V.L.Aksenov, E.V.Antipov[1], A.M.Balagurov, J.-J.Capponi[2],
V.P.Glazkov[3], I.N.Goncharenko[3], S.N.Putilin[1],
B.N.Savenko, V.A.Somenkov[3]

NEUTRON DIFFRACTION STUDY
OF THE HIGH-T_c SUPERCONDUCTOR
$HgBa_2CaCu_2O_{6.3}$ UNDER HIGH PRESSURE

[1]MSU, Moscow, Russia
[2]Lab.of Crystallography, CNRS, Grenoble, France
[3]RRC KI, Moscow, Russia

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Нейтронографическое исследование сверхпроводника HgBa₂CaCu₂O₆.₃ при высоком внешнем давлении

Кристаллическая структура высокотемпературного сверхпроводника $HgBa_2CaCu_2O_{6.3}$ исследована методом дифракции нейтронов при нормальном давлении и при $P = 3,0$ и 3,6 ГПа. Эксперименты проведены на импульсном реакторе ИБР-2 на дифрактометрах по времени пролета ДН-2, при нормальном давлении, и ДН-12 в камере с сапфировыми наковальнями. Результаты, полученные при $P = 0$, хорошо согласуются с моделью структуры Hg-1212, описанной в литературе. При повышенных давлениях заметно лучшее соответствие измеренных и вычисленных дифракционных спектров дает модель структуры с разупорядоченным вдоль диагоналей в плоскости (a, b) мостиковым кислородом. Из полученных структурных характеристик вычислены коэффициенты сжимаемости для параметров и объема элементарной ячейки и для отдельных межатомных и межслоевых расстояний.

Neutron Diffraction Study of the High-T_c Superconductor HgBa₂CaCu₂O₆.₃ under High Pressure

The pressure dependence of the crystal structure of a powder sample of $HgBa_2CaCu_2O_{6.3}$ ($T_c = 123$ K) was studied in the pressure range of 0 to 3.6 GPa, using the DN-12 time-of-flight diffractometer at the IBR-2 pulsed reactor and a sapphire anvil cell chamber. At $P = 0$ the results are in a good accordance with the published data. At $P = 3.0$ and 3.6 GPa the best fit of the experimental data was achieved using the structural model with apical oxygen disordered in the (a, b) plane. The compressibility values of the lattice constants and selected bonds were calculated from the structural data. The highest absolute value of compressibility was found for the distance between the Ba and O atom layers.

1. Introduction

In the recently discovered series of $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ compounds[1,2,3], as well as in other layered copper oxide high-temperature superconductors, a significant increase in the superconducting transition temperature is observed when high external pressure is applied[4,5]. For example, in the compound with n=3 (Hg-1223), T_c increases from 134 K at normal pressure to 150 K at P=11 GPa[6]. The T_c increase rate with pressure is almost the same for all representatives of the series: dT_c/dP=1.75, 2, and 1.7-1.8 K/GPa for n=1, 2, and 3, respectively (the data is presented in[7]). On the basis of this fact one may assume a similarity in the T_c increase mechanism, which could be connected with the similar structures of these compounds.

The first step towards ascertaining the reasons for the transition temperature increase is determination of the structural changes under external pressure. For oxide superconductors, it is especially important to determine the oxygen atom positions in the structure since the balance of distances between oxygen and other key structural atoms is the main factor in the development of superconductive properties. The most reliable direct method which provides information on the positions of the oxygen atoms in the structure is neutron diffraction since the accuracy of X-ray structural analysis is usually insufficient for this purpose.

