

# Antiferromagnetic ordering states of oxygen-deficient $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$ and $\text{Nd}_{1+y}\text{Ba}_{2-y}\text{Cu}_3\text{O}_{6+x}$ single crystals

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The paper describes a study of the antiferromagnetic ordering of oxygen-deficient  $\text{Nd}_{1+y}\text{Ba}_{2-y}\text{Cu}_3\text{O}_{6+x}$  single crystals. In pure, stoichiometric samples,  $y=0$ , with different oxygen contents  $x$  in the Cu(1) plane ( $0.02 < x < 0.2$ ), the antiferromagnetic I (AFI) phase appears to be stable down to 316 mK. The magnetic ordering within the Cu(2) sublattice of the pure  $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$  system is therefore similar to that of the pure  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  parent compound. With increasing oxygen content, the Néel temperature drops significantly and the critical exponent changes from 0.26 for  $\text{NdBa}_2\text{Cu}_3\text{O}_{6.09}$  to about 0.5 for  $\text{NdBa}_2\text{Cu}_3\text{O}_{6.23}$ . Magnetic ordering of the  $\text{Nd}^{3+}$  moments sets in at 1.7 K with a critical wave vector  $\mathbf{q}_{\text{Nd}} = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$ . Reordering to the AFII phase is observed in a crystal, which has a significant amount (4%) of  $\text{Nd}^{3+}$  ions substituted on the Ba sites. The relatively high temperature  $T_2 = 95$  K of this reordering suggests that the  $\text{Nd}^{3+}$  ions on Ba sites are very effective defects forcing the AFI  $\leftrightarrow$  AFII reordering. The mechanism of reordering is explained in terms of the creation of  $\text{Cu}^{2+}$  moments within the Cu(1) layer due to the  $\text{Nd}^{3+}$  ions on Ba sites, which via polarization lead to an effective ferromagnetic coupling between the moments on next-nearest neighboring Cu(2) layers. The  $\text{Nd}^{3+}$  doping on the  $\text{Ba}^{2+}$  sites increases the Néel temperature compared to the stoichiometric compound. [S0163-1829(99)02002-0]

## I. INTRODUCTION

The  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  system has attracted considerable attention due to its higher superconducting transition temperature  $T_c$  compared with  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .  $T_c$  values of up to 96 K, critical current densities of up to  $1.2 \times 10^5$  A/cm<sup>2</sup> at 77 K and 2.5 T, and irreversibility fields exceeding 13 T at 77 K can be achieved,<sup>1,2</sup> which move  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  into the range of interest for technical applications.

To understand the differences between the superconducting properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  it is important to identify any differences in their magnetic behavior, especially because  $\text{Nd}^{3+}$  ions can possess a magnetic moment while  $\text{Y}^{3+}$  ions cannot. A direct consequence of this is that magnetic ordering of the Nd sublattice occurs at low temperatures coexistent with superconductivity. Furthermore, previous investigations of the magnetic structure adopted by the Cu sublattice seemed to indicate that the magnetic ordering scheme in reduced  $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$  is strictly different from that of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ ,<sup>3-5</sup> even though the crystal structure of the two compounds is virtually identical.

It is well established that pure  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  shows a transition from the metallic and superconducting phase to the insulating and antiferromagnetically ordered antiferromagnetic I (AFI) phase upon successive reduction of the oxygen content  $x$  in the basal plane to below  $x \sim 0.4$ .<sup>6-8</sup> For  $0 < x < 0.2$  the Néel temperature  $T_N$  is slightly above 400 K and almost independent on  $x$ . This AFI phase is characterized by ordering of the moments on the Cu(2) sites within the  $\text{CuO}_2$  planes forming antiferromagnetic bilayers, which are separated by the weak-coupling path along the Cu(1) position occupied exclusively by nonmagnetic  $\text{Cu}^+$  for  $x=0$ . The AFI ordering scheme is characterized by a critical wave vector  $\mathbf{q}_{\text{AFI}} = (\frac{1}{2} \frac{1}{2} 0)$ . An average *ordered* moment on the Cu(2) site of  $0.55 \mu_B$  with a spin orientation perpendicular to the  $c$  axis has been reported in a  $\text{YBa}_2\text{Cu}_3\text{O}_{6.1}$  crystal,<sup>9</sup> while no *ordered* magnetic moment is present on the Cu(1) sites in the oxygen-deficient layer. Whereas in very pure  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  crystals the AFI phase is stable down to lowest temperatures,<sup>9</sup> reordering to a second antiferromagnetic phase AFII with characteristic wave vector  $\mathbf{q} = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$  has been reported in the doped Y system.<sup>3-5,9-22</sup> This AFII phase has a similar antiferromagnetic arrangement of the spins

within the Cu(2) bilayer as the AFI phase, but alternating AF magnetization of the bilayers stacked along the  $c$  axis, which is thus doubled with respect to the chemical unit cell.<sup>13</sup> The AFII phase was found to occur in  $\text{YBa}_2\text{Cu}_3\text{-}_z\text{M}_z\text{O}_{6+x}$  doped by trivalent ions like  $\text{Al}^{3+}$ ,<sup>9–11</sup>  $\text{Co}^{3+}$ ,<sup>14,15</sup>  $\text{Fe}^{3+}$ ,<sup>16–22</sup> or  $\text{Ga}^{3+}$ ,<sup>22</sup> which are known to substitute predominantly onto the Cu(1) sites.<sup>23–28</sup>

In contrast to the pure Y system, the AFII phase was frequently found in apparently undoped  $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$ .<sup>3–5</sup> Moudren *et al.*<sup>4</sup> reported that the AFII phase covers the whole antiferromagnetic region in their  $\text{NdBa}_2\text{Cu}_3\text{O}_{6.10}$  single crystal. Li *et al.*<sup>5</sup> observed the reordering from the AFI to the AFII phase at temperatures far below  $T_N$  with the reordering temperature  $T_2$  depending on the oxygen content  $x$ .

