JOURNAL OF SOLID STATE CHEMISTRY 109, 74–82 (1994)

Crystal Structure of the Incommensurately Modulated Nd-Containing Bi-2222 Phase

A. V. Mironov,*,† P. Coppens,[1,]* N. R. Khasanova,† E. V. Antipov,† and V. Petricek‡

*Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214; †Moscow State University, Moscow, Russia; and ‡Institute of Physics, Czechoslovak Academy of Science, Czechoslovakia

Received February 19, 1993; in revised form June 22, 1993; accepted June 23, 1993

A single crystal of $Bi_2Sr_{1.7}Nd_{1.8}Ce_{0.5}Cu_2O_{10+\delta}$ (2222 phase) was obtained and its structure refined, including parameters describing the structural modulation (orthorhombic system, four-dimensional space group $C:C2mb:111$, $\mathbf{a} = 5.5000(4)$ Å, $\mathbf{b} = 5.4846(7)$ Å, $\mathbf{c} = 17.873$ Å, $Z = 2$). The refinement of the average structure gave $R = 0.061$, while structure refinement including displacive and thermal modulation parameters resulted in $R = 0.042$ (overall) and $R = 0.030$ for the main reflections. The amplitudes and directions of modulation are very similar to those in the 2212 phase (1, 2), with displacements ranging up to 0.4 Å. The refinement shows extra oxygen to be located in BiO layers, and gives $\delta = 0.32(8)$, in reasonable agreement with previously reported values.

I. INTRODUCTION

Bi-2222 phases are related to the 2212 superconductors by replacement of the Ca layer by the R_2O_2 fluorite-like block (Fig. 1), where R is a rare earth element. It results in a shift of the CuO_2 layers adjacent to the fluorite blocks by $(a + b)/2$, and in an increase of the distance between these layers.

Bi-containing layered copper oxides generally have modulated structures. The modulation vector of the 2222 phase has been reported as $\mathbf{q} = 2/9\mathbf{a}^* + 0.5\mathbf{c}^*$ (3) (after allowing for the interchange of the **a**- and **b**-axis relative to the setting used here and in Ref. 1), while $\mathbf{q} = 0.210\mathbf{a}^*$ (or $\mathbf{q} = 0.210\mathbf{a}^* + \mathbf{c}^*$) for the 2212 phase (1). Since the **c**-axis length of the 2222 phase is about half that of 2212, the modulation vectors of the 2222 and 2212 phases are similar.

In previous work, average structures of 2222 phases have been refined with powder (3) and single crystal (4) X-ray data. The refinements showed very high and anisotropic thermal parameters for all atoms and unreasonably large Bi–O distances (about 2.7 Å). Such anomalous values of the atomic displacement parameters are typical for a refinement in which an existing structural modulation is ignored.

We present a determination of the structure of the 2222 phase including the modulation, and a comparison of the results with those for 2212.

II. EXPERIMENTAL

A mixture of Nd_2O_3, Bi_2O_3, CeO_2, $SrCO_3$, and CuO, corresponding to the composition $Bi_2Sr_2Nd_{1.65}Ce_{0.35}Cu_2O_{10+\delta}$, plus 90% excess of copper oxide, was ground under acetone in an agate mortar. It was heated in a beryllium oxide crucible up to 900°C in 9 hr and then to 980°C in 15 hr, kept at this temperature for 20 hr then slowly cooled to 800°C with a cooling rate of $2°hr^{-1}$, and to 400°C with a rate of $20°hr^{-1}$, and then furnace cooled to room temperature. Crystals grew as black plates. A single crystal with dimensions of $0.4 \times 0.1 \times 0.004$ mm^3 was chosen for data collection. A small part of the same crystal was used for analysis with a CAMEBAX-microBEAM instrument. Nd_2CuO_4, Bi_2CuO_4, Sr_2CuO_3, and CeO_2 were used as standards. Atomic percentages were determined at ten locations using the $K\alpha$ line for Cu, and $L\alpha$ lines of all other cations. The MBX COR program (ZAF-correction) was applied for the calculations (5). The average cation ratio was Bi:Sr:Nd:Ce = 33.3(9):24.6(1.2):33.6(1.2):8.5(2), with standard deviations in parentheses. This ratio, normalized for the sum over the cations to be six, led to the composition $Bi_{2.00(5)}Sr_{1.47(8)}Nd_{2.02(6)}Ce_{0.52(1)}Cu_2O_{10}$. The copper content was kept fixed at two, as its analysis suffered from severe fluorescence of other heavy atoms, and the calculation made for eight cations produced an unreasonably large excess of copper atoms. The starting composition used in refinement, $Bi_2Sr_{1.5}Nd_2Ce_{0.5}Cu_2O_{10}$, is within standard deviations equal to the analytical result. X-ray data collection and refinement are summarized in Table 1.