High-pressure neutron diffraction experiments have previously been performed on mercury-based superconductors in[7], where all three representatives of the series were investigated: for compounds with n=1, 2, and 3, an experiment was performed under pressures up to 0.6 GPa; for the compound with n=3, additional measurements were carried out for P=4.0 and 9.2 GPa. For Hg-1201 and Hg-1212, the dependence of the unit cell parameters and the main interatomic distances between the apical oxygen (O2) and the copper and mercury atoms turned out to be in agreement with expectations. Particularly, the Cu-O2 distance shortened with the pressure increase while the Hg-O2 distance remained almost constant. For Hg-1223, however, the result turned out to be just the opposite: the Cu-O2 distance remained constant or even grew slightly with pressure, while the Hg-O2 distance distinctly shortened (from 1.92 Å to 1.69 Å at
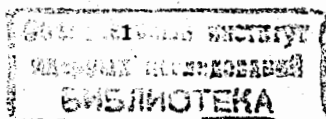
P=9.2 GPa). Another unexpected result was the fact that the compressibility of the CuO layer blocks appeared to be significantly lower (close to zero) than the interlayer compressibility. One of the problems which has emerged in[7] in the diffraction data analysis was the presence of an appreciable quantity of impurities, such as $BaCuO_{2+x}$, CaO and $Ba_2Cu_3O_{5+x}$, in the samples of compounds with n=2 and 3. In principle, their influence could have biased the structural analysis results. It is this factor that the authors of[7] emphasize to explain unusual behavior of the interatomic distances in Hg-1223. Thus, more experiments are needed to confirm these data.

In the present work, the results of the neutron diffraction experiment on the Hg-1212 compound under external pressures of 3.0 and 3.6 GPa are presented. A high-pressure cell with sapphire anvils was used in this experiment. To our knowledge, it was done for the first time at neutron TOF diffractometer so we consider the results as tentative.

2. Experiment

The experiments were performed on the $HgBa_2CaCu_2O_{6+x}$ compound, the synthesis and properties of which are given in[8]. The X-ray diffraction analysis has shown that there were practically no impurity phases in the sample, although traces of other representatives of the Hg-12(n-1)n series with n=1 and 3 were detected. Magnetic susceptibility measurements were performed at the frequency of 119 Hz in a 0.01 Oe field. They revealed the existence of a small jump at 133 K, which is connected with the presence of the Hg-1223 phase, and the wide transition into the superconducting phase beginning at 104 K. After additional treatment in an oxygen atmosphere at 300°C for 20 hours, the temperature of the main transition increased to 123 K. One of the samples of this series underwent neutron diffraction experiments at the reactor of NIST (USA) under normal pressure at room temperature and at 10 K. The results were published in[8].

Our neutron diffraction experiments were performed with the DN-2[9] and DN-12 time-of-flight diffractometers at the Laboratory of Neutron Physics of JINR. Both facilities have an average resolution $\Delta d/d \approx 0.015$ in the region of $d_{hkl}=2$ Å and high luminosity. The experiment at the DN-2 diffractometer was performed in order to determine the degree of phase homogeneity of the sample (the available amount of sample was about 0.2 g) and to refine its oxygen content. Fig. 1 shows the measured diffraction spectrum after Rietveld refinement. It was found that two phases were present in the sample: Hg-1212 and traces of metallic Au. Evidently, the later fell into sample during extraction from the container.
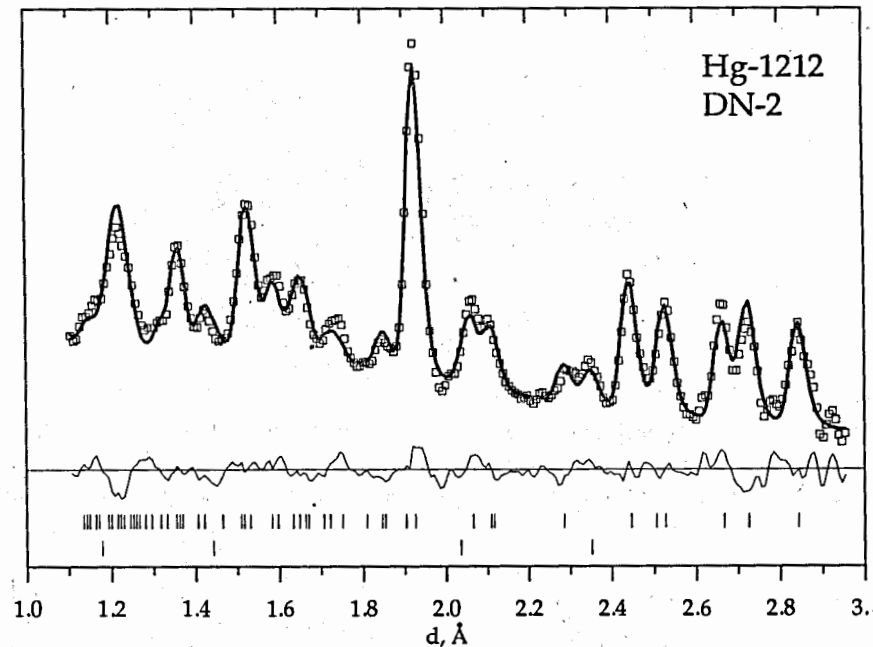

