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DIFFRACTION STUDY OF SOME HIGH-T_c SUPERCONDUCTORS WITH THE TIME-OF-FLIGHT NEUTRON DIFFRACTOMETER DN-2

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The results of neutron diffraction experiments performed on high-T_c superconductors of the 1-2-3 type by using the time-of-flight diffractometer are discussed. The test experiment on $YBa_2Cu_3O_{7-\delta}$ after profile refinement of the data has given us a well-known structure. The final profile R-factor is 2.7%. Neutron diffraction on $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ single crystals has been measured with the aim to reveal possible long-period modulation of the atomic structure. The diffraction patterns from these crystals do not involve any additional peaks commensurate with the main structure. The incommensurate peaks are also absent, the lowest limit for the period of modulation is as high as 400 Å. The structure of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ has been determined at x=0,0.06 and 0.10. Some indications of occupying (2q) positions in the centre of octahedra with Fe atoms have been received. The (1a) positions on Cu-O chains contain both Fe-atoms and vacancies.

The investigation has been performed at the Laboratory of Neutron Physics, JINR.

Нейтронографические исследования некоторых высокотемпературных сверхпроводников на дифрактометре ДН-2

А.М.Балагуров и др.

Обсуждаются результаты структурных экспериментов с ВТСП типа 1-2-3, проведенных на нейтронном дифрактометре по времени пролета: тестовый эксперимент с $YBa_2Cu_3O_{7-\delta}$, поиск длиннопериодной модуляции структуры монокристаллов $YBa_2Cu_3O_7$ и $GdBa_2Cu_3O_7$ и эксперимент с $YBa_2(Cu_{1-x}Fe_x)O_{7-\delta}$. Обработка нейтронограмм, полученных на хорошо аттестованном порошке $YBa_2Cu_3O_{7-\delta}$, привела к значениям структурных пара-

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метров, совпадающим с известными из литературы. Величина R-фактора по профилю составила 2,7%. В монокристаллических образцах никаких признаков дополнительных пиков от периодов, соизмеримых с основной структурой, не обнаружено вплоть до $d \cong 40$Å. Признаки несоизмеримой синусоидальной модуляции структуры отсутствуют вплоть до $d \leq 400$ Å. Для соединения с медью, частично замещенной железом, получены указания на заполнение железом позиций (2q) в центре усеченных кислородных октаэдров и наличие как атомов железа, так и вакансий в позициях (1a) на цепочках Cu-O вдоль оси кристалла.

Работа выполнена в Лаборатории нейтронной физики ОИЯИ.

The crystal structure of the high-temperature superconductors is intensively analysed now in all neutron centres of the world. Therefore, it is inevitable and even desirable to repeat identical experiments in order to obtain reliable results. New unusual information may be received on the spectrometers having the unique parameters. One of such spectrometers is the neutron time-of-flight diffractometer DN-2 /1/ at the pulsed reactor IBR-2. It has been designed for long-period crystal structure investigations, so the diffraction pattern is measured in the range of long d-spacing which is hard-to-reach for conventional diffractometers. Another unique feature of DN-2 is extremely small exposition time needed for data collection, so it permits carring out the real time diffraction investigations of noncyclic transient phenomena /2/.

In the present work some results of the first diffraction experiments with high-T_c SC ceramics and single crystals on the DN-2 are given.

1. The Features of the Experimental Method and Data Processing

Time-of-flight neutron diffraction data on the diffractometer DN-2 are collected using the one-dimensional position detector lying in horizontal plane. In such a case two-dimensional spectra are measured with scanning of wavelength and scattering angle. An available wavelength range of 1.2-20Å being combined with a scattering angle variation of 10°-160° permits one to have the d-spacing range of 1.6-100 Å. At the same time, the resolution ($\Delta d/d$) of DN-2 is not very high and in the best case it makes up 1% at $2\theta \geq 140°$ and $d \geq 3$ Å. Such poor resolution as well as some features of wavelength distribution of an incident neutron beam are not suitable for the precise powder dif-

fraction study. But it does not preclude from a Rietveld profile analysis /3/ of HTS ceramics due to their relative large unit cell and high symmetry. Certainly, in our case the Rietveld method gives temperature factors of atoms much worse than at conventional diffractometers, as the range of small d-spacing is inaccessible. But at the same time, including in the fitting only the reflections with $d \geq 1.4$ Å makes it possible to have no effect of uncertainties in thermal factors on other structure parameters. We use the version of the Rietveld method described in Ref. /4/.