[1] To whom correspondence should be addressed.

0022-4596/94 $6.00

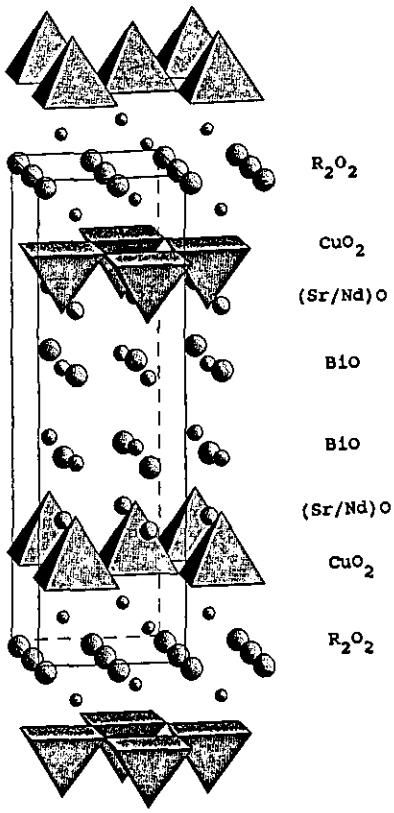

FIG. 1. Diagram of the average structure of the Bi-2222 phase.

TABLE 1
Summary of Crystallographic Information for $Bi_2Sr_{1.7}Nd_{1.8}Ce_{0.5}Cu_2O_{10+\delta}$

Molecular weight	1186.88
Color	Black
Crystal dimensions (mm)	0.4 × 0.1 × 0.004
Crystal system	Orthorhombic
Cell constants (Å)	a = 5.5000(4) b = 5.4846(7) c = 17.873(3)[a]
Modulation vector	$\mathbf{q} = 0.228(2)\mathbf{a}^* + 0.5\mathbf{c}^*$
Space group	C:$C2mb$:111[b]
Z	2
F(000)	1012
Calculated density (g/cm^3)	7.313
Absorption coefficient (cm^{-1})	55.10
Diffractometer	Enraf–Nonius CAD4, Mo$K\alpha$, graphite monochromator
Temperature	Ambient
Θ range (°)	2–40
Octants	h, $\pm k$, $\pm l$
Scan speed	Variable, depending on $\sigma(I)/I$
Structure refinement program	JANA92
Absorption correction	Analytical (crystal shape)
Measured reflections	8160
Independent reflection	
Main	515
First order satellites	626
Second order satellites	217
R_0(int)[c]	0.029
R_1(int)[c]	0.040 (m = 1) and 0.050 (m = −1)
R_2(int)[c]	0.073 (m = 2) and 0.120 (m = −2)
N_{ref}/N_{par}	8.33
R/R_w	0.042/0.045
R_0/R_{0w}	0.030/0.031
R_1/R_{1w}	0.046/0.049
R_2/R_{2w}	0.094/0.094
Weighting scheme	$w = \sigma^{-2}$

[a] As determined by refinement of 58 reflections; see text.
[b] Nonstandard setting of the space group A:$Abm2$:111 (No. 39b) according to (6)
[c] Here and below the index 0 refers to the main reflection, 1 refers to the first-order satellite, and 2 refers to the second-order satellite.

III. RESULTS

The lattice parameters and modulation (**q**) vector were determined by least-squares refinement of a set of 24 main reflections, and 32 first-order and 2 second-order satellites. The modulation vector was found to be $\mathbf{q} = 0.228(2)\mathbf{a}^* + 0.501(8)\mathbf{c}^*$. The $\mathbf{c}^*$ component was set to 1/2, as an irrational $\mathbf{c}^*$ component would lead to the monoclinic crystal system, for which no evidence was found in the averaging of the reflections. The exact value of the incommensurate $\mathbf{a}^*$ component is dependent on the type of rare earth element, and on cation and oxygen content. In a separate study we have found, for example, that for the Eu-containing 2222 phase with similar composition, the irrational part of the **q** vector equals $0.218(2)\mathbf{a}^*$. Similar conclusions were reached for $Bi_2(Sr_{1-x}Ln_x)(Gd_{1-y}Ce_y)Cu_2O_{10+\delta}$ by Nakai et al. (4).