Fig.1. Diffraction spectrum from $HgBa_2CaCu_2O_{6+x}$ measured with the DN-2 diffractometer. Experimental points, calculated profile, and difference curve (experiment - calculations) are shown. The positions of the Bragg peaks for the main phase and metallic Au are also indicated.

The DN-12 diffractometer is specifically intended for work with high-pressure cells based on sapphire anvils. A well collimated neutron beam passes through the sapphire single crystals, between which a sample is placed (Fig.2). Scattered neutrons are registered by the detector consisting of small counters positioned around the circle of a vertically standing ring. The ring as a whole can be moved relative to the sample along the beam direction providing scattering angles from 45° to 135°. The wavelength interval of DN-12 is 1.3 to 4.5 Å, therefore, at a scattering angle of 90°, the diffraction pattern can be measured in the d_{hkl} interval of 1 to 3 Å. The spectra are registered independently by each counter on the ring, summed, and normalized. Before summing, a necessary procedure is to examine the separate spectra for diffraction reflections from the sapphires. Sometimes these peaks can be subtracted from the spectrum without damaging the sample data, and sometimes the spectra from separate detectors are excluded from the summation. The measurements at DN-12 were performed on a sample with a mass of about 1 mg under pressures of P=0, 3.0 and 3.6 GPa;
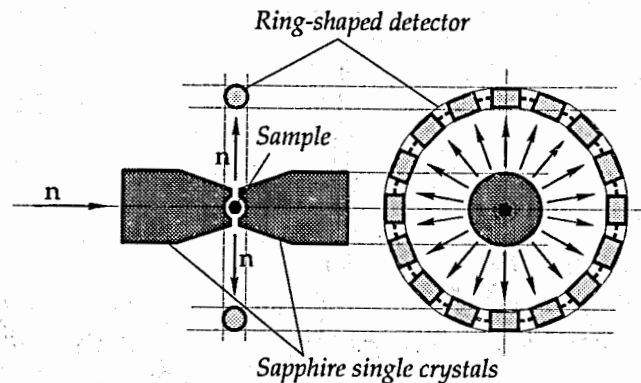
Fig.2. *Position of the high-pressure cell with the sample and the detector at the DN-12 diffractometer. The neutron beam passes through the sapphire single crystals. The neutrons scattered from the sample are registered by the ring-shaped detector assembled of separate counters.*
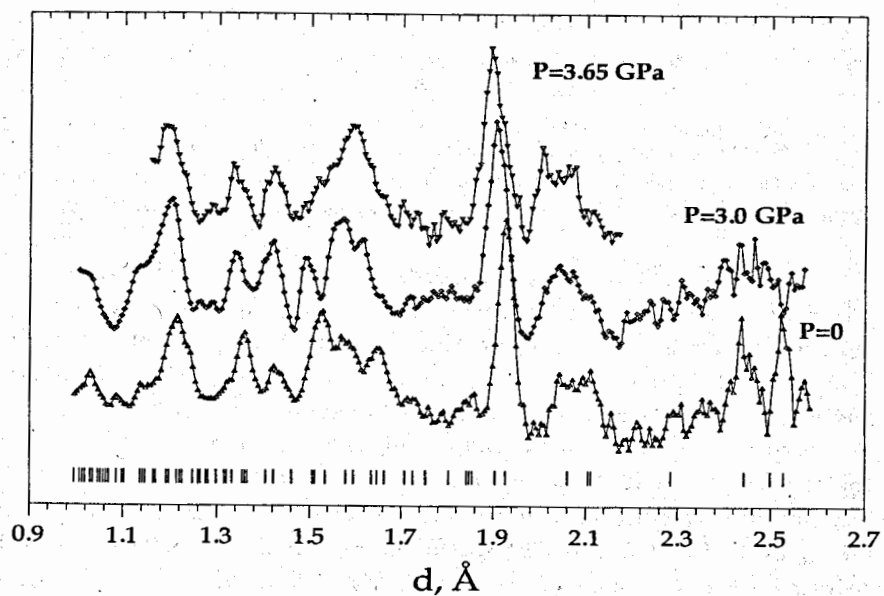