One difference between  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  and  $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$  is the fact that  $\text{Nd}^{3+}$  ions can substitute onto the Ba sites under particular preparation conditions yielding  $\text{Nd}_{1+y}\text{Ba}_{2-y}\text{Cu}_3\text{O}_{6+x}$ .<sup>29–31</sup> Furthermore, as mentioned above,  $\text{Nd}^{3+}$  carries a magnetic moment while  $\text{Y}^{3+}$  does not. It has been speculated that the AFI $\leftrightarrow$ AFII reordering in  $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$  is due to an ordering of  $\text{Cu}^{2+}$  moments within the Cu(1) layer, which is induced by the substitution of Nd on Ba sites.<sup>5</sup> For  $\text{YBa}_2\text{Cu}_3\text{-}_z\text{M}_z\text{O}_{6+x}$  the mechanism of reordering has been attributed to frustration of moments on the Cu(1) sites in the AFI phase.<sup>13,15–17</sup> However, the nuclear quadrupole resonance (NQR) results of Lütgemeier and Heinmaa<sup>22</sup> definitely rule out an ordered magnetic moment on Cu(1) sites in  $\text{YBa}_2\text{Cu}_3\text{-}_z\text{M}_z\text{O}_{6+x}$  doped by different trivalent cations. The AFI $\leftrightarrow$ AFII reordering is driven by the magnetic moment of a dopant and also by isolated  $\text{Cu}^{2+}$  moments created by the excess oxygen coordinating nonmagnetic dopants like  $\text{Al}^{3+}$  or  $\text{Ga}^{3+}$ .<sup>9–11,22</sup> Recently, Andersen and Uimin<sup>32</sup> presented a theoretical model that explains the AFI $\leftrightarrow$ AFII reordering via intermediate turn-angle phases by the formation of free  $\text{Cu}^{2+}$  spins in the Cu(1) basal planes. The free spins may be polarized and establish an effective ferromagnetic type of coupling between the adjacent  $\text{CuO}_2$  layers. It is suggested that trivalent cations on the Cu(1) site as well as the Ba site may give rise to the free  $\text{Cu}^{2+}$  spins.

In the oxygen-deficient  $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$  system it is still unclear if the reordering to the AFII phase is a general phenomenon or exclusively results from the  $\text{Nd}^{3+}$  ions on Ba sites. Therefore we studied the structural and magnetic properties of  $\text{Nd}_{1+y}\text{Ba}_{2-y}\text{Cu}_3\text{O}_{6+x}$  single crystals with stoichiometric composition as well as of crystals with a significant amount of  $\text{Nd}^{3+}$  on Ba sites.

## II. EXPERIMENT

Very pure, stoichiometric  $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$  single crystals were grown from a BaO/CuO flux in  $\text{SnO}_2$  crucibles by the slow-cooling method.<sup>33</sup> Powders of CuO,  $\text{BaCO}_3$ , and  $\text{Nd}_2\text{O}_3$  of a purity better than 99.99% were used. The growth was performed in air at a pressure of 70 mbar. Crystal growth was started at 1283 K, and the cooling rate during the growth was 0.8 K/h. The Nd/Ba-substituted crystals were grown in air atmosphere at 1 bar. For these crystals, Y-stabilized  $\text{ZrO}_2$  crucibles were used, which due to crucible

corrosion led to a slight contamination of Y on the Nd sites. Here the growth started at 1313 K with a cooling rate of 1 K/h.

The as-grown crystals were annealed in 1-bar flowing oxygen atmosphere between 873 K and 673 K during 500–660 h. The superconducting transition of the oxidized samples was found by ac susceptibility at  $T_c = 90.5$  K for the stoichiometric crystals and at 77.5 K for the Nd/Ba-substituted crystals, both with a width of about 1.5 K. The depression of  $T_c$  is attributed to the  $\text{Nd}^{3+}$  ions substituted on Ba sites.<sup>29–31</sup> Comparing this  $T_c$  value to the  $T_c$  versus  $y$  diagrams of Refs. 29–31 suggests a Nd content on Ba sites of roughly 10% in our crystals.

For the diffraction experiment the crystals were reduced using a gas volumetric technique.<sup>34</sup> For the determination of the oxygen content as well as the structural details, complete nuclear Bragg scattering single-crystal data sets were collected. The crystal  $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{6.23}$  was studied on the TAS2 four-circle diffractometer at the DR3 reactor at Risø National Laboratory with neutron wavelength  $\lambda = 1.047$  Å. Half a sphere of nuclear Bragg reflections up to  $\sin \theta/\lambda = 0.67$  Å<sup>-1</sup> were collected in the  $\theta$ - $2\theta$  mode leading to 225 independent observations. Analysis of the nuclear structural data was performed with the SHELX76 (Ref. 35) refinement program. The other two crystals  $\text{NdBa}_2\text{Cu}_3\text{O}_{6.09}$  and  $\text{Nd}(\text{Ba}_{1.92}\text{Nd}_{0.08})\text{Cu}_3\text{O}_{6.17}$  were measured on the four-circle diffractometer P110/5C2 at the reactor Orphée, CE-Saclay,<sup>36</sup> using neutrons with  $\lambda = 0.83$  Å, employing the  $\omega$ -scan technique. 908 reflections were collected up to  $\sin \theta/\lambda = 0.75$  Å<sup>-1</sup>, resulting in 242 symmetry independent observations. The structural analysis of these data sets was performed with the Prometheus program package. Numerical absorption and extinction corrections employing the Becker-Coppens model for secondary extinction of type I were applied.

Nonpolarized magnetic neutron-diffraction experiments were performed on the TAS1 triple-axis spectrometer at the DR3 reactor at Risø National Laboratory using incident neutrons of energy 13.7 meV ( $\lambda = 2.42$  Å) selected by a graphite monochromator. Higher-order neutrons were depressed by a pyrolytic graphite filter. The crystals were oriented with their  $[1\bar{1}0]$  axis vertical, so that the ( $hkl$ ) reflections were in the horizontal scattering plane. Details of the experimental setup are the same as those described in Ref. 10. For most of the work a standard <sup>4</sup>He cryostat was used for temperatures between 2 K and 300 K. For temperatures below 2 K, an Oxford Instruments Heliox He<sup>3</sup> cryostat was employed. The studies above room temperature were performed using a resistively heated furnace can.

The NQR spectra were recorded using a standard spin-echo technique with quadrature detection. The NQR spectra were measured by a frequency sweep. For measurements at 4.2 K and 1.2 K the crystals were mounted in an Oxford Instruments CF1200 He cryostat.

## III. RESULTS

### A. Nuclear structure

The significant 48% difference in neutron-scattering lengths of Nd (Ref. 37) and Ba (Ref. 38) makes neutron

TABLE I. Results of the structural refinement of three neutron Bragg data sets. The Debye-Waller factor has the form  $\exp-2\pi^2[a^{*2}(h^2U_{11}+k^2U_{22})+l^2c^{*2}U_{33}]$ , where the  $U_{ii}$  are the mean-square displacements.