2. The Test Experiment on $YBa_2Cu_3O_{7-\delta}$

The well-known sample of high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ having $T_c = 91$K and $\Delta T = 3.7$K was chosen for the test experiment. Earlier the refinement of the sample structure was done in Ref./5/ with the mini-SFINKS diffractometer. The main purpose of our measurements was to check the sensitivity of structure parameters, determined in Ref. /5/, by the fit covering the range from 0.9 to 2.0 Å if the range is shifted to $1.4 \leq d \leq 3$ Å.

The sample was carefully ground powder of 5.5 g, placed into a cylinder of diameter 8 mm made from Ti-Zr alloy with $b_{coh} = 0$. In order to reveal possible parasitic phases the measurements at low scattering angles (30° and 60°) were performed. It was shown that up to $d \leq 16$ Å there were no additional diffraction peaks. For profile analysis the data were measured with maximum resolution at $2\theta = 150°$ for about 10 hours. Data handling was done over the range of $1.4 \leq d \leq 3$ Å, which included 44 diffraction maxima compatible with the symmetry of the lattice (see Fig. 1.).

The results obtained after refinement of occupancy factors and coordinates of Cu- and O-atoms are shown in Table 1. These results agree well with the data from Ref. /5/.

One can see that the results of independent neutron diffraction experiments given in Refs. /5/ and /6/ are practically the same for coordinates of atoms, but the thermal parameters differ by a factor of 2.5. In order to test the influence of this difference on our results the fitting has been done with the varied occupancy of 04 and z-coordinate of Cu2; the other parameters are taken from /5/ or /6/ and are fixed. It is shown in Table 2 that both n(04) and z(Cu2), R-factors and χ_n are practically constant for these two cases. Only the parameter A_{12} which corrects the form of the effective spectrum of neutrons ($f_{cor} = d^{A_{12}-1}$) has marked change.