Starting parameters for the refinement were taken from (4) after correction for the **c**-axis doubling in this analysis (vide infra). Bi atoms were assumed to be located only at the Bi sites. Sr atoms were assumed to also occupy the Ce site in the fluorite block, while Nd was placed at both the Sr and Ce sites.

To eliminate the rational component of the **q** vector, the **c** cell parameter was doubled. Reflection conditions are $h + k = 2n$ and $L + m = 2n$ ($L = 2l$) for $hkLm$ reflections, and $k = 2n$ (corresponding to a $\left(\frac{b}{l}\right)$ plane), $m = 2n$ (corresponding to a $\left(\frac{m}{s}\right)$ plane), and thus $k + m = 2n$ (corresponding to a $\left(\frac{b}{s}\right)$ plane) for $hk0m$ reflections (6). Several four-dimensional space groups were tested. Only the space group C:$C2mb$:111 gave acceptable values for the satellite reflection R factor. The symmetry elements used are completely described by the symbol P:$X2mb$:$s1s$, which is equivalent to C:$C2mb$:111 (7). Here X represents four centering vectors (0 0 0 0), (1/2 1/2 0 0), (0 0 1/2 1/2), and thus (1/2 1/2 1/2 1/2).[2] Since the cations are located in mirror planes perpendicular to **b**, their modulation amplitude along **b** is symmetry re-

[2] This is the same as P:$X2mb$:111 with the origin shift (0 0 1/4) [7].

TABLE 2
Positional and Thermal Parameters (Å × 10^3) of the Basic Structure for $Bi_2Sr_{1.7}Nd_{1.8}Ce_{0.5}Cu_2O_{10+\delta}$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	−0.0084(7)	1/4	0.20755(3)	33.0(8)	30.4(4)	11.6(4)	0	−1(1)	0
	−0.000(2)	1/4	0.20742(4)	107(2)	30.1(9)	30.2(4)	0	7(3)	0
Sr/Nd[a]	−0.006(1)	3/4	0.13416(7)	14(1)	10.1(9)	17(1)	0	−9(2)	0
	0.017(2)	3/4	0.1338(1)	55(4)	10(2)	59(2)	0	18(4)	0
Cu	0.005(1)	1/4	0.08596(8)	6(1)	4.5(7)	22(2)	0	−14(2)	0
	0.006(3)	1/4	0.0857(2)	17(2)	4(1)	64(3)	0	3(5)	0
Nd/Ce[b]	0	3/4	0.03550(4)	10.2(4)	4.8(3)	14.2(6)	0	0	0
	0	3/4	0.03531(7)	9.2(6)	4.9(5)	54(1)	0	−15(1)	0
O1	0.250(5)	1/2	0	9(2)					
	0.0258(9)	1/2	0	5(12)	15(10)	56(13)	0	0	0
O2	0.256(3)	0.504(5)	0.0830(2)	7(2)					
	0.264(9)	0.50(1)	0.0827(5)	20(10)	8(7)	69(11)	−4(6)	20(14)	−14(19)
O3	−0.024(7)	1/4	0.1514(4)	20(4)					
	−0.047(9)	1/4	0.1503(5)	22(6)					
O4[c]	0.54(1)	0.143(3)	0.2008(5)	15					
	0.43(2)	0.19(5)	0.201(4)	215(86)					

Note. On the second line, values for the average structure, obtained without taking the modulation into account, are listed.
[a] Occupancy of Sr = 0.84(1), occupancy of Nd = 0.16(1)
[b] Occupancy of Nd = 0.74, occupancy of Ce = 0.26.
[c] Occupancy of O4 = 0.5.

stricted to be zero (8). This is very similar to the modulation in the 2212 phase (1) in which the **b**-axis modulation is symmetry allowed, but has amplitudes of about 3σ or less.

