First Observation of Superstructure Reflections by Neutron Diffraction Due to Oxygen Ordering in $YBa_2Cu_3O_{6.35}$

R. Sonntag and D. Hohlwein
Institut für Kristallographie der Universität, 7400 Tübingen, Federal Republic of Germany and Hahn-Meitner-Institut Berlin, Berlin, Federal Republic of Germany

T. Brückel
Institut Laue-Langevin, Grenoble, France

G. Collin
Laboratoire de Physique des Solides, Universite Paris-Sud, Orsay, France
(Received 5 October 1990)

We present results of a structural investigation of oxygen ordering in a 0.1-cm^3 $YBa_2Cu_3O_{6.35}$ single crystal. For the first time nonmagnetic superstructure reflections have been observed by neutron diffraction. From the intensities a $2\sqrt{2}a\times 2\sqrt{2}a\times c$ oxygen ordering model is derived. In this structure "half-filled" CuO chains alternate with "quarter-filled" chains. Only 15% of the basal-plane oxygen atoms contribute to the superstructure.

PACS numbers: 61.12.Ex, 74.70.Vy

The new oxide superconductors can be derived from well-ordered insulating compounds. Superconductivity results then from doping with defects. In $YBa_2Cu_3O_{6+x}$ the defects are characterized by the concentration x and the ordering of oxygen atoms, which depend strongly on the preparation condition. Both concentration and ordering are very important parameters for the structure, conductivity, and superconducting transition temperature T_c.[1,2]

The exact oxygen ordering in $YBa_2Cu_3O_{6+x}$ in the range of $0<x<1$ is still unknown. It is only for the two end members that the ordering and structure was clarified by neutron and x-ray diffraction (see, e.g., Refs. 3 and 4): The insulating $YBa_2Cu_3O_6$ has no oxygen atoms in the basal Cu planes, whereas in the 90-K superconductor $YBa_2Cu_3O_7$ ordered CuO chains exist along the b direction.

Many electron-diffraction studies have been published showing different kinds of superstructure reflections depending on oxygen concentration. Several oxygen ordering models have been proposed; see, e.g., Refs. 5–10. For the 60-K superconductor $YBa_2Cu_3O_{6.5}$, the so-called "ortho(II)" phase giving the second superconducting plateau,[11] a doubling of the a axis with every second CuO chain occupied along the b direction is postulated by electron microscopy.[10] In fact, with neutron-diffraction experiments these superlattice reflections have not been detected,[12–14] even though the electron-microscopy results indicate a well-ordered superstructure in three dimensions. This was explained by the presence of only a small fraction of ordered domains in the sample.[14]

To get a quantitative description of the oxygen structure and its degree of order we performed neutron-diffraction measurements on a large $YBa_2Cu_3O_{6.35}$ single crystal. For the first time we could clearly observe superstructure reflections and determine their intensities. An oxygen ordering model giving good agreement between calculated and observed intensities could be derived.

The investigated $YBa_2Cu_3O_z$ single crystal has dimensions of $5\times5\times4$ mm^3, an oxygen content of $z=6.35(0.05)$, and lattice constants $a=b=3.84$ Å and $c=11.75$ Å. The single crystal was prepared by the flux method using the eutectic composition 7BaO-18CuO with a ratio to $YBa_2Cu_3O_7$ flux of 0.25/0.75. The mixture was prereacted at 880 °C, melted at 990 °C, and then slowly cooled down to 900 °C in one week and finally to room temperature in two days.

Neutron-diffraction measurements were performed on the four-circle diffractometer D10 at the Institut Laue-Langevin (ILL) in Grenoble which is situated on a thermal neutron guide. Using a graphite (PG 002) monochromator the wavelength was $\lambda=2.359$ Å. The second-order contamination was reduced by a graphite filter and by using a PG 002 analyzer. Special care was taken to determine the remaining $\lambda/2$ and $\lambda/4$ contributions. Analyzer scans for these wavelengths and the comparison with the results obtained with a garnet test crystal yielded contaminations of 8×10^{-5} for $\lambda/2$ and 2×10^{-5} for $\lambda/4$. All observed superstructure and magnetic intensities have been corrected for these contributions.