Fig.3. *Regions of the diffraction spectra from Hg-1212 measured on DN-12 in the sapphire anvils cell at three different pressure values and later processed by the Rietveld method. The Bragg peaks of Hg-1212 at P=0 are shown by the tick marks.*

the measurement time for each pressure value was about 50 hours. The parts of the spectra measured at these three pressure values and processed later are shown in Fig.3. At the pressure of 3.6 GPa, sapphire diffraction peaks were present in almost all the spectra of the separate detectors in the region of 1.1 Å and in the d_{hkl} interval of 2.2 to 2.5 Å. Therefore, these regions were excluded from processing.

3. Results

The diffraction spectra were processed by the Rietveld method with the help of the MRIA[10] software. Data processing was performed in several stages. The spectrum measured at DN-2 was processed for the interval of $1.1<d_{hkl}<3.0$ Å which contained about 50 peaks from the tetragonal phase, space group P4/mmm. The data from[8] were used as the initial parameter values. The relatively low quality of the diffraction spectra (bad effect-to-background ratio and restricted possibilities of analyzing data in the region of small d_{hkl}) prevented the thermal atom parameters from being reliably evaluated. Therefore, we chose to fix them: B=0.5 Å² for Ba, Cu, and Ca; B=1.0 Å² for all oxygen atoms. Varying these parameters within the limits of 50% only slightly influenced the structural parameters of the atoms. The processing results are presented in Table 1, together with the structural data for the Hg-1212 compound obtained at NIST[8] and ANL[7]. Our data are presented in two sets which differ in their treatment of the mercury atom: in the first case, the occupancy factor was fixed to be n(Hg)=1 and the temperature factor $B_T(Hg)$ was varied. It turned out to be anomalously large: $B_T(Hg)=3.5$ Å². In the second case, the temperature factor was taken from[8] and fixed. In this case, n(Hg)=0.90±0.02, which agrees well with the result obtained with the help of synchrotron radiation[11].

While processing the spectra measured at DN-12, the thermal parameters, and the O3 oxygen content, n(O3)=0.3, were fixed. In addition, the lattice parameters at P=0, a=3.850 Å and c=12.629 Å, as determined by processing the data obtained at DN-2, were fixed as well. From the comparing measured and calculated profiles it follows that the spectrum fitting was quite good at zero pressure, but at higher pressures the fitting quality is definitely worse. Another conspicuous factor was the sharp shortening of the Hg-O2 bond length with the increase in pressure. That is why we undertook several attempts in order to change the initial model of the structure. The best result was obtained for the model with disordered O2 oxygen. Realistic values for the bond lengths were obtained on the assumption that O2 is disordered along the diagonals in the (a,b) plane, i.e., its position is described by the (x,x,z) coordinates. Data obtained for such a model are presented in Table 2. For the spectra measured at zero pressure,

Table 1. *Results of the structural analysis of* $HgBa_2CaCu_2O_{6+x}$. *Our data (JINR and JINR') and the results obtained at NIST[8] and ANL[7] are presented. The data given in the JINR and JINR' columns differ in the mercury atom treatment: n=1 was fixed for JINR, B_T=1.8 was fixed for JINR'. Also, some interatomic distances and distances between atom layers denoted as /l are presented.*

