

СООБЩЕНИЯ  
ОБЪЕДИНЕННОГО  
ИНСТИТУТА  
ЯДЕРНЫХ  
ИССЛЕДОВАНИЙ  
ДУБНА

E14-94-415

A.M.Balagurov, P.Fischer<sup>1</sup>, T.Yu.Kaganovich<sup>2</sup>, E.Kaldis<sup>3</sup>,  
J.Karpinski<sup>3</sup>, V.G.Simkin, V.A.Trounov<sup>2</sup>

PRECISION FOURIER NEUTRON DIFFRACTION  
STUDY OF THE HIGH-TEMPERATURE  
SUPERCONDUCTOR  $Y(^{44}\text{Ca})\text{Ba}_2\text{Cu}_4\text{O}_8$

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<sup>1</sup>Laboratory for Neutron Scattering, ETH PSI Villigen, Switzerland

<sup>2</sup>St. Petersburg Institute of Nuclear Physics, Gatchina, Russia

<sup>3</sup>Laboratory for Solid State Physics, ETH Zurich, Switzerland

Балагуров А. М. и др.  
 Прецизионное нейтронографическое исследование структуры  
 высокотемпературного сверхпроводника  $Y(^{44}\text{Ca})\text{Ba}_2\text{Cu}_4\text{O}_8$

Высокотемпературный сверхпроводник  $Y\text{Ba}_2\text{Cu}_4\text{O}_8$  с частичным замещением Y на Ca исследован на нейтронном фурье-дифрактометре высокого разрешения на реакторе ИБР-2 в широком диапазоне температур. Для увеличения нейтронного контраста для замещения использовался изотоп  $^{44}\text{Ca}$ . Структурный анализ проводился по спектрам, измеренным при 135, 165 и 293 К, температурная зависимость параметров решетки определялась по точкам, измеренным в диапазоне от 8 до 288 К. Подтверждено наличие структурной аномалии в области температур около 150 К. Она проявляется в резком изменении коэффициента расширения вдоль оси  $b$ , в нерегулярности поведения коэффициента орторомбичности и в заметном изменении некоторых длин связей. Наиболее заметно сокращение расстояния между атомом меди  $\text{Cu}_2$  и мостиковым кислородом O1, а также изменение расстояния между цепочками атомов кислорода в слое  $\text{CuO}_2$ .

Работа выполнена в Лаборатории нейтронной физики им. И. М. Франка ОИЯИ.

Сообщение Объединенного института ядерных исследований. Дубна, 1994

Balagurov A.M. et al.  
 Precision Fourier Neutron Diffraction Study  
 of the High-Temperature Superconductor  $Y(^{44}\text{Ca})\text{Ba}_2\text{Cu}_4\text{O}_8$

E14-94-415

The high-temperature superconductor,  $Y\text{Ba}_2\text{Cu}_4\text{O}_8$ , with partial substitution of Ca for Y was investigated with a high-resolution Fourier neutron diffractometer over a wide temperature range. The  $^{44}\text{Ca}$  isotope was used to increase neutron contrast. Structural analysis was performed for the spectra measured at 135, 165, and 293 K; the temperature dependence of the lattice parameters was determined from the points measured within the range of 8 to 288 K. The presence of a structural anomaly in the proximity of 150 K was confirmed. It manifests itself by a sharp change in the expansion coefficient along the  $b$  axis, irregular behaviour of the orthorhombicity coefficient, and a noticeable change in bond length. The most distinct change is a contraction of the distance between the  $\text{Cu}_2$  copper atom and the apical O1 oxygen, as well as change in the distance between the O2 and O3 atom chains in the  $\text{CuO}_2$  layer.

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

## 1. Introduction

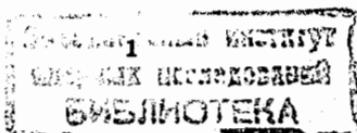
A partial substitution of Ca for Y (~10%) in the superconductor  $\text{YBa}_2\text{Cu}_4\text{O}_8$  leads to an increase in the superconducting transition temperature from 80 K to ~90 K and the occurrence of a phase transition at  $T \approx 150$  K. The phase transition was first found by means of elastic and specific heat measurements in a Ca doped compound<sup>/1/</sup>. Indications of its existence were also detected in the powder neutron diffraction study of  $\text{Y}(\text{Ca})\text{-124}$ <sup>/2/</sup> and the X-ray structure analysis<sup>/3/</sup> of  $\text{Y-124}$  and  $\text{Y}(\text{Ca})\text{-124}$  single crystals.