Measurements were done at room temperature and up to 410 K (above the Néel temperature of 390 K). All reciprocal-lattice points with $h,k=n,n/2,n/3,n/4$ (n integer) and $l=0$–6 (integer) were measured in the range $0<h,k<1.75$ from $2\theta_{min}=15°$ to $2\theta_{max}=90°$ in scattering angle 2θ to detect superstructure reflections.

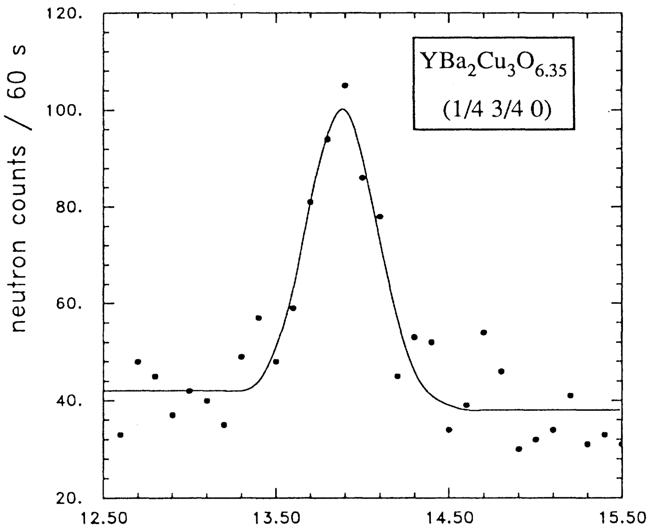

FIG. 1. Elastic neutron scattering (ω-$x\cdot 2\theta$ scan) of the $(\frac{1}{4}\,\frac{3}{4}\,0)$ superstructure reflection in $YBa_2Cu_3O_{6.35}$. The solid line presents a Gaussian curve fit with FWHM =0.47°.

In addition, magnetic reflections were measured to determine the magnetic structure, the magnetic moment of the Cu^{2+} ions, and the Néel temperature.

We have found five superstructure reflections in the ($hk0$) layer (see Table I), none for $l=1,2$, and five superstructure reflections about 10 times stronger in the third layer ($l=3$). Figures 1 and 2 show the observed $(\frac{1}{4}\,\frac{3}{4}\,0)$ and $(\frac{1}{2}\,\frac{1}{2}\,0)$ superstructure reflections. To check that the reflections are not of magnetic origin we

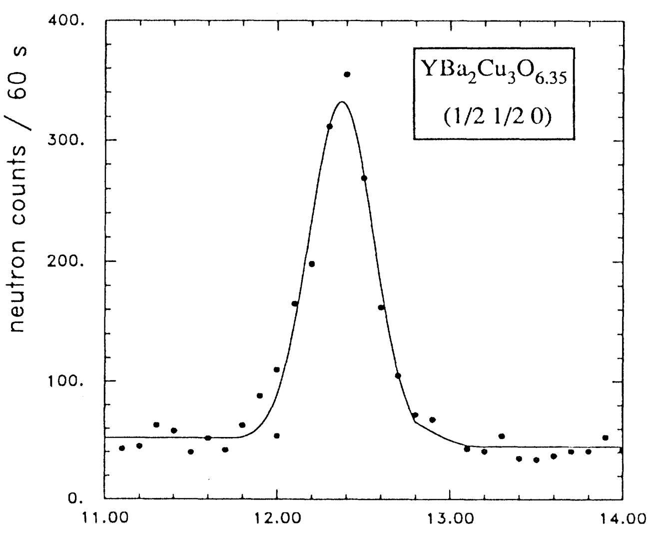

FIG. 2. Elastic neutron scattering (ω-$x\cdot 2\theta$ scan) of the $(\frac{1}{2}\,\frac{1}{2}\,0)$ superstructure reflection in $YBa_2Cu_3O_{6.35}$. The solid line presents a Gaussian curve fit with FWHM =0.46°.