Atom	Pos.	NIST	ANL	JINR	JINR'
Hg	0, 0, 0				
	n	1	1	1	0.90(2)
	B	1.8		3.5(6)	1.8
Ba	.5, .5, z				
	z	0.2175	0.2217	0.2170	0.2161
	B	0.6		0.5	0.5
Cu	0, 0, z				
	z	0.3751	0.3774	0.3756	0.3750
	B	-0.1		0.5	0.5
Ca	.5, .5, .5				
	B	0.1		0.5	0.5
O1	0, .5, z				
	z	0.3759	0.3773	0.3748	0.3748
	B	0.2		1.0	1.0
O2	0, 0, z				
	z	0.1564	0.1570	0.1550	0.1560
	B	0.7		1.0	1.0
O3	.5, .5, 0				
	n	0.35(2)		0.28(4)	0.30(4)
	B	1		1.0	1.0
a, Å		3.8526	3.8493	3.8504	3.8502
c, Å		12.6367	12.6461	12.6293	12.6287
Cu-O2, Å		2.764	2.787	2.786	2.766
Hg-O2, Å		1.976	1.985	1.976	1.970
Hg-Cu, Å		4.740	4.773	4.774	4.736
Cu-Cu, Å		3.157	3.101	3.142	3.157
Ba/l-O2/l, Å		0.772	0.818	0.783	0.759
Ba/l-Cu/l, Å		1.992	1.969	2.003	2.007
Ba/l-O1/l, Å		2.002	1.968	1.993	2.004
Ba/l-Hg/l, Å		2.748	2.804	2.741	2.729

Table 2. *Results of the structural analysis of the diffraction spectra from Hg-1212 measured at the DN-2 and DN-12 diffractometers under the ambient pressure, 3.0, and 3.6 Gpa. The model with disordered O2 along the diagonals in the (a,b) plane was used. The notation is the same as in Table 1.*

| Atom	Pos.	DN-2 P=0	DN-12 P=0	DN-12 P=3.0	DN-12 P=3.6
Hg	0, 0, 0				
	n	0.88(2)	0.9	0.9	0.9
	B	1.8	1.8	1.8	1.8
Ba	.5, .5, z				
	z	0.2141	0.2133	0.2001	0.1875
	B	0.5	0.5	0.5	0.5
Cu	0, 0, z				
	z	0.3751	0.3752	0.3625	0.3640
	B	0.5	0.5	0.5	0.5
Ca	.5, .5, .5				
	B	0.5	0.5	0.5	0.5
O1	0, .5, z				
	z	0.3739	0.3763	0.3746	0.3730
	B	1.0	1.0	1.0	1.0
O2	x, x, z				
	x	0.0490	0.0628	0.0820	0.1002
	z	0.1556	0.1577	0.1476	0.1420
	B	1.0	1.0	1.0	1.0
O3	.5, .5, 0				
	n	0.39(4)	0.30	0.30	0.3
	B	1.0	1.0	1.0	1.0
a, Å		3.8501	3.8501	3.814	3.799
c, Å		12.6300	12.6300	12.409	12.338
a/a_o			1	0.9906	0.9867
c/c_o			1	0.9825	0.9769
Cu-O2, Å		2.785	2.768	2.703	2.791
Hg-O2, Å		1.983	1.996	1.884	1.833
Hg-Cu, Å		4.737	4.738	4.498	4.491
Cu-Cu, Å		3.155	3.152	3.412	3.356
Ba/l-O2/l, Å		0.739	0.702	0.651	0.561
Ba/l-Cu/l, Å		2.033	2.045	2.015	2.178
Ba/l-O1/l, Å		2.018	2.058	2.041	2.289
Ba/l-Hg/l, Å		2.704	2.694	2.483	2.313
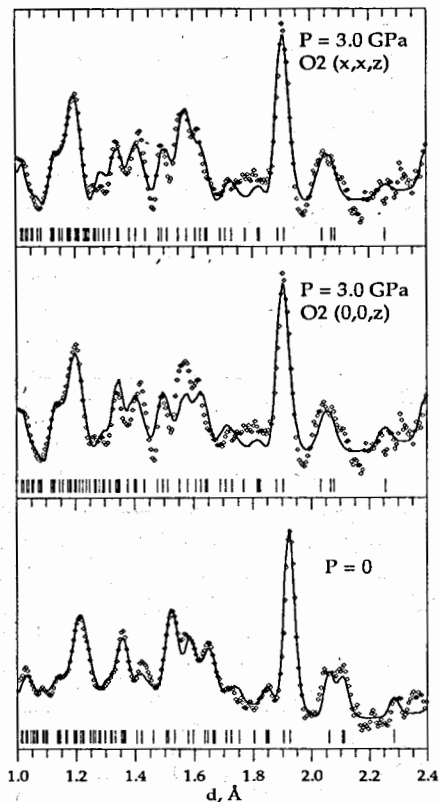
Fig.4. Diffraction spectra from Hg-1212 at P=0 and 3.0 GPa processed by the Rietveld method. For the spectrum at P=3 GPa, profiles calculated for two different models, with ordered and disordered O2 oxygen, are shown.