Site	Position	Stoichiometric crystal			
		NdBa <sub>2</sub> Cu <sub>3</sub> O <sub>6.09</sub>	NdBa <sub>2</sub> Cu <sub>3</sub> O <sub>6.23</sub>	Nd/Ba-substituted crystal Nd <sub>1.08</sub> Ba <sub>1.92</sub> Cu <sub>3</sub> O <sub>6.17</sub>	
Nd	1 <i>d</i>	Occupancy	1.023(7)	1.00(2)	1.023(7)
		$U_{11}$	0.0032(3)	0.0040(8)	0.0044(3)
		$U_{33}$	0.0062(3)	0.0073(11)	0.0083(5)
Ba	2 <i>h</i>	Occupancy	0.997(7)	1.00(1)	1.020(7)
		$z$	0.19246(9)	0.19262(21)	0.19160(9)
		$U_{11}$	0.0076(4)	0.0099(9)	0.0089(4)
		$U_{33}$	0.0072(5)	0.0099(12)	0.0111(6)
Cu(1)	1 <i>a</i>	Occupancy	1.022(8)	0.98(2)	0.972(7)
		$U_{11}$	0.0111(4)	0.0142(10)	0.0181(5)
		$U_{33}$	0.0086(5)	0.0083(11)	0.0084(5)
Cu(2)	2 <i>g</i>	$z$	0.35374(6)	0.35353(14)	0.35362(6)
		$U_{11}$	0.0034(2)	0.0044(5)	0.0040(2)
		$U_{33}$	0.0086(3)	0.0094(7)	0.0110(3)
O(1)	2 <i>g</i>	Occupancy	0.998(6)	0.98(2)	0.973(6)
		$z$	0.15210(9)	0.15189(22)	0.15311(10)
		$U_{11}$	0.0148(3)	0.0284(10)	0.0226(4)
		$U_{33}$	0.0096(5)	0.0112(12)	0.0111(6)
O(2)	4 <i>i</i>	$z$	0.37181(6)	0.37099(14)	0.37194(7)
		$U_{11}$	0.0058(2)	0.0054(7)	0.0074(3)
		$U_{22}$	0.0038(2)	0.0085(7)	0.0047(3)
		$U_{33}$	0.0096(3)	0.00109(7)	0.0124(3)
O(4)	2 <i>f</i>	Occupancy	0.090(7)	0.23(2)	0.175(8)
		$U_{11}$	0.025(14)	0.047(17)	0.039(10)
		$U_{22}$	0.003(10)	0.016(12)	0.031(9)
		$U_{33}$	0.026(16)	0.015(12)	0.016(8)
		$a$	3.898(6) Å	3.900(2) Å	3.890(4) Å
		$c$	11.882(24) Å	11.790(7) Å	11.814(25) Å
		$R$	2.4%	2.8%	2.6%
		$R_W$	2.8%	3.8%	2.9%

diffraction a suitable tool for determining the content of Nd on Ba sites. Table I gives the results of our structure refinements. For the crystals grown under reducing conditions, the refined occupancy of the Ba site is very close to unity. Wavelength dispersive x-ray microprobe (WDX) investigations on crystals of the same batch also showed no deviation from the Nd:Ba ratio of 1:2.<sup>39</sup> We conclude that under reducing growth conditions the Nd<sup>3+</sup> ions do not enter the Ba sites. The oxygen occupancy on the O(4) site of these two stoichiometric crystals was refined to  $x=0.09$  and  $x=0.23$ , respectively. Although the apical oxygen O(1) shows a slight deficiency, in the following we will call these crystals Nd<sub>1</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6.09</sub> and Nd<sub>1</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6.23</sub>, respectively, according to the oxygen content  $x$  within the Cu(1) layer.

In contrast, the crystal prepared in 1 bar air shows a refined Ba occupancy significantly larger than 1. Taking into account the scattering length of both elements, one finds a Nd content of 4% on Ba sites. The occupancy  $x$  of the oxygen O(4) within the Cu(1) layer is 0.17, so that in the following we will call this crystal Nd(Ba<sub>1.92</sub>Nd<sub>0.08</sub>)Cu<sub>3</sub>O<sub>6.17</sub>. The Nd:Ba ratio obtained from the structural refinement is also consistent with careful WDX analysis.<sup>39</sup>

## B. Magnetic properties of stoichiometric Nd<sub>1</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub>

In all our reduced stoichiometric Nd<sub>1</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> crystals, the spin system orders into the AFI structure below  $T_N$ , as indicated by magnetic superlattice peaks with wave vector  $\mathbf{q}_{AFI}=(\frac{1}{2}\frac{1}{2}0)$ . The superlattice peaks are sharp in all directions implying three-dimensional (3D) and long-range order.

Figure 1 illustrates the temperature dependence of the integrated intensity of the magnetic  $(\frac{1}{2}\frac{1}{2}2)$  peak of Nd<sub>1</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6.09</sub>. The transition from the paramagnetic phase to AFI sets in at  $T_N=376(1)$  K. The integrated intensity shows a power-law behavior  $I\sim I_0(T_N-T)^{2\beta}$  with a critical exponent  $\beta=0.25(1)$ , fitted between 300 K and  $T_N$ . From 11 accessible magnetic superlattice peaks, the ordered magnetic moment on Cu(2) at 4.2 K was refined to  $0.59(5)\mu_B$ , oriented within the (001) plane.

Below about 1.7 K additional magnetic peaks with  $\mathbf{q}=(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  appear. While the intensity of the  $(\frac{1}{2}\frac{1}{2}\frac{3}{2})$  peak strongly increases with decreasing temperature below 1.7 K, the  $(\frac{1}{2}\frac{1}{2}2)$  peak remains unaffected to within experimental error. Two different origins of  $\mathbf{q}=(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  ordering are

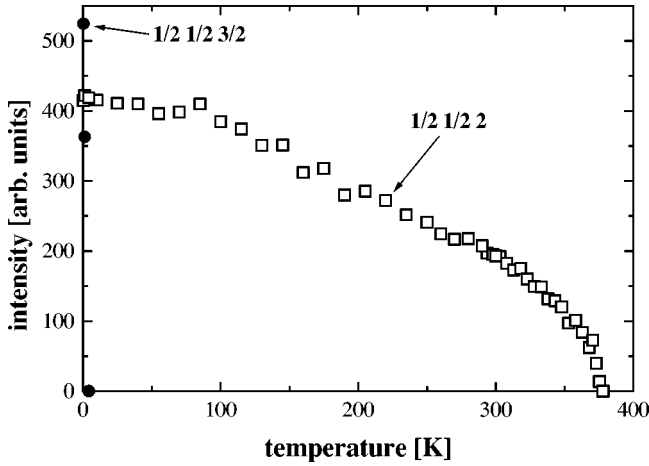


FIG. 1. Temperature dependence of the integrated intensity of the  $(\frac{1}{2}\frac{1}{2}2)$  magnetic reflection for  $\text{NdBa}_2\text{Cu}_3\text{O}_{6.09}$ . The AFI ordering sets in at the Néel temperature  $T_N=376$  K. Below 1.7 K peaks of the type  $(h+\frac{1}{2}, k+\frac{1}{2}, l+\frac{1}{2})$  occur, which are due to an antiferromagnetic ordering of the  $\text{Nd}^{3+}$  moments; the three datapoints (full circles) were obtained at 1.7 K, 1.5 K, and 1.2 K. Note that the  $\text{Nd}^{3+}$  magnetic ordering at wave vector  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  does not affect the ordering of the  $\text{Cu}^{2+}$  moments at  $(\frac{1}{2}\frac{1}{2}0)$ .