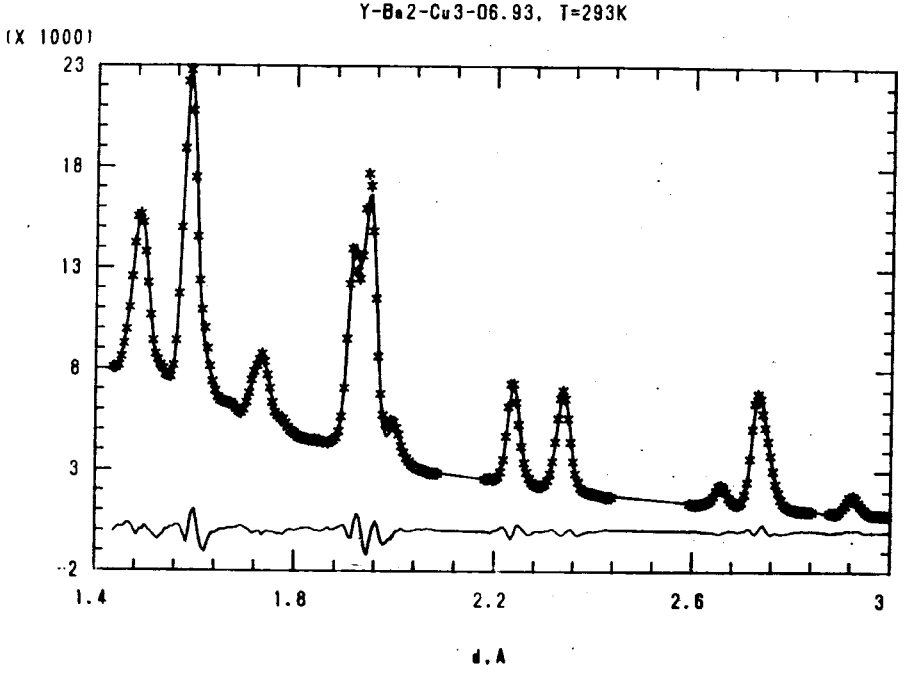


Fig. 1. The observed (stars) and calculated (solid line) neutron profile intensities for $YBa_2Cu_3O_{7-\delta}$ with the difference marked below. The total number of points are 245, R = 2.7%, the expected agreement index R_e = 1.8%.

Table 1

The results (agreement indexes, atom positions and occupancies) for an orthorhombic PmmmYBa$_2$Cu$_3$O$_{7-\delta}$. The thermal parameters and z-coordinate of Ba are taken from Ref./5/ and are fixed. R-factors in %, $\chi_n = (\chi^2/m)^{1/2}$, m is a degree of freedom.

R_p	R_b	R_w	χ_n	n(Cu1)	n(Cu2)	z(Cu2)
2.7	7.3	4.9	3.61	1.02(2)	2.02(2)	0.356(2)
	z(01)		z(02)	z(03)	n(04)	
	0.155(1)		0.372(3)	0.383(3)	0.97(3)	

In conclusion, the analysis of data from $YBa_2Cu_3O_{7-\delta}$ gives, firstly, an excellent fit between 1.4 and 3 Å and shows, secondly, that the results are week functions of the variation of thermal parameters. In some limits the change is completely compensated by a common corrective factor.

Table 2

The results of fitting for set parameters from Ref./5/ (1) and Ref. /6/ (2). Only z(Cu2) and n(04) were varied. The attempt to fit n(05) was also made (3).

	R_p	R_B	R_w	χ^2	z(Cu2)	n(04)	n(05)	A_{12}
(1)	2.7	7.4	4.9	3.61	0.3566(5)	0.974(30)	----	0.57(3)
(2)	2.7	7.4	4.9	3.59	0.3563(5)	0.967(30)	----	0.68(3)
(3)	2.7	7.4	4.8	3.58	0.3563(5)	0.925(40)	0.07(4)	0.58(3)

3. The Search for the Long-Period Modulations

We have measured neutron diffraction from $YBa_2Cu_3O_7$ and $GaBa_2Cu_3O_7$ single crystals to have evidence for possible long-period modulation of the atomic structure both commensurate and incommensurate with the main period. The single crystals were prepared by melting initial materials with Cu excess, and had superconducting properties (T_c = 70-75K). We did not separate the single crystals from a crucible and therefore, had the plates of good quality with the area of ~ 20 mm^2, large enough for the experiment. But on the other hand, the diffraction pattern could be measured near $\vec{c}^*$-direction only.

All reflections from a (001)-plane up to the twelfth order ones have been measured on both crystals at room and liquid nitrogen temperature (Figs. 2 and 3). The commensurate modulation of the structure must give additional maxima either between diffraction orders or at $d > d_{001}$. But no evidences of such peaks were found. On the other hand, the incommensurate modulation of the sinusoidal type must give satellites near main peaks. If the modulation vector has the $\vec{c}^*$-direction, then the gap between the satellite position d_s and the main peak position d_0 is $\Delta d = d_0^2/d_s$. The rough minimum estimations of d_s may be obtained for the (001) reflex. The width of this reflex makes one possible to see some additional peaks if $\Delta d \geq 0.3$ Å. From this it follows that if an incommensurate modulation exists, its period will be more than 400 Å.