TABLE I. Observed and calculated integrated intensities of oxygen superstructure reflections in $YBa_2Cu_3O_{6.35}$. An additional 27 reflections with $I_{obs} < \sigma$ with $\sigma = 10$ are omitted.

hlk	I_{obs}	I_{calc}
$\frac{1}{2}\,0\,0$	40	60
$\frac{1}{2}\,\frac{1}{2}\,0$	420	400
$\frac{1}{4}\,\frac{3}{4}\,0$	50	40
$\frac{1}{2}\,\frac{3}{2}\,0$	30	155
$\frac{3}{2}\,\frac{3}{2}\,0$	150	115

measured the temperature dependence of the intensities. The results give clear evidence for a nonmagnetic origin of the superstructure reflections as demonstrated in Fig. 3 together with the temperature behavior of some magnetic reflections. The crystal was of good quality with a mosaic spread of about 0.45° (FWHM). Scans around the superstructure reflections did not show any additional diffuse scattering or any broadening in the three directions of reciprocal space. The intensities are about 10^4–10^5 times smaller than the main Bragg reflections.

The intensities of the magnetic reflections at room temperature agree well with the known 3D antiferromagnetic structure of the Cu^{2+} ions in the CuO_2 layers with spin direction along (110).[15,16] From the temperature behavior of the magnetic reflections in Fig. 3 a Néel

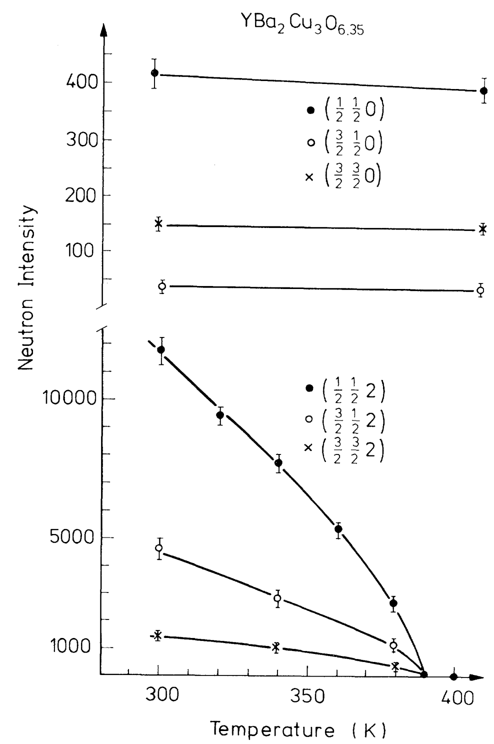

FIG. 3. Temperature behavior of integrated neutron intensities (15 min/reflection) of magnetic (lower) and oxygen superstructure (upper) reflections in $YBa_2Cu_3O_{6.35}$.

temperature of 390(5) K is obtained. We find a magnetic moment of $0.4(0.05)\mu_B$ per Cu^{2+} ion. These results are consistent with other work.[15,16]

The observed superstructure reflections in the $(hk0)$ layer can be indexed with a $2\sqrt{2}a \times 2\sqrt{2}a \times c$ (diagonal) superlattice cell which is 8 times larger than the original one. We used

$$I = |F_{hkl}|^2[1/\sin(2\theta)]\exp(-2w)$$

with an anisotropic temperature factor in the form

$$w = 2\pi^2(h^2a^{*2}U_{11}^2 + k^2b^{*2}U_{22}^2 + l^2c^{*2}U_{33}^2)$$

to calculate intensities for different oxygen ordering models on this superlattice. The best agreement with the observed intensities is reached with the oxygen ordering model given in Fig. 4. This model was also proposed on the basis of superstructure reflections observed by electron microscopy on a $YBa_2Cu_3O_{6.375}$ sample.[9] In comparison with the fully occupied CuO chains along the b direction in $YBa_2Cu_3O_7$, there are only "half-filled" CuO chains alternating with "quarter-filled' chains. Pure oxygen chains are formed in the 45° direction. In this structure each oxygen atom has oxygen vacancies as first and second neighbors. Theoretical calculations of the oxygen ordering phase diagram which have been done so far by Monte Carlo simulation[11,17] have to be extended to explain the observed superstructure.