known: (i) reordering of the copper spins to the AFII phase and (ii) ordering of the spins on the rare-earth site. As can be seen from Fig. 1, the AFI  $\mathbf{q}=(\frac{1}{2}\frac{1}{2}0)$  ordering component is not affected by the  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  component. Thus the AFII ordering of the  $\text{Cu}(2)$  moments can be excluded as the origin of the  $\mathbf{q}=(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  intensities in the present case, as AFII is necessarily competitive to AFI and depresses the  $\mathbf{q}=(\frac{1}{2}\frac{1}{2}0)$  intensities when the AFII order parameter increases.<sup>13,10,17,11,32</sup> Further, the  $\text{Cu}(1)$  NQR line at 1.2 K shows no sign of line

splitting or broadening, which it would if AFII ordering or the intermediate turn-angle phase were present.<sup>11</sup> As AFII ordering is thus ruled out, the  $\mathbf{q}=(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  magnetic ordering in our stoichiometric  $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{6.10}$  is most probably related to ordering of the rare-earth sites. Antiferromagnetic ordering of the rare-earth moments occurs typically at Néel temperatures  $T_N^{RE}$  of 1–2 K.<sup>40–44</sup> For  $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$  ordering of the  $\text{Nd}^{3+}$  moments has been reported with  $T_N^{RE}=1.7$  K for  $x<0.2$ .<sup>43,44</sup> Clinton *et al.*<sup>40</sup> postulated a long-range, 3D antiferromagnetic structure formed by the  $\text{Nd}^{3+}$  moments with an average ordered moment  $\langle\mu_z\rangle$  of  $0.85\mu_B$  and the moment direction tilted by  $45^\circ$  with respect to the  $c$  axis. Details of the ordering of the  $\text{Nd}^{3+}$  moments in our sample will be reported elsewhere.<sup>45</sup>

The Néel temperature  $T_N$  of AFI ordering depends on the oxygen content  $x$  within the  $\text{Cu}(1)$  layer. While the  $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{6.09}$  crystal has a  $T_N$  of 376 K,  $T_N$  drops to 289 K for the  $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{6.23}$  crystal and the critical exponent  $\beta$  becomes 0.53(2) (cf. Fig. 2). Further, in the  $x=0.23$  sample the AFI order parameter goes through a maximum at about 70 K and decreases almost linearly with decreasing temperature below 70 K. As refined from 11 accessible magnetic superlattice peaks, the average ordered magnetic moment on the  $\text{Cu}(2)$  site at 70 K is  $0.35(3)\mu_B$ . As down to 2 K no  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ -type reflections were observed, the decrease of the AFI order parameter is not related to a turn-angle reordering to AFII. For the pure  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  system with  $x\geq 0.2$  a reentrant behavior of the AFI order parameter has frequently been reported and has been related to a small amount of localized oxygen  $2p$  holes transferred to the  $\text{Cu}(2)$  layers, which build up static disorder between the antiferromagnetic bilayers.<sup>46,47</sup>

### C. Magnetic properties of Nd/Ba-substituted $\text{Nd}(\text{Ba}_{1.92}\text{Nd}_{0.08})\text{Cu}_3\text{O}_{6.17}$

The Nd/Ba-substituted crystal  $\text{Nd}(\text{Ba}_{1.92}\text{Nd}_{0.08})\text{Cu}_3\text{O}_{6.17}$  shows a completely different magnetic behavior compared to

TABLE II. Comparison between observed and calculated square of the structure factors  $F^2$  for the AFI and AFII magnetic Bragg reflections for  $\text{Nd}_{1.08}\text{Ba}_{1.92}\text{Cu}_3\text{O}_{6.17}$ . The data collections for the two phases have been performed at 100 K and 4.2 K, respectively. For the calculation, the direction of the spins on  $\text{Cu}(2)$  sites have been assumed to be perpendicular to the  $c$  axis.

AFI ( $T=100$ K)				AFII ( $T=4.2$ K)			
$hkl$	$\kappa$ ( $\text{\AA}^{-1}$ )	$F_{obs}^2$ ( $10^3$ b)	$F_{calc}^2$ ( $10^3$ b)	$hkl$	$\kappa$ ( $\text{\AA}^{-1}$ )	$F_{obs}^2$ ( $10^3$ b)	$F_{calc}^2$ ( $10^3$ b)
$\frac{1}{2}\frac{1}{2}0$	1.140	<1	0.0	$\frac{1}{2}\frac{1}{2}0$	1.140	<1	0.0
$\frac{1}{2}\frac{1}{2}1$	1.258	19.5	20.3	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	1.171	7.7	7.8
$\frac{1}{2}\frac{1}{2}2$	1.559	34.9	34.3	$\frac{1}{2}\frac{1}{2}\frac{3}{2}$	1.391	45.3	47.2
$\frac{1}{2}\frac{1}{2}3$	1.960	5.0	4.4	$\frac{1}{2}\frac{1}{2}\frac{5}{2}$	1.751	28.6	28.5
$\frac{1}{2}\frac{1}{2}4$	2.412	12.9	12.7	$\frac{1}{2}\frac{1}{2}\frac{7}{2}$	2.182	1.1	1.0
$\frac{1}{2}\frac{1}{2}5$	2.892	37.8	38.1	$\frac{1}{2}\frac{1}{2}\frac{9}{2}$	2.650	a	42.4
$\frac{1}{2}\frac{1}{2}6$	3.387	12.7	13.6	$\frac{1}{2}\frac{1}{2}\frac{11}{2}$	3.138	a	42.4
$\frac{1}{2}\frac{1}{2}7$	3.391	<1	2.1	$\frac{1}{2}\frac{1}{2}\frac{13}{2}$	3.638	1.9	2.0
$\frac{3}{2}\frac{3}{2}1$	3.461	5.0	5.2	$\frac{3}{2}\frac{3}{2}\frac{1}{2}$	3.431	2.3	2.3
$\frac{3}{2}\frac{3}{2}2$	3.582	7.7	7.6	$\frac{3}{2}\frac{3}{2}\frac{3}{2}$	3.512	10.5	10.9
$\frac{3}{2}\frac{3}{2}3$	3.774	<1	1.0	$\frac{3}{2}\frac{3}{2}\frac{5}{2}$	3.669	6.1	6.4
$R=2.8\%$				$R=2.9\%$			
$\mu_{\text{Cu}(2)}=0.47(1)\mu_B$				$\mu_{\text{Cu}(2)}=0.54(1)\mu_B$			
				$\mu_{\text{Cu}(1)}=0.007(10)\mu_B$			

<sup>a</sup>Al powder line.

