splitting of the CuO bond distances can be estimated to 0.01 Å. A smaller splitting, even though too small to be detected by powder diffraction, might have a strong impact on the electronic band structure.

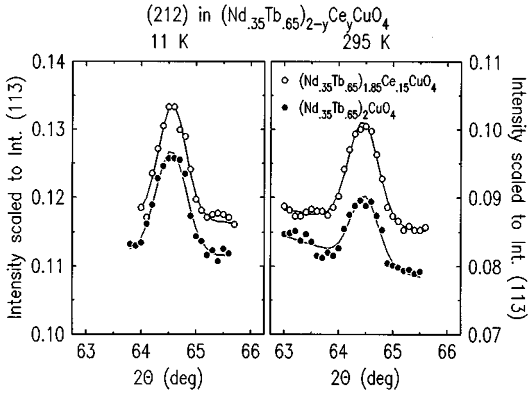

FIG. 3. Comparison of the profiles of the (212) superstructure reflection peaks in $(Nd_{0.35}Tb_{0.65})_{1.85}Ce_{0.15}CuO_4$ and $(Nd_{0.35}Tb_{0.65})_2CuO_4$ at 11 and 295 K (neutron diffraction G4.1). The measured intensities were scaled with the peak height of the (113) fundamental reflection obtained by fitting with a Gaussian and shifted vertically for clarity.

As a consequence of the rotation transition at higher Tb contents several bond lengths are strongly modified. The Cu-O(1) distance decreases with increasing Tb content as long as the samples stay in the ideal T' structure in accordance with the relatively smaller ionic radius of the Tb ion. For higher Tb contents the rotation of the CuO_4 squares gives rise to an elongation of the Cu-O(1) bond when compared to the value extrapolated from the $I4/mmm$ plane. In this system with a Ce concentration of 0.15 the Cu-O(1) bond does not go below 1.958 Å. The elongation of the Cu-O(1) bond in the distorted phase was also observed for the tilt transition in the T phase.[10] So, a similar bond-length mismatch between the R-O and Cu-O subsystems might be responsible for the rotation transition in the T' phase in agreement with the pronounced dependency on the R ionic radius.[1,11] However, a more detailed analysis with respect to the rather an-

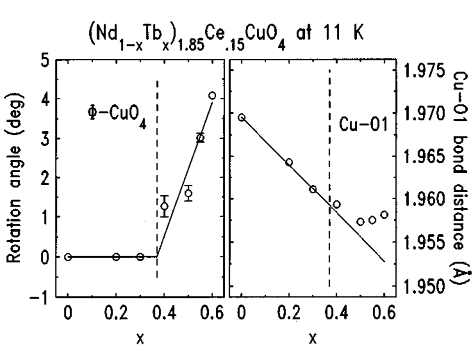

FIG. 4. Rotation angle and Cu-O(1) bond distance at 11 K as a function of the Tb concentration x. The broken vertical lines indicate the critical Tb concentration for the transition into the $Acam$ phase at 11 K. Other lines are guides to the eye. The $x=0$ data point was obtained from Ref. 23.

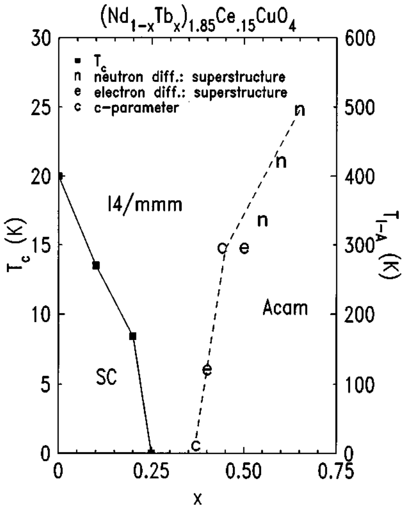

FIG. 5. Phase diagram of $(Nd_{1-x}Tb_x)_{1.85}Ce_{0.15}CuO_4$. The superconducting transition temperatures were obtained by resistivity and/or susceptibility measurements (left scale). *n* denotes structural transition temperatures (right scale) obtained by temperature-dependent neutron-diffraction studies. *e* represents the sample with lowest Tb concentration which shows the superstructure peaks in electron diffraction. *c* represents the critical Tb concentrations determined by the kink in the Tb dependency of the *c* lattice parameter.

isotropic coordinations reveals a more complex driving mechanism.[12]

The influence of Ce doping on the transition has been studied by comparing the superstructure reflection intensities in $(Nd_{0.35}Tb_{0.65})_{1.85}Ce_{0.15}CuO_4$ and $(Nd_{0.35}Tb_{0.65})_2CuO_4$, see Fig. 3. There is only a small effect: for the Ce containing sample the intensity has been measured as a function of temperature thereby determining the transition temperature from the I-centered high-temperature phase to the $Acam$ phase, $T_{I-A}=505(5)$ K; extrapolation of the intensities measured for the Ce-free sample gives $T_{I-A}=450(15)$ K. The obtained shift in T_{I-A} agrees to a recent measurement on $Gd_{2-x}Ce_xCuO_4$ single crystals.[13] Qualitatively the increase of T_{I-A} is explained by the smaller ionic radius of Ce^{4+} and the charge transfer into the planes which should enhance the equilibrium Cu-O distances. Quantitatively, the 15% Ce doping shifts the transition temperature by about +50 K, whereas in the case of La_2CuO_4 the Sr doping by the same amount reduces the transition by about 350 K. The strongly reduced influence of the electronic doping in case of the T' phase might indicate that the charge transfer is incomplete in respect to the amount of Ce substitution.