Although the existence of the structural phase transition in  $\text{Y}(\text{Ca})\text{-124}$  is considered to be reliably established, the conditions of its occurrence and its specific manifestations are not altogether clear. In particular, it is contended<sup>/3/</sup> that the temperature dependence of lattice parameters  $a$  and  $c$  show a kink at  $T \approx 150$  K, while parameter  $b$  remains almost the same over the entire temperature range studied. On the other hand paper<sup>/2/</sup> shows a kink in the temperature dependence of parameter  $b$  but no clear effects at  $T \approx 150$  K were observed in the dependence of  $a$  and  $c$  or concerning the interatomic distances, while paper<sup>/3/</sup> asserts a significant contraction of the  $\text{Cu2-O1}$  bond length and a shortening of the  $\text{Y-O}_{2,3}$  and  $\text{Y-Ba}$  distances below 150 K.

We have attempted to clarify the situation by carrying out an experiment on the same sample studied earlier in<sup>/2/</sup>. We performed our experiment with the high-resolution neutron Fourier diffractometer (HRFD) put into operation recently at the IBR-2 pulsed reactor in Dubna<sup>/4/</sup>. The resolution of HRFD is approximately 2.5 times better than that of the mini-SFINKS diffractometer in Gatchina where the results of Ref.<sup>/2/</sup> were obtained.

## 2. Experiment

The neutron diffraction experiment was performed on powdered  $\text{YBa}_2\text{Cu}_4\text{O}_8$  that had 10% of its Y replaced by  $^{44}\text{Ca}$ . The coherent scattering length of the  $^{44}\text{Ca}$  isotope (1.42 F) differs appreciably from that of Y and Ba ( $b_{\text{Y}}=7.75$  F,  $b_{\text{Ba}}=5.07$  F) thus facilitating the problem of identifying Ca atoms in the positions of Y or Ba. The X-ray phase analysis revealed the presence of small amounts of  $\text{CuO}$



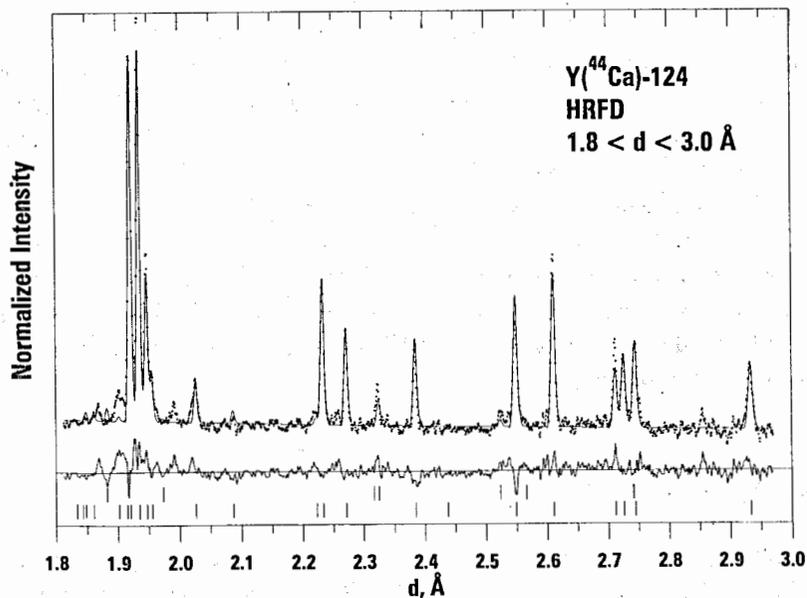
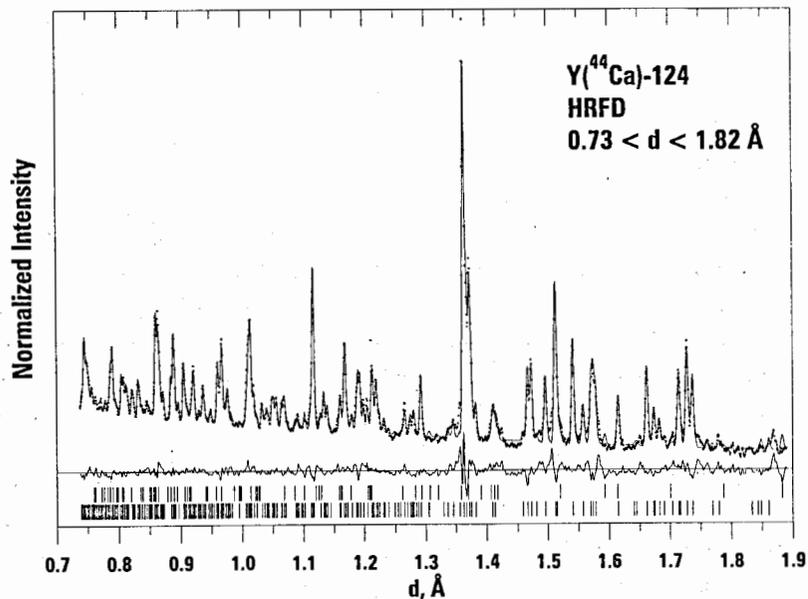