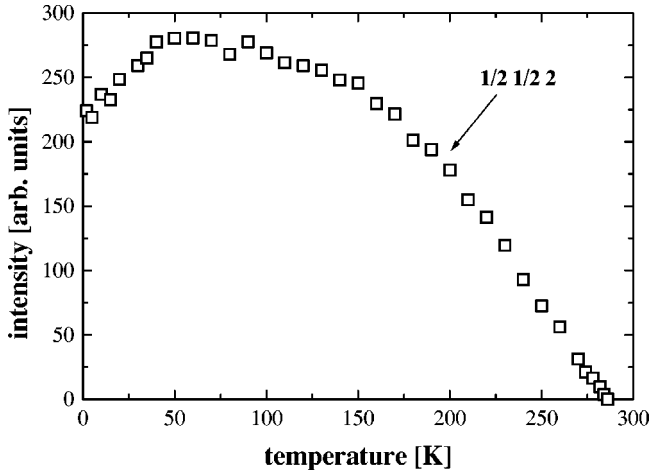


FIG. 2. Temperature dependence of the integrated intensity of the  $(\frac{1}{2}\frac{1}{2}2)$  Bragg peaks for  $\text{NdBa}_2\text{Cu}_3\text{O}_{6.23}$ . The transition from the paramagnetic phase to the AFI phase occurs at 289 K. Although the AFI order parameter decreases below 70 K with decreasing temperature, no  $(h + \frac{1}{2}, k + \frac{1}{2}, l + \frac{1}{2})$  peaks occur down to 2 K, excluding the presence of the AFII phase.

the two stoichiometric crystals. Between  $T_N = 385$  K and 95 K only magnetic peaks of the  $\mathbf{q} = (\frac{1}{2}\frac{1}{2}0)$  type are observed, indicating the presence of the AFI phase. Below  $T_2 = 95$  K magnetic superlattice peaks appear with  $\mathbf{q} = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$ . Between 95 K and 35 K both types of magnetic peaks coexist, while below 35 K only the  $\mathbf{q} = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$  type of ordering is present. The magnetic Bragg reflections in this low-temperature phase are also resolution limited, implying 3D long-range ordering. Table II reports the refinement results for the magnetic intensities of  $\text{Nd}_{1.08}\text{Ba}_{1.92}\text{Cu}_3\text{O}_{6.17}$  and Table III gives the magnetic moments in comparison to those of other  $\text{Nd}_{1+y}\text{Ba}_{2-y}\text{Cu}_3\text{O}_{6+x}$  crystals. In Fig. 3 the temperature dependence of the integrated intensity of the  $(\frac{1}{2}\frac{1}{2}2)$  and  $(\frac{1}{2}\frac{1}{2}\frac{3}{2})$  peaks is displayed. The AFI ordering component follows a power-law with a critical exponent  $\beta$  of 0.25(1), which is identical to that found for the stoichiometric  $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{6.09}$  crystal. In the temperature range between 95 K and 35 K, however, the intensity of the  $(\frac{1}{2}\frac{1}{2}2)$  peak decreases monotonically, while the  $(\frac{1}{2}\frac{1}{2}\frac{3}{2})$  peak increases monotonously.

TABLE III. Comparison between the magnetic transitions of the  $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$  single crystals with data from literature. Moudén *et al.* (Ref. 4) reported that their  $\text{NdBa}_2\text{Cu}_3\text{O}_{6.10}$  crystal orders directly from the paramagnetic state into the AFII phase. The averaged *ordered* moments on the Cu(1) and Cu(2) sites have been determined at different temperatures  $T_{meas}$ .

Sample	$T_N$ (K)	$T_2$ (K)	$\mu_{\text{Cu}(2)}$ ( $\mu_B$ )	$\mu_{\text{Cu}(1)}$ ( $\mu_B$ )	$T_{meas}$ (K)
$\text{NdBa}_2\text{Cu}_3\text{O}_{6.09}$ <sup>a</sup>	376		0.59(5)		4.2
$\text{NdBa}_2\text{Cu}_3\text{O}_{6.23}$ <sup>a</sup>	289		0.35(3)		70
$\text{Nd}_{1.08}\text{Ba}_{1.92}\text{Cu}_3\text{O}_{6.17}$ <sup>a</sup>	385	95	0.47(1)		100
$\text{Nd}_{1.08}\text{Ba}_{1.92}\text{Cu}_3\text{O}_{6.17}$ <sup>a</sup>	385	95	0.54(1)	0.007(10)	4.2
$\text{NdBa}_2\text{Cu}_3\text{O}_{6.10}$ <sup>b</sup>	385	385	0.40(2)	0.04(2)	80
$\text{NdBa}_2\text{Cu}_3\text{O}_{6.10}$ <sup>c</sup>	430	80	0.83	0.32	20
$\text{NdBa}_2\text{Cu}_3\text{O}_{6.35}$ <sup>c</sup>	230	10	0.27	0.23	5

<sup>a</sup>This work.

<sup>b</sup>Moudén *et al.* (Ref. 4).

<sup>c</sup>Li *et al.* (Ref. 5).