The average structure was refined first with anisotropic thermal parameters for all atoms except the oxygen atoms O3 in the SrO and O4 in the BiO layers. Thermal parameters of these two atoms became quite large, especially in the case of O4. The refinement and successive difference Fourier synthesis excluding O4 showed this atom to be located off the mirror plane. In the further refinement this was accounted for with an occupancy factor of 0.5 for each site; the O4 thermal parameter was fixed at $U = 0.015$ Å; other oxygens were also treated isotropically. R factors for this refinement are $R = 0.061$, $R_w = 0.072$. For some atoms the thermal parameters along the **a**-axis were up to several times larger than those along **b**; the ratio decreased from the SrO layer to the fluorite block. Thermal parameters along **c** were always much higher than those along **b**. The only exception is Bi, due to the high value of U_{22} in comparison with the other atoms. These observations confirmed that the modulation displacements are mainly in the *ac* plane. Occupancy refinement of the Bi site showed no evidence for vacancies. Occupancy refinement of Sr and Nd in the Sr/Nd site gave occupancies only slightly different from that of the starting composition. The composition of the final refinement was $Bi_2Sr_{1.7}Nd_{1.8}Ce_{0.5}Cu_2O_{10}$. The results of this refinement are listed in Table 2 (second line for each cell).

In the subsequent refinement the modulation was taken into account. The function used to describe the positional modulation of all atoms but O4 is

$$\mathbf{U} = \sum_{l=1}^{m} [\mathbf{U}_s^l \sin(2\pi l x_4) + \mathbf{U}_c^l \cos(2\pi l x_4)], \qquad [1]$$

where $\mathbf{U}_s^l$ and $\mathbf{U}_c^l$ are amplitude vectors of the sin and cos waves of the lth harmonic, and x_4 is the coordinate in the fourth (internal) dimension, which describes the position along the modulation vector. The first and second harmonics were included (i.e., $m = 2$). The difference Fourier section of the four-dimensional density parallel to **a** through the O4 site (Fig. 2) is very similar to that of the corresponding atom in the 2212 phase (1, 2). As in Ref. (1), a sawtooth-like function was used to describe the modulation of O4,

$$\mathbf{U} = 2\mathbf{U}_0 (x_4 - x_4^0)/\Delta, \qquad [2]$$

where $\mathbf{U}_0$ is the amplitude of modulation and Δ is the period of the function. If Δ is greater than 1, adjacent sawteeth overlap by $(\Delta - 1)/2$, which implies that an additional $(\Delta - 1)$ oxygen atoms exist in the overlapping region. For the Bi atom the modulation of the thermal parameters was also refined. Resulting R factors are (0.046|0.030, 0.051, 0.106) (here and below these values stand for R_{overall}, R_0, R_1, R_2). The resulting equivalent