Fig.5. Dependences of the Hg-1212 lattice parameters on pressure, normalized to the values at P=0. Points obtained on DN-12 and SEPD are shown. Lines are drawn by the least square method. The lines drawn for c through both sets of data are indistinguishable.

introduction of parameter x for O2 did not notably change values of the z-coordinate of the atoms and did not improve the fitting quality. For the spectra measured at P=3.0 and 3.65 GPa, we obtained visible improvement, especially in the region around d=1.6 Å (Fig.4).

The most easily evaluated and reliable results of our measurements are the dependencies of the Hg-1212 lattice parameters on pressure. They are shown in Fig.5 as normalized to P=0 together with the data from[7] obtained at the SEPD diffractometer. For our data, values are shown for the models with ordered and disordered O2. Lines, obtained with the help of the least square method, are drawn only for the second model. The least square line is also drawn for parameter a according to the SEPD data. For parameter c, this line is indistinguishable from ours. The compressibility values, determined as
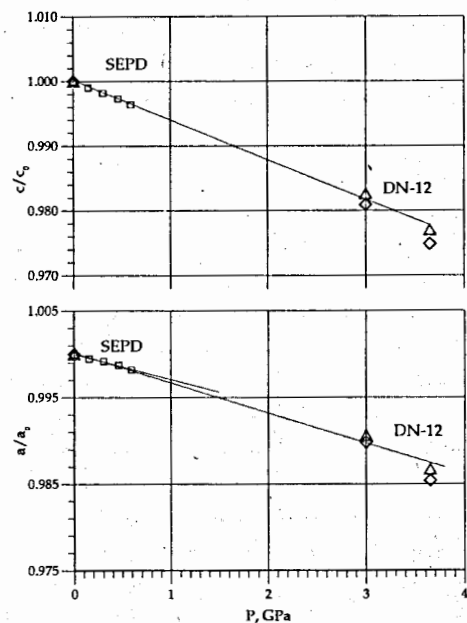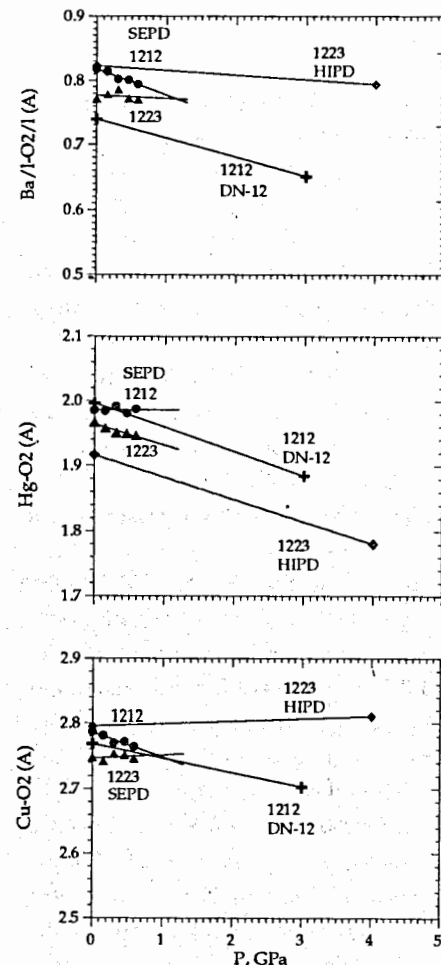

Fig.6. Interatomic distances in Hg-1212 and Hg-1223 as determined from the measurements on DN-12, SEPD, and HIPD. The lines are drawn by the least square method.

Table 3.

Compressibilities of the lattice constants and selected bonds of Hg-1212, measured with DN-12 (up to 3 GPa) and SEPD (up to 0.6 GPa), and Hg-1223, measured with HIPD (up to 9.2 GPa).