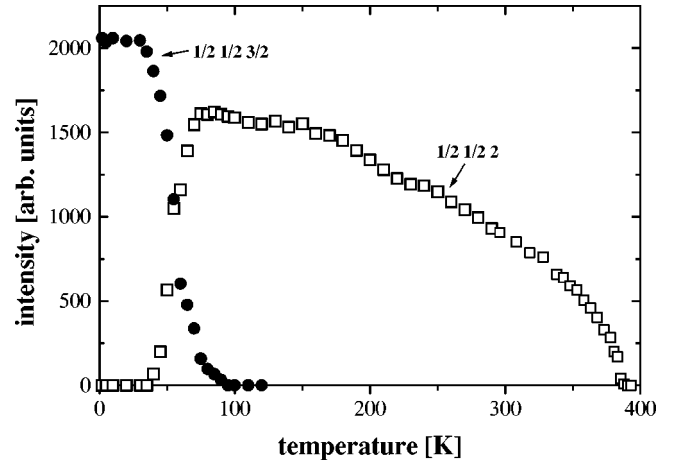


FIG. 3. Temperature dependence of the integrated intensity of the  $(\frac{1}{2}\frac{1}{2}2)$  and  $(\frac{1}{2}\frac{1}{2}\frac{3}{2})$  magnetic Bragg peaks for  $\text{Nd}_{1.08}\text{Ba}_{1.92}\text{Cu}_3\text{O}_{6.1}$ . The AFI ordering sets in at  $T_N = 385$  K. The order parameter follows a power law with a critical exponent  $\beta = 0.25(1)$ . The transition to the turn-angle phase  $\text{AFI} \oplus \text{AFII}$  occurs at  $T_2 = 95$  K. Reordering to the AFII phase is completed at 35 K.

This characteristic temperature dependence indicates the presence of the turn-angle phase  $\text{AFI} \oplus \text{AFII}$ ,<sup>11</sup> via which the reordering to the AFII phase takes place.<sup>32</sup> Figure 4 shows the NQR spectrum at 4.2 K in the frequency range between 24 MHz and 35 MHz for that crystal. The NQR line of the  $^{63}\text{Cu}$  isotope shows a Zeeman splitting which is typical for AFII ordering.<sup>11,20–22</sup> The hyperfine field at the Cu(1) site equals 0.2 T, which is very similar to those values found in  $\text{YBa}_2\text{Cu}_{3-z}\text{Fe}_z\text{O}_{6+x}$  ceramics<sup>21,22</sup> as well as in  $\text{YBa}_2\text{Cu}_{3-z}\text{Al}_z\text{O}_{6+x}$  single crystals in the AFII phase.<sup>11</sup>

#### IV. DISCUSSION

Our study on  $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$  has shown that substitution of  $\text{Nd}^{3+}$  on Ba sites in this material occurs only if the crystal growth takes place under oxidizing conditions<sup>30,31</sup> while the substitution is prevented if growth is performed under reducing atmosphere. Further, we showed that substitution of  $\text{Nd}^{3+}$  for  $\text{Ba}^{2+}$  is accompanied by the uptake of oxygen on the O(4) site in the Cu(1) layer to maintain charge balance in

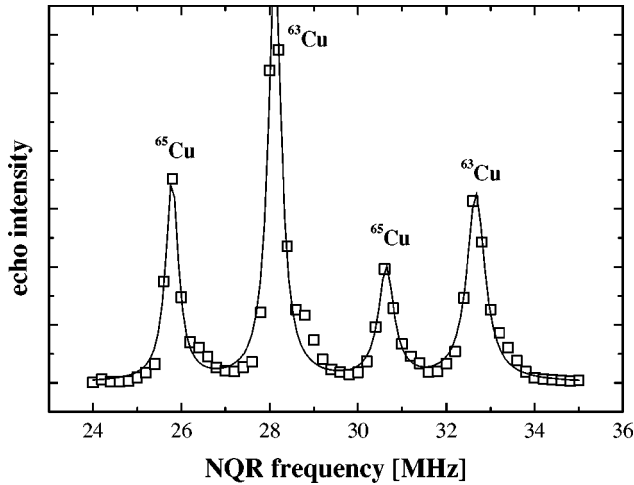


FIG. 4. Cu(1) NQR spectrum of  $\text{Nd}_{1.08}\text{Ba}_{1.92}\text{Cu}_3\text{O}_{6.17}$  at 4.2 K indicating Zeeman splitting of the NQR lines of the two isotopes. The Zeeman splitting reveals a hyperfine field at the Cu(1) site and thus indicates the presence of the AFII phase. For  $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{6.09}$  and  $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{6.23}$ , there is no Zeeman splitting, while the lines are equally sharp.

the structure. Consequently, the  $\text{Nd}^{3+}$  ions are able to enter the Ba sites only if the oxygen partial pressure is high enough during growth. Excess oxygen in the basal layer is also reflected by the observed orthorhombic-tetragonal phase transition with increasing amount of Nd on Ba sites.<sup>5,30</sup> The smaller ionic size of  $\text{Y}^{3+}$  (89.2 pm) (Ref. 48) compared to  $\text{Nd}^{3+}$  (99.5 pm) may explain, why the former does not substitute for  $\text{Ba}^{2+}$  (136 pm) in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ .

In both stoichiometric  $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$  crystals investigated here, the spin system orders from the paramagnetic state to the AFI or  $\mathbf{q} = (\frac{1}{2} \frac{1}{2} 0)$  structure, and the AFI arrangement is stable to lowest temperatures forming the magnetic ground state with respect to the Cu spin system, which is complemented by  $\mathbf{q} = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$  ordering of the  $\text{Nd}^{3+}$  moments.  $T_N$  is slightly depressed compared to the  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  compound: while we find  $T_N = 376$  K for  $x = 0.09$  and 289 K for  $x = 0.23$ , respectively, the expected  $T_N$  values are about 410 K and 380 K for  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  with the same values of  $x$ .<sup>46</sup> The smaller  $T_N$  may be due to the slightly larger cell of  $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$  compared to  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  at the same  $x$ , which reduces the coupling of the  $\text{Cu}^{2+}$  moments between the antiferromagnetic Cu(2) bilayers. Moreover, a lowering of  $T_N$  is expected because the tendency for the oxygen to order in chains and thereby to dope the Cu(2) layers with charge carriers is smaller in  $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$  than in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ .<sup>49,50</sup>

While the AFI ground-state ordering of the  $\text{Cu}^{2+}$  moments in stoichiometric  $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$  is similar to that of pure  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  crystals, the slight Nd/Ba substitution in our  $\text{Nd}(\text{Ba}_{1.92}\text{Nd}_{0.08})\text{Cu}_3\text{O}_{6.17}$  crystal induces reordering to the AFII phase via the turn-angle phase, setting in at  $T_2 = 95$  K. This magnetic reordering, in turn, is similar to that occurring in  $\text{M}^{3+}$  ( $=\text{Co}^{3+}, \text{Fe}^{3+}, \text{Al}^{3+}, \dots$ )-doped  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ .<sup>9-11,14-22</sup>

AFII ordering has been reported in nominally stoichiometric  $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$ ,<sup>3-5</sup> and it has been suggested that AFII ordering is an intrinsic property of the  $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$