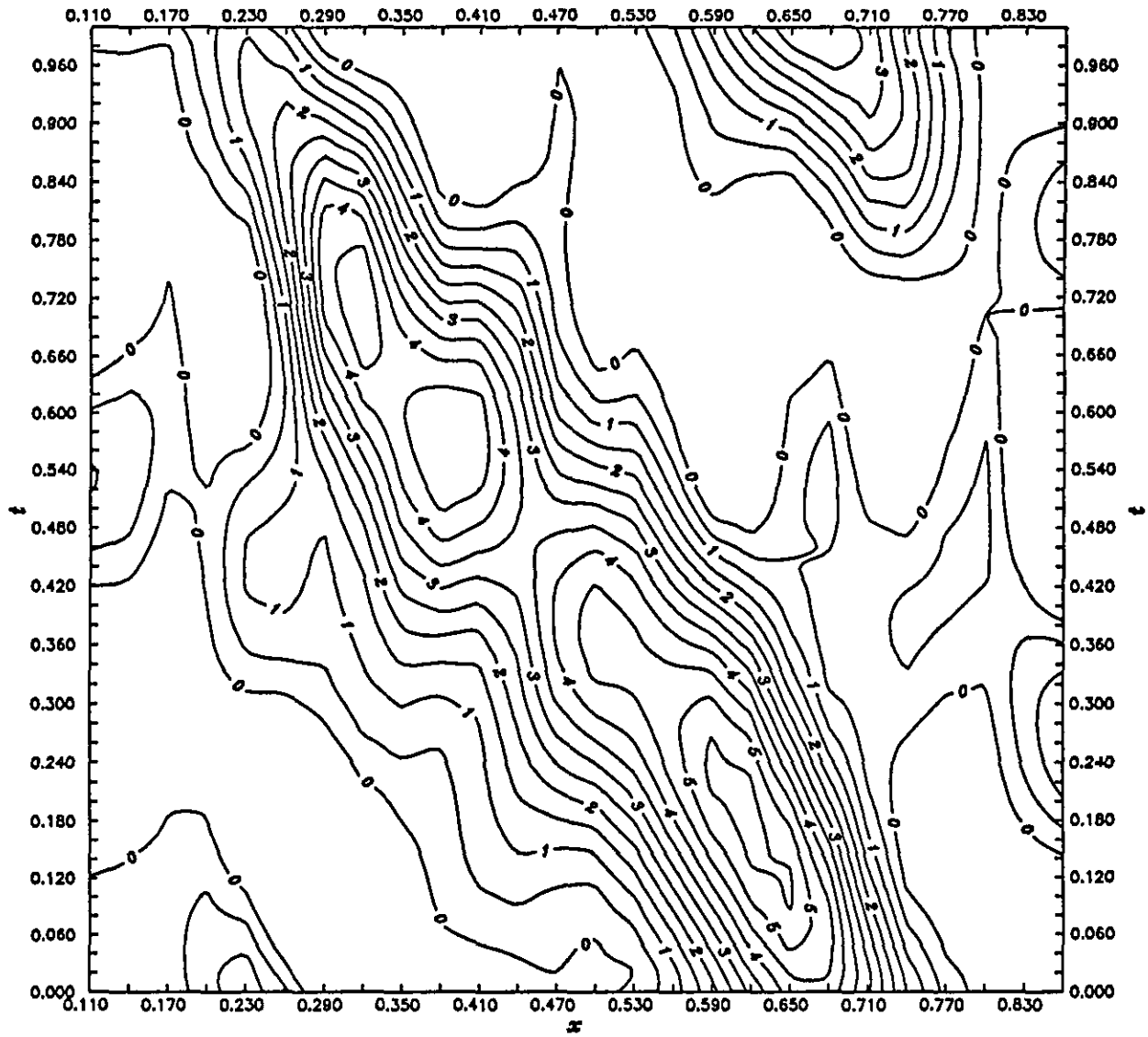

FIG. 2. x–t section of the four-dimensional difference Fourier map showing the modulation of the oxygen atom O(4) at $y = 0.145$, $z = 0.202$. Contours at intervals of 0.5 $e/Å^{-3}$.

isotropic thermal parameter for Cu was slightly negative (by less than 1σ).

Additional refinement including the modulation of the Sr/Nd thermal parameter modulation gave slightly lower R factors (0.045|0.031, 0.050, 0.101). A final refinement with thermal parameter modulation for all cations yielded R factors of (0.042|0.030, 0.046, 0.094). In all refinements, the thermal parameter for copper remained slightly negative, as was the case for the 2212 phase (1). An occupancy refinement of the Bi site again showed no evidence for vacancies. The results of this last refinement are given in Tables 2–3 while interatomic distances are listed in Table 4.

The O4 difference density (Fig. 2) shows the existence of extra oxygen for some t sections, corresponding to specific unit cells along the modulation vector.[3] The value of $\Delta = 1.16(4)$ corresponds to $\delta = 0.32(8)$ in the *stoichiometric formula.*

Since the Sr/Nd site is occupied by two atom types with different ionic radii, the occupancy of the site itself may be modulated, i.e., the probability of finding a particular atom type on the site may be dependent on the structural displacements. The Sr/Nd thermal parameter U_{11} is slightly negative in some unit cells (with a minimum of $-0.009(6)$ Å^2). In an alternate refinement the occupancy modulation of the Sr/Nd site was refined rather than the

[3] $t = x_4 - \mathbf{q}\cdot\mathbf{r}$, where $\mathbf{r}$ is the position vector of the atom. Positions of different atoms can be compared for one and the same t for both atoms, that is for one and the same three-dimensional section of four-dimensional space.

TABLE 3
Amplitudes (Å) of the Positional and Thermal Parameter (Å × 10^3) Modulations for $Bi_2Sr_{1.7}Nd_{1.8}Ce_{0.5}Cu_2O_{10+\delta}$