Fig. 1. Diffraction spectrum from the powdered  $Y_{0.9}^{44}Ca_{0.1}Ba_2Cu_4O_8$  measured on the high-resolution Fourier diffractometer at the IBR-2 pulsed reactor showing the experimental points, profile calculated by the Rietveld method, and the difference curve.

and  $Y_2O_3$  in the sample. The temperature of the superconducting phase transition was 87 K.

The HRFD diffractometer is a time-of-flight correlation neutron spectrometer using a Fourier chopper for modulation of the intensity of neutrons striking the sample. In the theory applying the Fourier chopper to neutron diffraction technique<sup>4,5/</sup> it has been shown that the correlation analysis of the scattered neutron intensity allows neutron diffraction pattern to be reconstructed. The resolution depends on the frequency of the intensity modulation and the geometric contribution related to the primary beam collimation, imperfect response of the detector system, etc. For the HRFD, the attainable time-of-flight resolution is  $\Delta t/t=0.00025$  at  $d=2$  Å. The presence of the geometric contribution widens the diffraction peaks, so the diffractometer resolution was 0.0012 at the moment of performing the experiment. This value turned out to be optimal for the experiment on  $Y^{(44}Ca)-124$  because the widths of the diffraction peaks from the sample were  $\sim 30\%$  greater than the resolution function width.

The diffraction spectra were measured with good statistical accuracy at temperatures of 135, 165, and 293 K; structural analysis was then performed with these data. Additional measurements were performed at nine temperature points in the interval of 8 to 288 K. These data were only used for determining the temperature dependence of the lattice parameters. The spectra were measured with high resolution by the detector at a fixed mean scattering angle of  $2\theta=152^\circ$  in the  $d$ -spacing range of 0.75 to 3.0 Å. Simultaneously, the diffraction spectra were measured at  $2\theta=90^\circ$  for analysis of the neutron diffraction pattern in the  $d_{hkl}$  interval of 3 to 6.0 Å. Besides the diffraction peaks from  $CuO$ , weak peaks at  $d=3.482, 3.079, 2.856, 1.991, 1.705,$  and  $1.651$  Å, which do not correspond to the basic phase of  $Y^{(44}Ca)-124$ , were found in the spectra. They can neither be attributed to the compound  $Y_2O_3$ , to which the X-ray data pointed, nor to  $Y-123$ , whose presence could have been assumed.

The unit cell parameters were refined using the data from the interval of  $1.35 \text{ Å} \leq d \leq 2.97 \text{ Å}$ ; Rietveld structural analysis was performed on the interval from  $0.73 \text{ Å} \leq d \leq 2.97 \text{ Å}$ . Fig.1 shows portions of the spectrum with the experimental points, calculated profile, and the difference curve.

### 3. Results

In the analysis of the measured diffraction spectra, two phases were taken into account:  $Y-124$  and  $CuO$ . For  $Y^{(44}Ca)Ba_2Cu_4O_8$ , the space group  $Am\bar{m}$  and the initial values of the parameters from<sup>6/</sup> were used. For the  $CuO$  phase, the

following data were taken from<sup>17/</sup>: space group C2/c,  $a=4.6837 \text{ \AA}$ ,  $b=3.4226 \text{ \AA}$ ,  $c=5.1288 \text{ \AA}$ ,  $z=4$ ,  $y_O=0.4184$ .