The phase diagram of NTCCO has been established combining the different diffraction techniques with the resistivity and susceptibility measurements, see Fig. 5.[12] The superconducting T_c diminishes rapidly with the Tb substitution, superconductivity (SC) could not be detected for Tb concentrations higher than 0.25. For an only slightly higher Tb content we observed the rotation distorted phase, with the characteristic superstructure reflections appearing in electron and neutron diffraction, furthermore the plot of the c lattice parameters obtained at 11 K presents the characteristic kink at 0.36(3). For $x=0.55$, 0.60, and 0.65 the transition temperatures were determined on analyzing the superstructure reflection intensities as a function of temperature by means of neutron diffraction; for $x=0.4$ the corresponding intensities appeared in the electron-diffraction pattern on cooling. The exclusion between SC and the structural distortion in NTCCO resembles the interplay between superconductivity and the LTT phase in $La_{2-x-y}Nd_xSr_yCuO_4$.[5] In the case of $(Nd_{1-x}Tb_x)_{1.85}Ce_{0.15}CuO_4$ the superdonducting phase is separated from the rotation phase by a region of nonsuperconducting samples not presenting a long range superstructure. However, the strong difference of the Nd and Tb ionic radii might favor a local distortion in the samples around $x=0.3$, which is very difficult to detect in a diffraction experiment.

For several T' compounds the appearance of weak ferromagnetism (WFM) has been reported.[14] However, WFM is incompatible with the ideal structure with space group $I4/mmm$ and necessitates a structural distortion. The $Acam$ structure described by the rotation of the CuO_4 squares easily explains the occurrence of WFM and the alignment of the ferromagnetic moment parallel to the CuO_2 planes. It, therefore, seems reasonable to assume that all T' compounds presenting WFM possess the $Acam$ superstructure. Hence, it is possible to compare the structural distortion in NTCCO to the magnetic phase diagrams of similar systems. Oseroff *et al.*[14] observe at low temperatures indications for WFM in Eu_2CuO_4. Our conjecture that Eu_2CuO_4 undergoes a structural phase transformation is supported by the appearance of additional Raman lines.[15] A direct proof of the distortion in Eu_2CuO_4 was recently obtained by neutron diffraction.[16] As Ce increases the transition temperature $Eu_{1.85}Ce_{0.15}CuO_4$ should present the superstructure, too; however, this compound is still superconducting though its T_c is already reduced.[2] Furthermore, Fuchs *et al.* observe SC and WFM in the same $Eu_{1.75}Gd_{0.1}Ce_{0.15}CuO_4$ sample.[17] In all published phase diagrams, SC disappears close to the composition where WFM appears, and where a lattice parameter anomaly similar to the one in Fig. 2 is observed.[17–20] Hence, we suggest the following interpretation: the rotation distortion might not suppress SC but only reduce the T_c. However, the increased distortion in the samples with the smallest R's might enhance such an effect leading to the observed suppression.

Such a relation to the SC reflects the continuous character of the rotation transition. Furthermore, it corresponds to the current understanding of the influence of the tilt transition in the LTO-T phase: the LTO tilt was also shown to reduce and not to suppress T_c.[21] However, it cannot be ruled out that the suppression of SC in the T' compounds with small R's is due to an inefficient or incomplete reduction of the oxygen content. It seems worthwhile to remind that for our samples the reduction step had to be performed at lower temperature for increasing Tb content. So, a less effective reduction appears possible. However, it was verified that the oxygen content has only a minor influence on the rotation transition by analyzing an oxidized sample.[12] Manthiram and Zhu argue that an inherent instability in the case of the smaller ionic radii would prevent a proper reduction.[22]

In conclusion we have analyzed the structural distortion and the superconducting properties in NTCCO. The smaller ionic radius of the Tb ions causes the rotation transition with strong impacts on several bond distances. Especially the

Cu-O bonds are elongated. The driving force of the transition seems to be more complex in nature than the isotropic bond-length mismatch which can account quantitatively for the tilt transitions in the T phase.

The phase diagram of NTCCO exhibits an exclusion between SC at low-Tb concentrations, and the rotation distorted phase at large concentrations. For some intermediate concentrations neither SC or a long-range structural deformation can be detected. Our data together with the published phase diagrams on the WFM were interpreted by the assumption that the rotation of the CuO_4 squares reduces T_c continuously resulting into a rather strong effect for larger rotation angles. The question whether such an effect is responsible for the nonexistence of SC in $R_{2-x}Ce_xCuO_4$ samples with small R's needs further analysis on the role of the oxygen content and on the character of the charge transfer in these compounds.

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