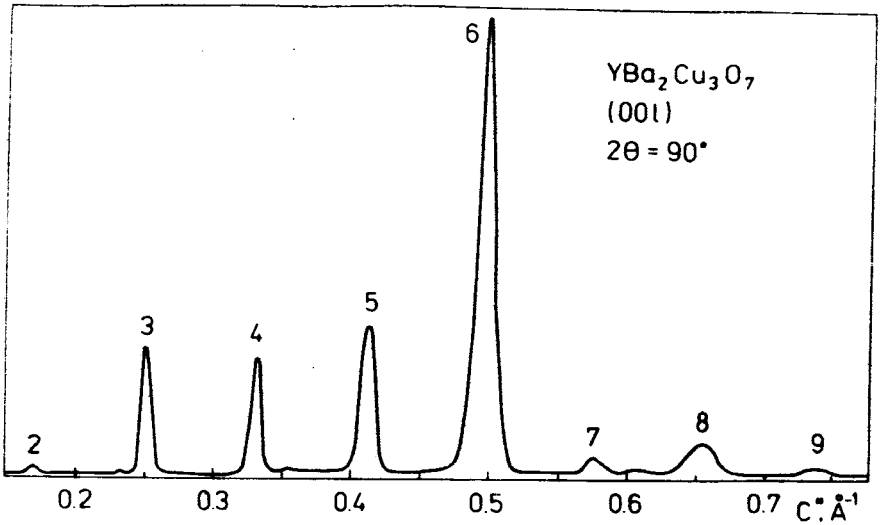


Fig. 2. The orders of the reflection from (001) plane of the $YBa_2Cu_3O_7$ single crystal.

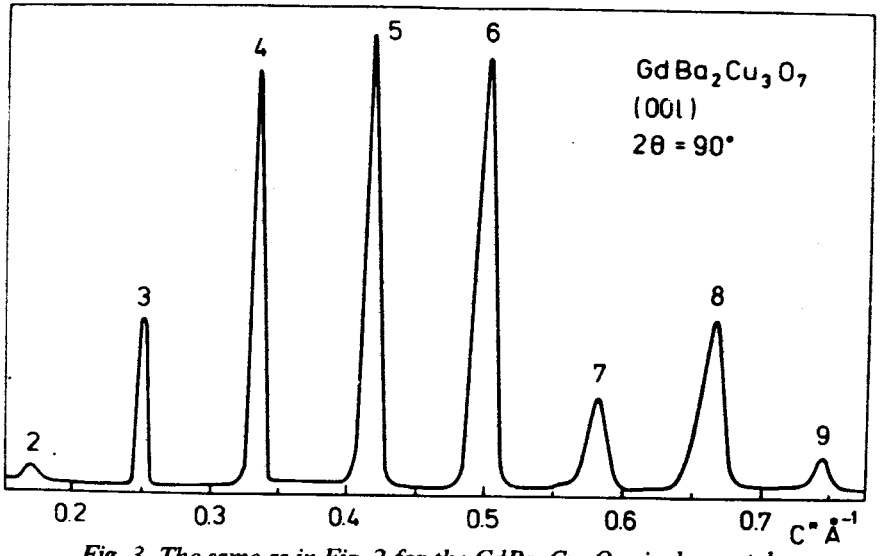


Fig. 3. The same as in Fig. 2 for the $GdBa_2Cu_3O_7$ single crystal.

4. On the Substitution of Copper for Iron

The problem of substitution of copper in 1-2-3 ceramics for a neighbouring elements of the 4th period from iron to gallium and silver is discussed in many papers /7 – 12/. There is detailed information on the modification of T_c, symmetry and lattice parameters in

$YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ depending on x [8,10,11]. But at the same time, there is no reliable data on the possibility of the favourable substitution of one of the nonequivalent structure position (1a) and (2q) of copper for iron.