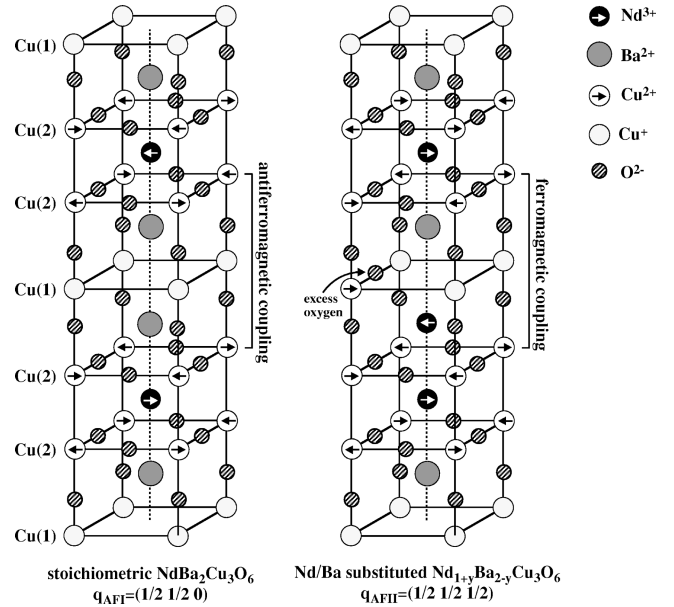


FIG. 5. Crystallographic and magnetic structure of  $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$  and  $\text{Nd}_{1+y}\text{Ba}_{2-y}\text{Cu}_3\text{O}_{6+x}$ . In the stoichiometric compound the AFI phase exists. In the Nd/Ba-substituted compound, from charge balance considerations substitution of  $\text{Ba}^{2+}$  by  $\text{Nd}^{3+}$  results in one  $\text{O}^{2-}$  ion built in at the O(4) site, which oxidizes one of its Cu(1) neighbors to  $\text{Cu}^{2+}$ . The associated free spin within the Cu(1) layer establishes an effective ferromagnetic coupling that frustrates the arrangement of spins on Cu(2) sites in the AFI phase and thus induces the reordering to the AFII phase.

compound. Li *et al.*<sup>5</sup> explained the  $\text{AFI} \leftrightarrow \text{AFII}$  reordering in their  $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$  single crystals with an ordering of moments within the Cu(1) layer, which in their opinion are created by substitution on either the Cu(1) sites or the Ba sites. However, in our refinement of the AFII structure we did not observe any *ordered* magnetic moment on Cu(1) sites within experimental error. Furthermore, our NQR measurements also exclude an *ordered* magnetic moment on Cu(1) sites.

On the other hand we have strong indications that the  $\text{AFI} \leftrightarrow \text{AFII}$  reordering is related to the  $\text{Nd}^{3+}$  ions substituted on  $\text{Ba}^{2+}$  sites. Since the reordering temperature  $T_2$  for  $\text{Nd}_{1.08}\text{Ba}_{1.92}\text{Cu}_3\text{O}_{6.17}$  is relatively high, the magnetic effect of  $\text{Nd}^{3+}$  on the Ba site is very large. There are two possibilities to explain how the  $\text{Nd}^{3+}$  ions on Ba sites may induce the AFII ordering. The first possibility is the magnetic moment of the  $\text{Nd}^{3+}$  ions themselves. It is quite conceivable that the  $\text{Nd}^{3+}$  ions on the Ba sites may couple magnetically to the moments on Cu(2) sites, resulting in an effective ferromagnetic coupling of the adjacent Cu(2) layers, and thus precipitating AFII ordering. However, the coupling mechanism itself not is at all obvious.

The other possible mechanism is related to the creation of free spins within the Cu(1) layer by the excess oxygen, which is introduced at the O(4) site to charge balance the  $\text{Nd}^{3+}$  substituted for  $\text{Ba}^{2+}$  (cf. Fig. 5). This balance requires one negative elementary charge. The second elementary charge on the  $\text{O}^{2-}$  is balanced by the oxidation of one neighboring  $\text{Cu}^+$  on a Cu(1) site, creating a  $\text{Cu}^{2+}$  with a free spin. If these local moments couple magnetically to the moments on neighboring Cu(2) sites, there will be an effective ferromagnetic coupling between the adjacent antiferromagnetic

Cu(2) layers, which triggers the reordering to the AFII phase. This postulated mechanism for the Nd compound is very similar to that postulated for the Al-doped system,<sup>10,11</sup> and has also been treated in the theoretical work by Andersen and Uimin.<sup>32</sup> Note that in pure, stoichiometric  $\text{Nd}_1\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$  or  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  the excess oxygen on the O(4) site oxidizes two neighboring  $\text{Cu}^+$  to  $\text{Cu}^{2+}$  that are spin-paired by superexchange, and thus no free spins are created.

Although we are suggesting a similar mechanism for the reordering, it must be borne in mind that the  $T_2$  values observed in the  $\text{Nd}_{1+y}\text{Ba}_{2-y}\text{Cu}_3\text{O}_{6+x}$  system are much higher than those of the Al-doped  $\text{YBa}_2\text{Cu}_{3-z}\text{Al}_z\text{O}_{6+x}$  system.

While the onset of AFII order induced by  $\text{Al}^{3+}$ -doping ever exceeds 25 K,<sup>10,11</sup>  $T_2$  values reported for nominally stoichiometric  $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$  scatter between 0 and 80 K (Table III) and Moudén *et al.*<sup>4</sup> even found a transition from the paramagnetic phase directly into the AFII phase at 385 K for their nominal  $\text{NdBa}_2\text{Cu}_3\text{O}_{6.10}$ . While the large values and also the large scatter in  $T_2$  are quite unlikely due to  $\text{M}^{3+}$  contamination, we believe that the methods employed by these authors to determine the elemental composition of their crystals are not sensitive enough to detect a small Nd/Ba nonstoichiometry,<sup>51</sup> to which we attribute the AFII ordering. Further, we believe that the distribution of the free spins on  $\text{Cu}^{2+}$  ions within the Cu(1) layer has a significant influence on  $T_2$ .<sup>10,28</sup> For  $\text{Nd}_{1+y}\text{Ba}_{2-y}\text{Cu}_3\text{O}_{6+x}$  variations in the growth procedure are likely to produce differences in the distribution of  $\text{Nd}^{3+}$  ions on  $\text{Ba}^{2+}$  sites, which in turn may have a strong influence on the stabilization of the AFII phase. If two neighboring Ba sites within the (001) plane are substituted by  $\text{Nd}^{3+}$ , the amount of free spins in the Cu(1) layer and thus  $T_2$  is expected to be lower than in the case of randomly distributed, isolated  $\text{Nd}^{3+}$  ions. Indeed, Kramer *et al.*<sup>31</sup> recently reported that also the superconducting transition temperature  $T_c$  strongly depends on the degree of  $\text{Nd}^{3+}$  pairing and that the width of the transition reflects the uniformity of the distribution.