Table 1. Lattice constants of  $Y(^{44}\text{Ca})$ -124 as a function of temperature.

T, K	a, Å	b, Å	c, Å
8	3.83514(10)	3.86613(9)	27.1750(9)
75	3.83631(6)	3.86636(5)	27.1923(5)
100	3.83687(7)	3.86649(6)	27.2000(5)
125	3.83742(6)	3.86678(6)	27.2081(5)
150	3.83814(11)	3.86698(11)	27.2148(11)
175	3.83870(13)	3.86756(13)	27.2212(13)
200	3.83954(14)	3.86788(14)	27.2299(14)
225	3.84023(13)	3.86837(12)	27.2381(13)
288	3.84212(11)	3.86982(10)	27.2620(10)

The refined unit cell parameters as a function of temperature are summarized in Table 1 and illustrated in Fig.2. Fig.3 shows the temperature dependences of the orthorhombicity coefficient  $\omega = (b-a)/(b+a)$  and the unit cell volume  $V_c$ . For  $b$ ,  $c$ , and  $V_c$ , the linear dependences determined by the least square method before and after 150 K are drawn. One can see that in the proximity of 150 K the temperature behavior of both these quantities and  $\omega$  changes. This change is especially clear for parameter  $b$ .

The structural characteristics of  $Y(^{44}\text{Ca})$ -124 as determined for three temperature values are given in Table 2. At room temperature, the  $z$ -coordinates, thermal parameters  $B_T$  of all independent atoms, and the occupancy factor  $n$  of the Y and Ba positions were refined. The thermal parameters of the atoms turned out to be plausible except the  $B_T$  of Y and O3, with the thermal parameter of Y remaining negative for all variants of the data processing (varying the  $d_{hk}$  interval, changing the weight scheme, etc.) A correlation between  $n$  and  $B_T$  resulted in  $n(\text{Y})$  being obviously undervalued. At the fixed  $B_T(\text{Y})=0.5$ ,  $n(\text{Y})$  was found to be 0.889(5), which is practically equal to the nominal value of 0.9. The population factor of the Ba position coincides with the nominal value within the limits of error, which confirms the conclusion made earlier<sup>12,6/</sup> that it is the Y position and not Ba that is replaced by Ca. This points to the main role in the substitution mechanism being played by the small ion radius of  $\text{Ca}^{2+}$ , which practically coincides with the  $\text{Y}^{3+}$  radius, and not by its valency, which is equal to that of Ba.

Table 2. Structural parameters of  $Y(^{44}\text{Ca})$ -124 for  $T=293, 165$  and  $135 \text{ K}$ . (Two phases: 1 - Y124, 2 - CuO;  $d$ -range:  $0.74 - 2.97 \text{ \AA}$ ). \*Fixed values.

	Posit. / T	293 K	165 K	135 K
Y	.5,5,0			
	n	0.82(1)	0.90	0.90
	B	-0.56(6)	0.2*	0.2*
Ba	.5,5,z			
	n	1.96(2)	2	2
	z	0.13490(8)	0.1347(2)	0.1348(2)
	B	0.54(7)	0.2*	0.2*
Cu1	0,0,z			
	z	0.21256(5)	0.2125(1)	0.2129(1)
	B	0.36(3)	0.2*	0.2*
Cu2	0,0,z			
	z	0.06100(5)	0.0618(1)	0.0616(1)
	B	0.40(3)	0.2*	0.2*
O1	0,0,z			
	z	0.14621(6)	0.1454(1)	0.1454(1)
	B	0.65(4)	0.4*	0.4*
O2	.5,0,z			
	z	0.05250(5)	0.0540(1)	0.0542(1)
	B	0.27(4)	0.4*	0.4*
O3	0,.5,z			
	z	0.05288(6)	0.0520(1)	0.0517(1)
	B	0.06(4)	0.4*	0.4*
O4	0,.5,z			
	z	0.21869(6)	0.2197(1)	0.2195(1)
	B	0.94(5)	0.4*	0.4*
a, Å		3.84106(3)	3.8379(1)	3.8372(1)
b, Å		3.86908(3)	3.8673(1)	3.8669(1)
c, Å		27.2590(3)	27.213(1)	27.204(1)
$\chi^2$		2.3	2.4	2.9
$R_p$		0.097	0.117	0.144
$R_w$		0.085	0.120	0.139
$R_e$		0.091	0.099	0.113