Atom	Wave	U_x	U_y	U_z	U_{11}	U_{22}	U_{33}	U_{13}
Bi	$\sin(2\pi x_4)$	0.317(2)	0	0.017(5)	26(2)	−1(3)	−2(2)	2.2(7)
	$\cos(2\pi x_4)$	0	0	0.102(2)	25(1)	−5.6(8)	2.7(5)	−2(2)
	$\sin(4\pi x_4)$	0.003(3)	0	0.026(7)	−3(2)	−1(4)	−5(2)	−2.2(7)
	$\cos(4\pi x_4)$	0.048(6)	0	−0.031(3)	2(1)	−3(1)	−0.3(9)	−1(2)
Sr/Nd	$\sin(2\pi x_4)$	0.243(3)	0	0.05(1)	−17(2)	6(3)	18(4)	−3(1)
	$\cos(2\pi x_4)$	−0.05(1)	0	0.251(4)	12(2)	−5(2)	−7(2)	8(3)
	$\sin(4\pi x_4)$	0.034(6)	0	0.04(1)	−6(4)	−3(6)	−12(4)	2(2)
	$\cos(4\pi x_4)$	−0.097(8)	0	0.047(6)	6(2)	2(3)	1(2)	2(2)
Cu	$\sin(2\pi x_4)$	0.086(4)	0	0.06(2)	14(3)	−2(7)	5(6)	−8(2)
	$\cos(2\pi x_4)$	0.052(9)	0	0.243(5)	−5(2)	1(2)	4(2)	−6(2)
	$\sin(4\pi x_4)$	0.022(7)	0	0.02(1)	16(3)	−5(6)	−6(6)	−2(2)
	$\cos(4\pi x_4)$	0.04(1)	0	0.018(7)	−5(3)	−3(4)	−11(3)	1(3)
Nd/Ce	$\sin(2\pi x_4)$	0042(2)	0	0.019(8)	−3(2)	−2(3)	−10(3)	−3.7(6)
	$\cos(2\pi x_4)$	−0.019(6)	0	0.246(2)	1.8(8)	0.1(9)	1(1)	1(2)
	$\sin(4\pi x_4)$	−0.006(2)	0	0.036(7)	−5(2)	−2(4)	3(3)	3(1)
	$\cos(4\pi x_4)$	−0.015(5)	0	0.006(4)	0.9(8)	−1(1)	−3(1)	6(2)
O1	$\sin(2\pi x_4)$	0	0.00(2)	0.16(3)				
	$\cos(2\pi x_4)$	0	−0.08(5)	0.24(2)				
	$\sin(4\pi x_4)$	−0.05(3)	0	0				
	$\cos(4\pi x_4)$	0.01(4)	0	0				
O2	$\sin(2\pi x_4)$	0.07(1)	−0.01(2)	0.00(3)				
	$\cos(2\pi x_4)$	0.06(3)	0.00(4)	0.27(3)				
	$\sin(4\pi x_4)$	0.04(2)	0.00(2)	−0.14(2)				
	$\cos(4\pi x_4)$	0.05(3)	−0.05(4)	0.06(2)				
O3	$\sin(2\pi x_4)$	0.41(3)	0	−0.01(7)				
	$\cos(2\pi x_4)$	−0.24(5)	0	0.15(2)				
	$\sin(4\pi x_4)$	0.16(6)	0	−0.06(6)				
	$\cos(4\pi x_4)$	−0.32(5)	0	0.05(4)				
O4	U_0	−1.6(6)	0.10(4)	0.33(3)				
	x_4^0, Δ	0.41(2)	1.16(4)	—				

thermal parameter modulation. The R factors remain practically the same (0.042|0.030, 0.045, 0.097), as do the other variables in the refinement. Sr occupancy modulation parameters are significantly different from zero, and are given in Table 5, for five unit cells along the **a** axis.

IV. DISCUSSION

It is clear that the modulations in the 2222 and 2212 structures are quite comparable, which may be expected as the mismatch between the BiO and CuO_2 layers is the likely cause of the modulation (9). The modulation amplitudes for corresponding atoms are remarkably similar in the two structures.

Compared with the average structure reported by Nakai *et al.* (4), the present results give more reasonable Bi–O distances and thermal parameters. The oxygen modulation function (Eq. [1]) is very similar to that found for the 2212 structure. As Δ in Eq. [2] is larger than 1, some unit cells contain two O4 atoms instead of one, as is the case in the 2212 phase. The overlapping region of the function (Eq. [2]) corresponds to t sections between 0.84–0.90. This t range corresponds to approximately every seventh–ninth unit of each –Bi–O–Bi–O– row parallel to **a**, in agreement with results of Le Page *et al.* for the commensurate analogue $Bi_{10}Sr_{15}Fe_{10}O_{46}$ (10), and of Petricek *et al.* (1) and Gao *et al.* (2) for the 2212 phase. The excess oxygen content, described by δ, equals 0.32(8), which agrees within experimental error with results on related compounds obtained by iodometric titration. For example, for $Bi_2Sr_2(Ln_{1.7}Ce_{0.3})Cu_2O_{10+\delta}$, a value $\delta = 0.24 \pm 2$ was reported (3), while for a series of Eu-containing phases values ranged from 0.03–0.21(3) (11).