Our experiments were performed on three samples of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ with x = 0.0, 0.06 and 0.10, which were prepared with standard ceramics technique at the Institut of Physics, Warsaw. Diffraction patterns were measured at $2\theta = 154°$ for about 2-4 hours. The initial values of parameters for profile analysis were taken from Ref./8/. The typical parts of diffraction pattern, where one can see the transition from orthorombic symmetry for x = 0 to a tetragonal one for x = 0.06 and x = 0.10, are shown in Fig. 4. The results of data analysis (R-factors and the values of varied parameters) are given in Table 3. For the sample without iron the two versions are given. They are different by the thermal parameter values, but one can see that the occupancies stay in both cases invariable. For the x = 0.06 sample the two versions of data processing are given too: for $a \neq b$ and a = b cases. In the second case there is the insignificant increasing of R-factors; the structure parameters have not changed.

Table 3

The results for $YBa_2(Cu_{1-x}Fe_x)_3O_7$ with x = 0.0, 0.6 and 0.10. The sets (1) and (2) for 0% Fe are differentiated by thermal factors: (1) — from Ref. /5/, (2) — from Ref./13/.

	0% Fe		6% Fe		10% Fe
	1	2	$a \neq b$	a = b	a = b
R_p	6.0	5.8	5.7	5.9	6.9
R_w	8.0	7.8	7.5	7.8	9.5
χ^2_n	1.94	1.88	1.47	1.53	2.58
a, Å	3.816	3.817	3.861	3.862	3.864
b, Å	3.881	3.882	3.874	3.862	3.864
c, Å	11.663	11.665	11.641	11.631	11.618
n_e (1a)	1.02(1)	1.00(1)	0.92(2)	0.91(2)	0.96(2)
n_e (2q)	1.97(2)	1.98(2)	2.05(2)	2.06(2)	2.06(2)
z_{Cu} (2q)	0.360(1)	0.359(1)	0.363(2)	0.362(2)	0.362(2)
n(O4)	0.92(2)	0.89(2)	0.97(2)	0.98(2)	1.00(2)

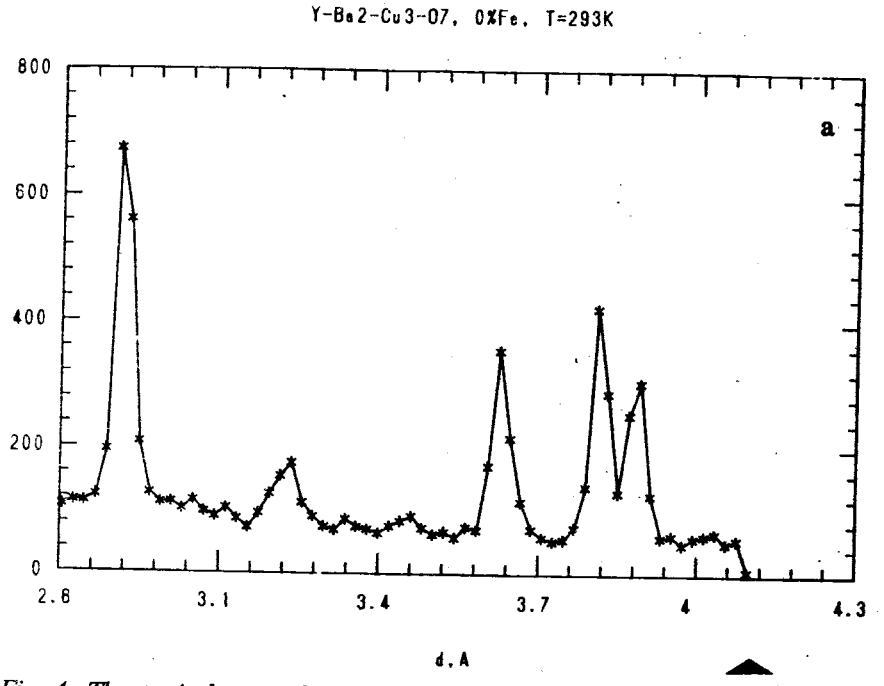
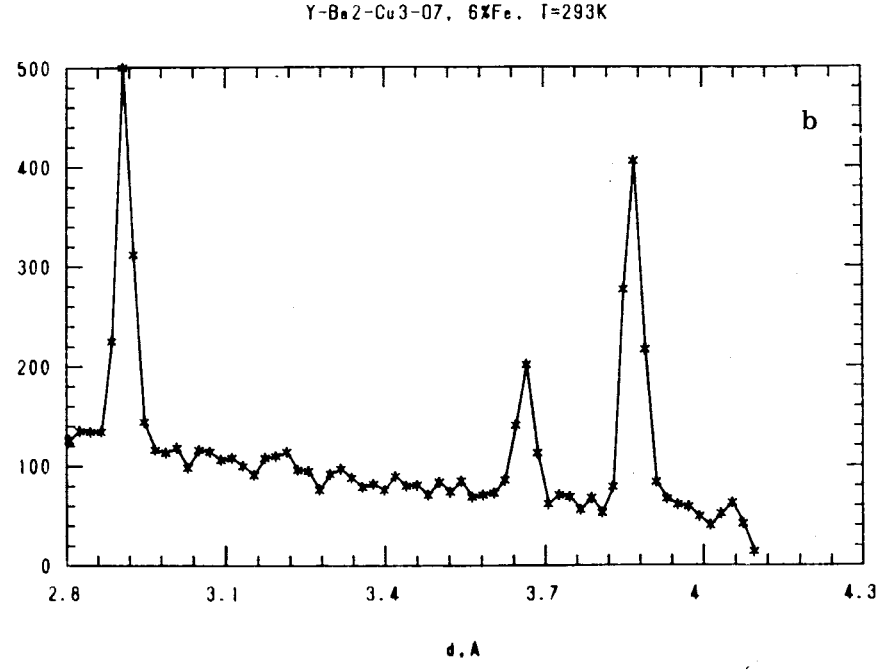