Lütgemeier<sup>21</sup> found in his studies on  $\text{YBa}_2\text{Cu}_{3-z}\text{Fe}_z\text{O}_{6+x}$  ceramics, that the AFII ordering is suppressed by an excess of oxygen in the Cu(1) layer. As such a mechanism could also have suppressed AFII order in the undoped, stoichiometric crystals with  $x=0.09$  and  $x=0.23$  studied here, we reduced another crystal of the same batch under conditions to get the oxygen content as low as possible. The reduction was performed at 800 °C at an oxygen pressure of  $2.8 \times 10^{-4}$  bars, for which, according to the oxygen isotherms published by Lee *et al.*,<sup>52</sup> the oxygen content should be approximately  $x=0.04$ . From the intensity of the 24 MHz NQR line, which is directly related to threefold coordinated Cu(1) ions,<sup>50</sup> i.e., to Cu ions with one neighboring  $\text{O}^{2-}$  ion within the Cu(1) layer, we estimated the oxygen content  $x$  within the Cu(1) layer for that crystal as less than 0.02. Furthermore, at 1.2 K the Cu-NQR spectrum between 27 MHz and 31 MHz gave extremely sharp lines for both isotopes without any sign of Zeeman splitting, implying that the AFI phase is present. Therefore, we conclude that in the pure, stoichiometric Nd compound, the AFI ordering scheme of the Cu

moments is stable down to lowest temperature and, supplemented by ordering of the  $\text{Nd}^{3+}$  spins, forms the ground-state phase. This means that the magnetic ordering of the Cu moments in the stoichiometric Nd system is very similar to that of pure, oxygen-deficient  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ .

## V. CONCLUDING SUMMARY

We have demonstrated that Nd/Ba-substituted  $\text{Nd}_{1+y}\text{Ba}_{2-y}\text{Cu}_3\text{O}_{6+x}$  crystals are obtained when growth takes place under oxidizing conditions, while a reduced oxygen fugacity leads to stoichiometric  $\text{NdBa}_2\text{Cu}_3\text{O}_{6+x}$ . Magnetic ordering in the reduced pure stoichiometric  $\text{Nd}_{1+y}\text{Ba}_{2-y}\text{Cu}_3\text{O}_{6+x}$  system occurs from the paramagnetic state to the antiferromagnetic AFI structure of the  $\text{Cu}^{2+}$  moments, which remains the stable configuration down to lowest temperatures, where it is supplemented by  $\mathbf{q}_{\text{Nd}} = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$  ordering of the  $\text{Nd}^{3+}$  moments below 1.7 K. The nonstoichiometric  $\text{Nd}_{1+y}\text{Ba}_{2-y}\text{Cu}_3\text{O}_{6+x}$  system, however, shows a reordering from the AFI to the antiferromagnetic AFII phase via the intermediate turn-angle phase  $\text{AFI} \oplus \text{AFII}$  below  $T_2 = 95$  K. We attribute the  $\text{AFI} \leftrightarrow \text{AFII}$  reordering in  $\text{Nd}_{1+y}\text{Ba}_{2-y}\text{Cu}_3\text{O}_{6+x}$  to the creation of *isolated* magnetic  $\text{Cu}^{2+}$  ions within the Cu(1) layer, which are formed by the one excess  $\text{O}^{2-}$  ion for each  $\text{Nd}^{3+}$  ion substituted for  $\text{Ba}^{2+}$ . Coupling of these free  $\text{Cu}^{2+}$  spins to the moments on the neighboring Cu(2) layers results in an effective ferromagnetic coupling between the adjacent antiferromagnetic Cu(2)O<sub>2</sub> layers, which forces the AFII reordering via an intermediate turn-angle phase upon decreasing temperature. The suggested mechanism is similar to that proposed for the Al-doped  $\text{YBa}_2\text{Cu}_{3-z}\text{Al}_z\text{O}_{6+x}$  system.<sup>10,11,32</sup> The higher reordering temperature  $T_2$  and thus the larger coupling strength in the  $\text{Nd}_{1+y}\text{Ba}_{2-y}\text{Cu}_3\text{O}_{6+x}$  system compared to  $\text{YBa}_2\text{Cu}_{3-z}\text{Al}_z\text{O}_{6+x}$  may indicate a more random distribution of  $\text{Cu}^{2+}$  ions within the Cu(1) layer. An alternative or additional ferromagnetic coupling via the  $\text{Nd}^{3+}$  moments on Ba sites also cannot be ruled out. Since the  $\text{AFI} \leftrightarrow \text{AFII}$  reordering is induced already by a small amount of  $\text{Nd}^{3+}$  on Ba sites, we suggest that the observation of the magnetic reordering can be used as a sensitive probe to detect  $\text{Nd}^{3+}$  on Ba sites. Apart from the  $\text{Nd}^{3+}$  magnetic ordering, however, the pure, stoichiometric Nd compound shows very similar magnetic AFI ordering as the pure Y compound.

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- <sup>51</sup>Due to the well-known influence of magnetic  $M^{3+}$  dopants in the  $YBa_2Cu_3O_{6+x}$  system, the possibility of contamination by impure chemicals or by crucible corrosion may be considered as

the origin of the  $T_2$  differences of nominally  $NdBa_2Cu_3O_{6+x}$  crystals (Table III). However, to explain the high- $T_2$  values of the  $NdBa_2Cu_3O_{6+x}$  in Refs. 4 and 5, a Fe contamination of  $y_{>0.06}$  would be necessary according to the  $z$ - $T_2$  phase diagrams of Mirebeau *et al.* (Ref. 17) and Lyubutin *et al.* (Ref. 19). Such a degree of contamination with  $Fe^{3+}$  or  $Co^{3+}$  would have been easily detected by the electron-probe microanalysis and Rutherford backscattering employed by these authors. However, the precision in determining the Nd/Ba ratio by microprobe techniques requires excellent standards and is hampered by an overlap of the  $K$  lines of Nd and Ba, so that the weaker  $L$  lines have to be taken. The Rutherford backscattering edges of Nd and Ba can be separated only with difficulties, as the difference in atomic mass is only about 5%. Thus we can show that these methods are hardly sensitive enough to determine Nd doping on Ba sites unless very special measures are taken.

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