TABLE 4
Interatomic Distances for $Bi_2Sr_{1.7}Nd_{1.8}Ce_{0.5}Cu_2O_{10+\delta}$

Atoms	Average structure	Minimum–maximum distances
Bi–O4	3.07(6)	2.50–3.86
	2.58(6)	2.28–3.60
	2.19(2)	2.16–2.30
	3.34(6)	3.29–3.48
Bi–O4[a]	3.34(6)	3.14–3.46
Bi–O3	2.01(2)	1.88–2.21
Sr–O4	2.47(2)	2.18–2.69
Sr–O3	2.72(4)	2.30–3.25
	2.814(4) 2×	2.77–2.87
	2.92(4)	2.42–3.62
Sr–O2	2.69(2) 2×	2.49–2.96
	2.64(2) 2×	2.46–2.83
Cu–O3	2.35(2)	2.16–2.53
Cu–O2	1.96(3) 2×	1.91–2.01
	1.93(3) 2×	1.89–1.99
Nd–O2	2.59(2) 2×	2.43–2.81
	2.57(2) 2×	2.43–2.74
Nd–O1	2.32(2) 2×	2.25–2.40
	2.32(2) 2×	2.23–2.47

[a] Oxygen of the adjacent BiO layer.

TABLE 5
Sr Occupancy Modulation in $Bi_2Sr_{1.7}Nd_{1.8}Ce_{0.5}Cu_2O_{10+\delta}$

Unit cell	1	2	3	4	5
Sr occupancy[a]	0.45(7)	0.19(7)	0.55(7)	0.43(7)	0.62(7)

[a] Sr occupancy function determined by refinement, with standard deviations in parentheses: $g = 0.5*[0.86(1) - 0.29(4)*\sin(2\pi x_4) - 0.08(2)*\cos(2\pi x_4) - 0.28(4)*\sin(4\pi x_4) + 0.11(4)*\cos(4\pi x_4)]$.

The modulation of the cations along the **a** and **c** directions are illustrated in Figs. 3a and 3b. In agreement with results on the 2212 phase (1), the modulation amplitude of the Bi atoms is three times larger along **a** and along **c**, while for the CuO_2 plane block the displacements of the cations are larger along **c** than along **a**. The latter is also true for the R_2O_2 (R = Nd, Ce) layer. The covalent bonds in the CuO_2 layer are sufficiently rigid to prevent significant distortions in directions parallel to the layer. The displacements in this layer along the perpendicular, **c**, direction apparently cause similar distortions in the fluorite block. The displacements in the SrO layer are similar in both **a** and **c** directions. The largest modulation amplitude for O4 (1.62 Å) is in the **a**-axis direction.

The occupation of the Sr/Nd site by two different atoms (Sr and Nd) may give rise to occupancy modulation.