Integrated intensities for the observed and calculated superstructure reflections are given in Table I. In the measured 2θ range there are 27 additional reflection positions where we could not find intensities larger than the statistical error $\sigma = 10$. These "unobserved intensities," which are not listed in Table I, are also consistent with the model. By comparison with the intensities of the main Bragg reflections, we found that only 15% of all oxygen atoms in the basal $CuO_{0.35}$ layers contribute to the superstructure reflections. These 15% of the oxygen atoms can be situated in fully (super)ordered regions of the crystal while other regions are completely disordered, or, more likely, there is one phase with a fractional long-range order or a long-range order parameter less than 1.

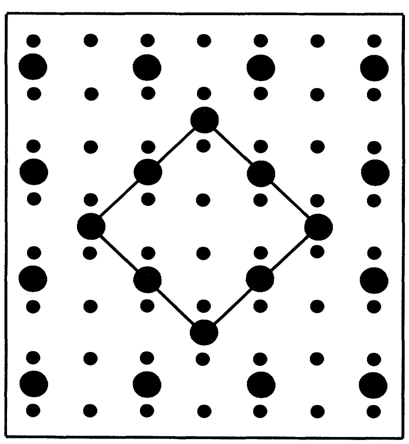

FIG. 4. Derived $2\sqrt{2}a \times 2\sqrt{2}a \times c$ oxygen superstructure in the basal plane of $YBa_2Cu_3O_{6.35}$ (small circles denote Cu, big circles denote O).

The absence of these superstructure reflections in higher layers can be explained by large anisotropic temperature factors of the ordered oxygen atoms in the c^* direction (large U_{33}^2) which then suppress diffraction intensities in higher layers. This is the case for $U_{33}^2 = 0.25$ Å^2. For the intensities in Table I, $U_{11}^2 = U_{22}^2 = 0.04$ Å^2 has been determined. Neutron powder diffraction on oxygen-deficient $YBa_2Cu_3O_{6+x}$ yielded similar large temperature factors for these oxygen atoms.[13,14]

As already mentioned, the superstructure reflections are about 10^4–10^5 times weaker in integrated intensities as compared to the main Bragg peaks. Therefore large single crystals and long measuring times are necessary and might be one reason for the former unsuccessful experiments.

Now we briefly discuss the additional reflections in the third layer. The observed integrated neutron intensities at $(\frac{1}{2}\,\frac{1}{2}\,3)$, $(\frac{3}{2}\,\frac{1}{2}\,3)$, $(\frac{1}{4}\,\frac{3}{4}\,3)$, $(\frac{5}{4}\,\frac{1}{4}\,3)$, and $(\frac{7}{4}\,\frac{3}{4}\,3)$ are about 10 times stronger than for the superstructure reflections in the zero layer. We believe that these superstructure reflections are not caused directly by the described oxygen ordering but by induced displacements of other atoms along c. In fact, the index $l = 3$ is evidence for a substructure which divides the original unit cell into three equidistant structural elements along the c axis. In $YBa_2Cu_3O_{6+x}$ there are three approximately equidistant CuO layers. The lattice constant c depends strongly on the oxygen concentration. By this the oxygen ordering in the basal plane will produce displacements along the c axis in the neighboring CuO layers. These displacements cannot be seen in the $(hk0)$ layer and are probably the reason for the observed superstructure reflections with $l = 3$. Up to now a quantitative model could not be found.