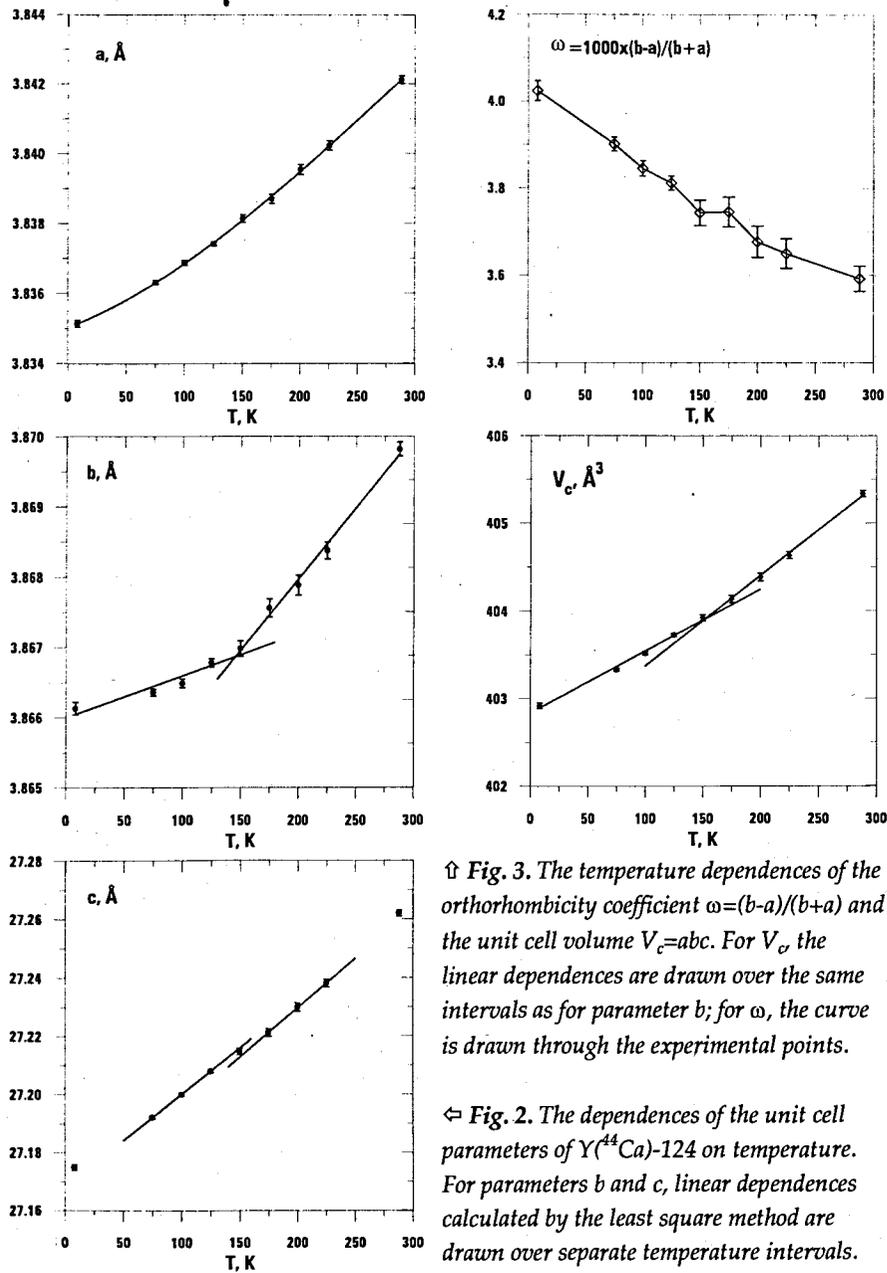


Fig. 3. The temperature dependences of the orthorhombicity coefficient  $\omega = (b-a)/(b+a)$  and the unit cell volume  $V_c = abc$ . For  $V_c$  the linear dependences are drawn over the same intervals as for parameter  $b$ ; for  $\omega$ , the curve is drawn through the experimental points.