Compres-sibilities	1212_{DN-12}	1212_{SEPD}	1223_{HIPD}
κ_a	3.48	2.94	2.28
κ_c	6.15	6.04	4.7
κ_v	13.0	11.9	9.1
κ_{Cu-O2}	7.9	14	2
κ_{Hg-O2}	19	0	14
κ_{Ba-O2}	25	50	10

$\kappa_q=-(1/q)\delta q/\delta P$ $(10^{-3}/GPa)$, where q is the parameter, calculated for the crystallographic axes and for the unit cell volume are given in Table 3.

As already mentioned, processing our diffraction spectra using the standard model of the Hg-1212 structure lead to unrealistic values for the interatomic distances at higher pressure. Therefore, we show only the data obtained with the use of the model of O2 disordered in the (a,b) plane. Fig.6 shows the dependences of the Cu-O2 and Hg-O2 distances on pressure, which are interesting concerning the apical oxygen behavior, and the changes in the magnitude of splitting between the barium and O2 oxygen layers. The points obtained at P=3.6 GPa are not shown because we are not sure for the quality of Rietveld refinement at this pressure. The compressibility values for the distances are given in Table 3. For comparison, the data from[7] on Hg-1212 and Hg-1223 are also presented in that table.

4. Discussion

The structural characteristics of the Hg-1212 compound as determined by three laboratories (Table 1) agree with each other quite well. For all data sets, the distances between atoms and between layers generally coincide within an accuracy of 0.01 Å. Our results agree better with those presented in[8], which can naturally be attributed to the identity of the samples. The negative or obviously undervalued thermal factors of Cu, Ca, and O2 atoms obtained in[8] are still not clearly explained. Further progress on this issue can be achieved by investigating high-quality samples on high resolution neutron diffractometers.

The compressibility values that we obtained along the crystallographic axes only slightly exceed the corresponding values in[7], which were determined under pressures up to 0.6 GPa, but are outside the error limits (especially for a). Therefore, one may assume that within the pressure interval of 0.6 to 3 GPa a deviation from the linear dependence of the a and c parameters on pressure takes place.

Our results for the compressibility values of the Cu-O2 and Hg-O2 interatomic distances noticeably differ from the data in[7]: κ_{Cu-O2} is two times smaller, κ_{Hg-O2} is large. For Hg-O2 bound our result, in fact, correspond better to the result for Hg-1223. In[7], the data for Hg-1223 are regarded as unexpected and the assumption was made that the diffraction spectrum analysis results were distorted by the impurity phases in the sample. One can admit that a similar systematic error is present in our work, but it should be noted that these results were obtained on different samples and diffractometers. Another possible explanation could be in a change in the character of the dependence of these interatomic distances in Hg-1212 under pressures higher than 1 GPa. It is also possible that the presence of O3 oxygen in any quantity noticeably affects the specific values of compressibility.

The greatest absolute values of compressibility were obtained for the distances between the Ba-O2 and Ba-Hg atom layers. Despite a relatively broad spread in specific values, the general tendency is beyond doubt. In[12], it is noted that the magnitude of the Coulomb splitting of the cation - anion layers is very sensitive to changes both in the compound content and in external conditions, when the ambience charge is asymmetrical (Ba and O2 layers in our case). The results of our experiment and the data in[7] confirm this conclusion. Defining more exactly the cause of the large compressibility values for these distances, one may say that they are due, to a great extent, to the motion of Ba atoms towards the Hg atom plane.

5. Conclusion

In the present work results of the neutron diffraction investigation of the Hg-1212 compound under normal conditions and under external pressures of up to 3.6 GPa are presented. Comparing them with the results for Hg-1212 (up to 0.6 GPa) and Hg-1223 (up to 9.2 GPa) presented in[7] reveals an agreement in many aspects. There are significant disagreements, however, which are especially obvious for the behavior of κ_{Hg-O2} compressibility. Further experiments are also needed to clear up the situation regarding occupancy of the Hg positions and the mercury temperature factors. This is especially interesting in light of data obtained recently on the possibility of carbon atoms occupying these positions.

Acknowledgments

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