Fig. 4. The typical part of diffraction pattern for the Fe contained samples: a – 0%, b – 6%, c – 10%.

It should be noted that tetragonalization occurres with an increase of Fe content and is accompanied by a decrease of the value $g = c/3 - (a+b)/2$, where a, b and c are the lattice parameters. It is known that in the case of the falling of 04 occupancy from 1 to 0 in pure $YBa_2Cu_3O_7$ the lattice becomes also tetragonal, but the g-value increases.

Given in Table 3 occupancies of copper are normalized on the coherent scattering amplitude $b_{Cu} = 0.772 \cdot 10^{-12}$cm. For $x = 0$ they are in good agreement with multiplicity of positions (1a) and (2q), where the atoms Cu1 and Cu2 are situated. To determine the concentration of impurity in these positions, one must know the probabilities of the substitution. Initially assuming equiprobable substitution of Cu for Fe both in (1a) and (2q) and having in mind that $b_{Fe} = 0.954 \cdot 10^{-12}$cm, one can have for $x = 0.10$ $n(1a) = 1.024$ and $n(2q) = 2.047$. The experimental value n_e (1a) is essentially less than 1.024, while n_e (2q) is equal to 2.047 in the limit of errors. This fact allows one to assume that the (2q)-position is filled in by Fe-atoms in the right concentration, while in the (1a)-position there are some number of vacancies. One can calculate the occupancies of (1a) and (2q) positions for Cu, Fe and vacancies (see Table 4) taking into account the possibi-