Fig. 2. The dependences of the unit cell parameters of  $Y(^{44}\text{Ca})\text{-124}$  on temperature. For parameters  $b$  and  $c$ , linear dependences calculated by the least square method are drawn over separate temperature intervals. For parameter  $a$ , experimental points were approximated by a parabola.

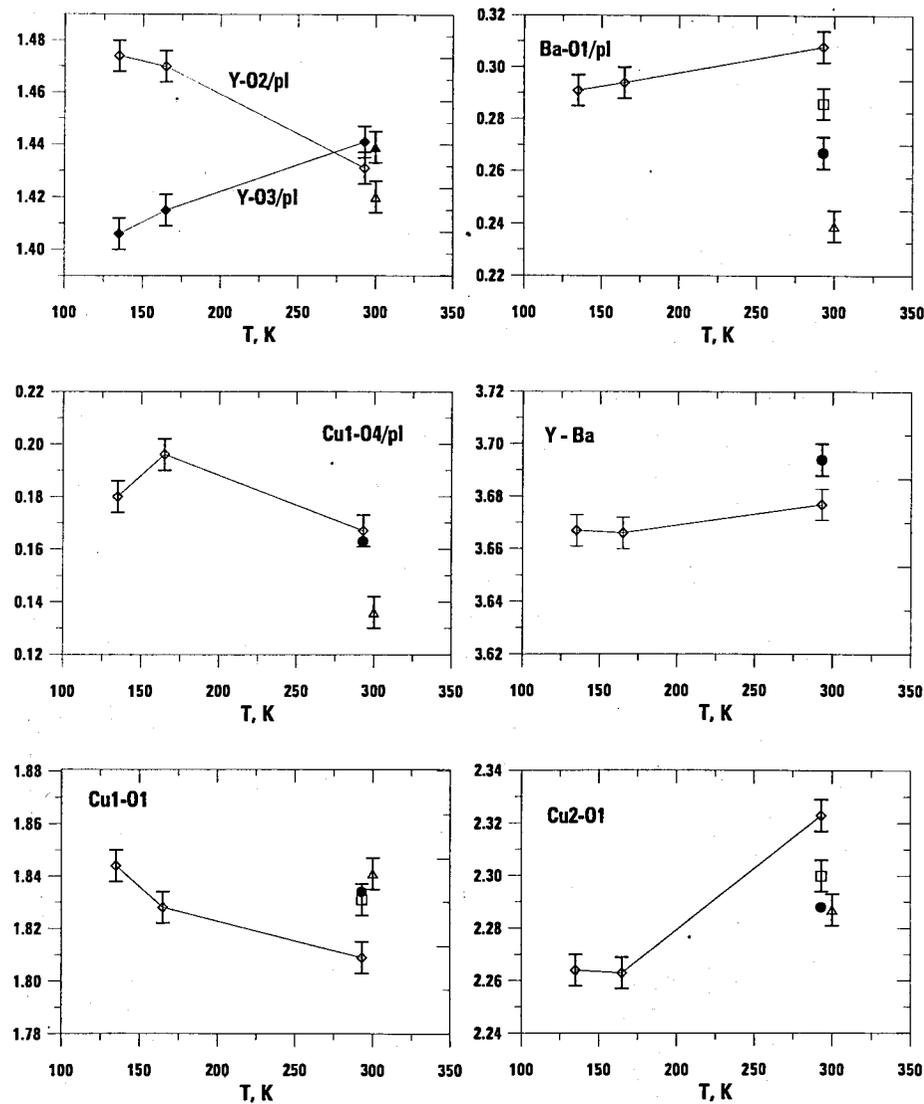


Fig. 4. Experimental values for the main interatomic bond lengths and distances (in Å) between atom layers (denoted by the index /pl). Shown are the points obtained in this study ( $\diamond$  and  $\blacklozenge$ ), in Ref./2/ ( $\triangle$ ) and Ref./3/ ( $\bullet$ ). The symbol  $\square$  marks the points calculated with the O1 atom coordinate taken from /2/.

In processing the spectra measured at the temperatures of 135 K and 165 K, the occupancy of the Y and Ba positions was fixed; thermal parameters were not refined and were set to equal 0.2 and 0.4 Å<sup>2</sup> for the metal and oxygen atoms, respectively.