In conclusion, we first observed nonmagnetic superstructure reflections in a $YBa_2Cu_3O_{6+x}$ compound by neutron diffraction. A partial long-range oxygen ordering model could be derived showing that only an amount of about 15% of the oxygen atoms in the basal $CuO_{0.35}$ layers are contributing to these reflections. For the structure derived each oxygen atom has oxygen vacancies as first and second neighbors. The results are important for the determination of interaction energies between the oxygen atoms in the basal plane which are the charge reservoir for the superconducting carriers. Theoretical calculations of the oxygen ordering phase diagram have to be extended to explain the observed superstructure.

We thank Dr. N. Pyka, Kernforschungszentrum Karlsruhe, for selecting the crystal. This investigation has been supported financially by the Bundesministerium für Forschung und Technologie under Project No. 03-PR1TUE-6 and 13N 5482/0.

Note added.— After submission of this paper we noticed that Lin *et al.*[18] recently reported about an indication of oxygen order in $YBa_2Cu_3O_{6+x}$ with $x=0.5$ and 0.6 by neutron powder diffraction.

[1]R. J. Cava, B. Batlogg, K. M. Rabe, E. A. Rietman, P. K. Gallagher, and L. W. Rupp, Jr., Physica (Amsterdam) **156C**, 523 (1988).

[2]T. Wolf, W. Goldacker, B. Obst, G. Roth, and R. Flükiger, J. Cryst. Growth **96**, 1010 (1989).

[3]J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, and M. S. Kleefisch, Phys. Rev. B **36**, 3608 (1987).

[4]P. K. Gallagher, H. M. O'Bryan, S. A. Sunshine, and D. W. Murphy, Mater. Res. Bull. **22**, 995 (1987).

[5]M. A. Alario-Franco, C. Chaillout, J. J. Caponi, and J. Chenavas, Mater. Res. Bull. **22**, 1685 (1987).

[6]D. J. Werder, C. H. Chen, R. J. Cava, and B. Batlogg, Phys. Rev. B **37**, 2317 (1988).

[7]G. Van Tendeloo, H. W. Zandbergen, and S. Amelinckx, Solid State Commun. **63**, 389 (1987).

[8]J. L. Hodeau, P. Bordet, J. J. Capponi, C. Chaillout, and M. Marezio, Physica (Amsterdam) **153–155C**, 582 (1988).

[9]J. Reyes-Gasga, T. Krekels, G. Van Tendeloo, J. Van Landuyt, S. Amelinckx, W. H. M. Bruggink, and H. Verweij, Physica (Amsterdam) **159C**, 831 (1989).

[10]C. Chaillout, M. A. Alario-Franco, J. J. Capponi, J. Chevenas, P. Strobel, and M. Marezio, Solid State Commun. **65**, 283 (1988).

[11]D. de Fontaine, M. E. Mann, and G. Ceder, Phys. Rev. Lett. **63**, 1300 (1989).

[12]R. Sonntag, D. Hohlwein, K. Herz, W. Prandl, G. Eckold, and T. Wolf, J. Cryst. Growth **102**, 957 (1990).

[13]R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, W. F. Peck, Jr., and L. W. Rupp, Jr., Physica (Amsterdam) **165C**, 419 (1990).

[14]J. D. Jorgensen, B. W. Veal, A. P. Paulikas, L. J. Nowicki, G. W. Crabtree, H. Claus, and K. Kwok, Phys. Rev. B **41**, 1863 (1990).

[15]J. M. Tranquada, D. E. Cox, W. Kunnmann, H. Moudden, G. Shirane, M. Suenaga, P. Zolliker, D. Vaknin, S. K. Sinha, M. S. Alvarez, A. J. Jacobson, and D. C. Johnston, Phys. Rev. Lett. **60**, 156 (1988).

[16]D. Petitgrand and G. Collin, Physica (Amsterdam) **153–155C**, 192 (1988).

[17]D. de Fontaine, G. Ceder, and M. Asta, Nature (London) **343**, 544 (1990).

[18]Y. P. Lin, J. E. Greedan, A. H. O'Reilly, J. N. Reimers, and C. V. Stager, J. Solid State Chem. **84**, 226 (1990).