Y-Ba2-Cu3-O7, 6%Fe, T=293K
500
400
300
200
100
0
b
2.8
3.1
3.4
3.7
4
4.3
d, A

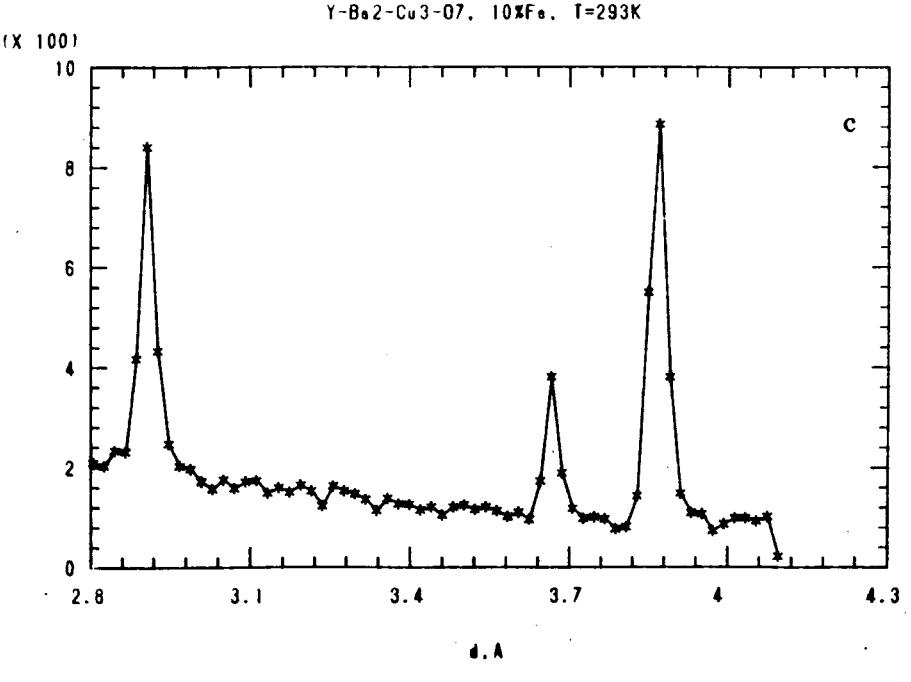

Y-Ba2-Cu3-O7, 10%Fe, T=293K
(X 100)
10
8
6
4
2
0
c
2.8
3.1
3.4
3.7
4
4.3
d, A

Table 4

The occupancies of (1a) and (2q) sites by Cu and Fe atoms and vacancies. The calculation was made assuming that $n_{Cu} = k(1 - x)$, $n_{Fe} = kx$.

	(1a)		(2q)	
x	0.06	0.10	0.06	0.10
n_e	0.92	0.96	2.05	2.06
k	0.91	0.94	2.02	2.01
n_{Cu}	0.85	0.85	1.90	1.81
n_{Fe}	0.05	0.09	0.12	0.20
n_{vac}	0.10	0.06	-0.02	-0.01

lity of vacancies and assuming that Cu and Fe are present in the samples in right concentration, i.e. $n_{Cu} \sim (1 - x)$ and $n_{Fe} \sim x$. It is obvious, that Table 4 is correct only for a (2q) position due to $n_{vac} = 0$. For the (1a) position the experimental value n_e can be explained by various ways: one can decrease n_{Fe}, simultaneously increasing n_{Cu} and n_{vac}. In this sense, the values of n_{Fe}(1a) given in Table 4 are the upper limit. It should be noted that n_{Fe} both for (1a) and (2q) positions are practically equal to the iron concentration in initial composition. The visible decrease of Cu1 is still obscure though there is information of such kind in other papers. For example, in the $YBa_2Cu_3O_{6.6}$ single-crystal structure analysis by X-Ray /13/ it was reported that n_{Cu}=(1a) = = 0.862.

5. Conclusions

The results of the present paper confirm the good possibilities of structure investigations of high-T_c superconductors with the TOF-diffractometer DN-2. The Rietveld method gives reliable information about the positional parameters and occupancies of atoms. The oxygen content is determined with the accuracy of (0.02-0.03) atom per unit cell. Including in the fitting of data the diffraction peaks with d-spacing greater than 1.4 Å makes the correlations between thermal and occupancy parameters not so important.

A likely explanation of our measurements on $YBa_2(Cu_{1-x}Fe_x)_3O_7$ can be done if one concludes that Fe impurities are present in both Cu1 and Cu2 site in accordance with 1/3 and 2/3 probabilities. Simul-

taneously the vacancies (6-10%) are present in Cu1 site. The search for long-period modulations of single crystal structures of $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ has not given any evidences of additional diffraction peaks. We have found that the lowest limit of possible incommensurate modulation is as high as 400 Å.

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