At room temperature, the z-coordinates of the atoms are in good agreement with values obtained in<sup>/8/</sup> for Y-124 without substitution. The differences between relative coordinates are no more than 0.0002 – 0.0005 Å except for the O1 atom. At 135 K, the z-coordinate values are very close to those obtained in Ref.<sup>/6/</sup> for the same sample at the temperature of 9 K. Table 3 presents the main interatomic bond lengths and distances between atom layers illustrated in Fig.4. For comparison, it also contains the corresponding quantities obtained in<sup>/2,8/</sup>. In the column for T=293 K, two values are given for the distances involving the O1 atom: the first was obtained for  $z_{O1}=0.1462$  (our data) and the second was calculated for  $z_{O1}=0.1454$  which was taken from Ref.<sup>/6/</sup>. This was done to estimate possible systematic errors caused by the influence of impurities that were not taken into account.

**Table 3.** Selected interatomic and interlayer (denoted by the index /pl) distances [in Å] of Y(<sup>44</sup>Ca)-124 for 135, 165 and 293 K. Data obtained at room temperature from papers<sup>/2, 8/</sup> are also given.

	135 K	165 K	293 K	from <sup>/2/</sup>	from <sup>/8/</sup>
Cu2-O1	2.264	2.263	2.323/2.300	2.287	2.288
Cu1-O1	1.844	1.828	1.809/1.831	1.841	1.834
Y-Ba	3.667	3.666	3.677	3.772	3.694
Y-O2/pl	1.474	1.470	1.431	1.420	1.427
Y-O3/pl	1.406	1.415	1.441	1.439	1.438
Ba-O1/pl	0.291	0.294	0.308/0.286	0.239	0.267
Cu1-O4/pl	0.180	0.196	0.167	0.136	0.163

#### 4. Discussion and conclusion

The results of this work confirm the presence of a structural anomaly in Y-124 doped with Ca in the proximity of 150 K. It manifests itself by a sharp change in the expansion coefficient along the *b* axis, irregularity of the orthorhombicity coefficient, and a noticeable change in some bond lengths. According to the X-ray investigation<sup>/3/</sup>, the most pronounced indication of phase transition is the

shortening of the distance between the Cu2 atom and the apical O1 oxygen atom as well as a contraction of the Y-O2,3 and Y-Ba distances. It follows from our data that the Cu2-O1 bond indeed changes the most obviously. Even with all possible systematic errors being taken into account, the contraction is about 0.03 Å. The change in the Y-Ba bond manifests itself less clearly, although it also appears to take place. Of interest seems to be the situation regarding the distance between the base plane of the structure (Y layer) and the O2 and O3 atoms. In Ref.<sup>/1/</sup>, it was assumed that the phase transition at 150 K is connected with a change in the shape of the CuO<sub>2</sub> plane (atoms Cu2, O2 and O3). Our data indicate that the distance between the chains formed by the O2 and O3 atoms in this layer increases along the z-axis from 0.01 Å at the room temperature to 0.05 Å in the region of the phase transition.

These results, as well as the data obtained in Ref.<sup>/2/</sup>, demonstrate that the structural distinctions of the phase transition in Y(<sup>44</sup>Ca)-124 can be investigated with the help of high-resolution neutron powder diffraction. The disagreement in the behavior of parameters *a* and *b* between our data and data from<sup>/3/</sup> remains unclear. One of the possible causes could be the ordering of the admixture calcium atoms along one or another direction in the lattice, which in principle is possible. Another explanation may be based on the difference between ceramic powder (our and Ref.<sup>/2/</sup> case) and single crystal (Ref.<sup>/3/</sup> case) data from the point of view of preparation and internal stresses. For further clarification, a fine scanning over temperature must be performed in close proximity to the phase transition using a sample with a smaller amount or, preferably, without any impurities.

#### Acknowledgments

This research was supported by the Russian National Program of Fundamental Research (grant No.93-02-2530) and by the Swiss National Science Foundation. The authors are grateful to V.V.Chernyshev for sample testing and are deeply indebted to Prof. V.L.Aksenov for helpful discussions. Thanks also to A.Schaeffer for text editing.

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Received by Publishing Department  
on October 25, 1994.