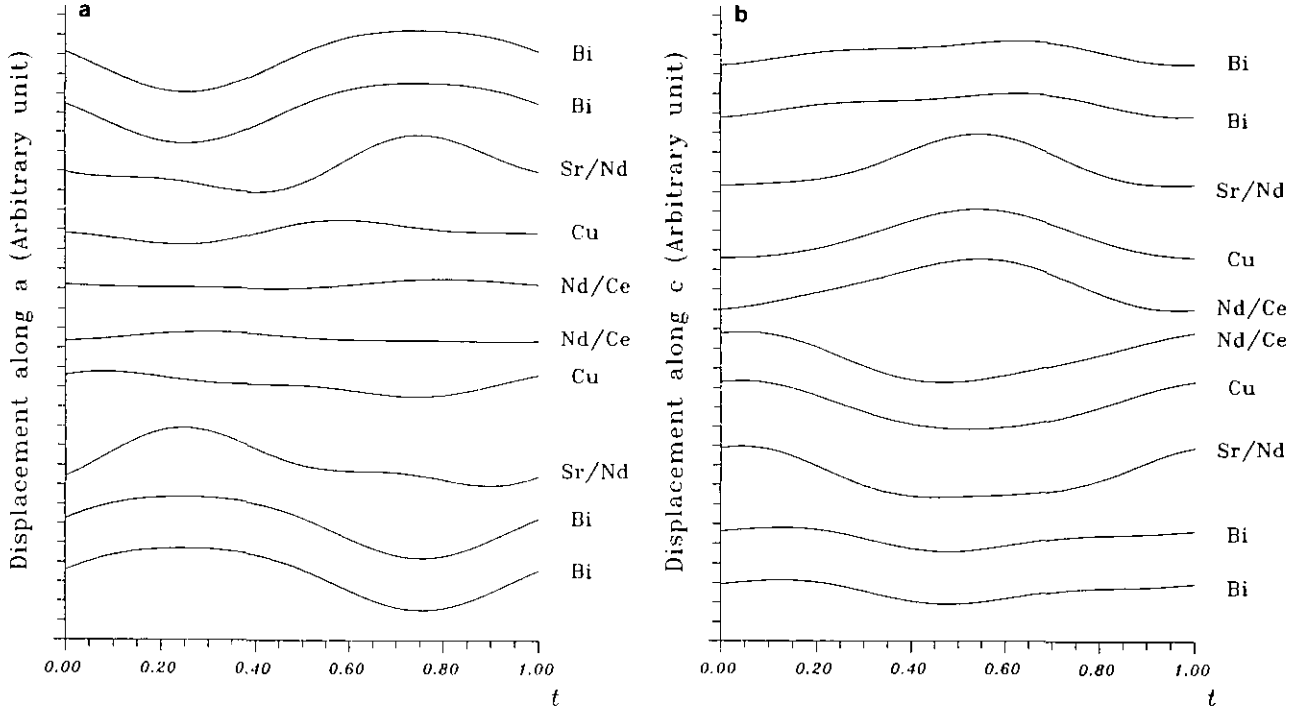

FIG. 3. Displacive modulation of the cations as a function of t. Displacement amplitudes are in arbitrary units. The difference between neighboring unit cells corresponds to the difference $\Delta t \approx 0.228$. (a) Displacement along **a**; (b) diplacement along **c**.

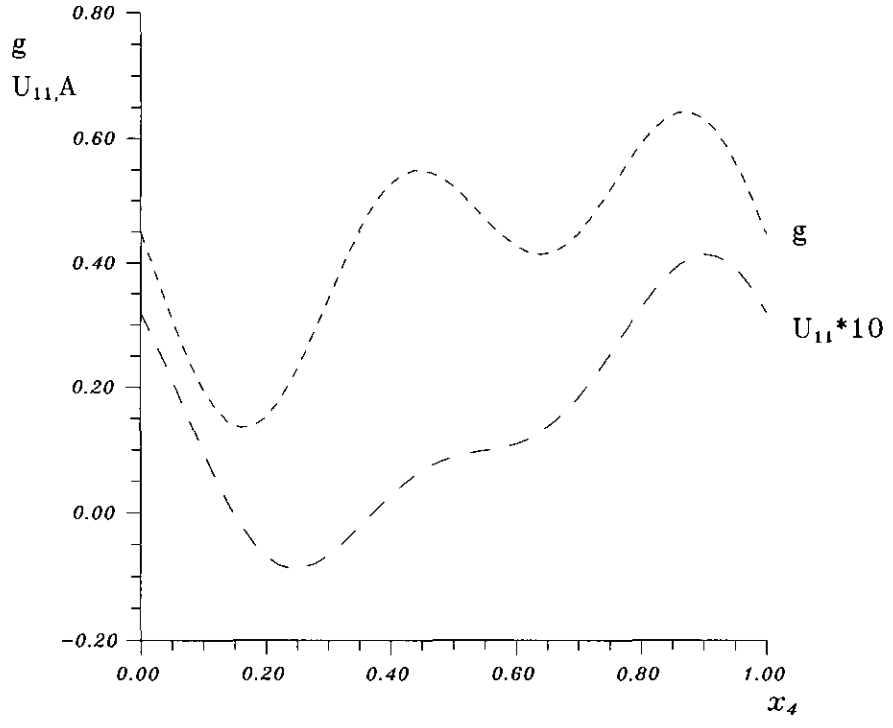

FIG. 4. The dependence of the Nd/Sr site occupancy (g) and U_{11} displacement parameter on the internal coordinate x_4.

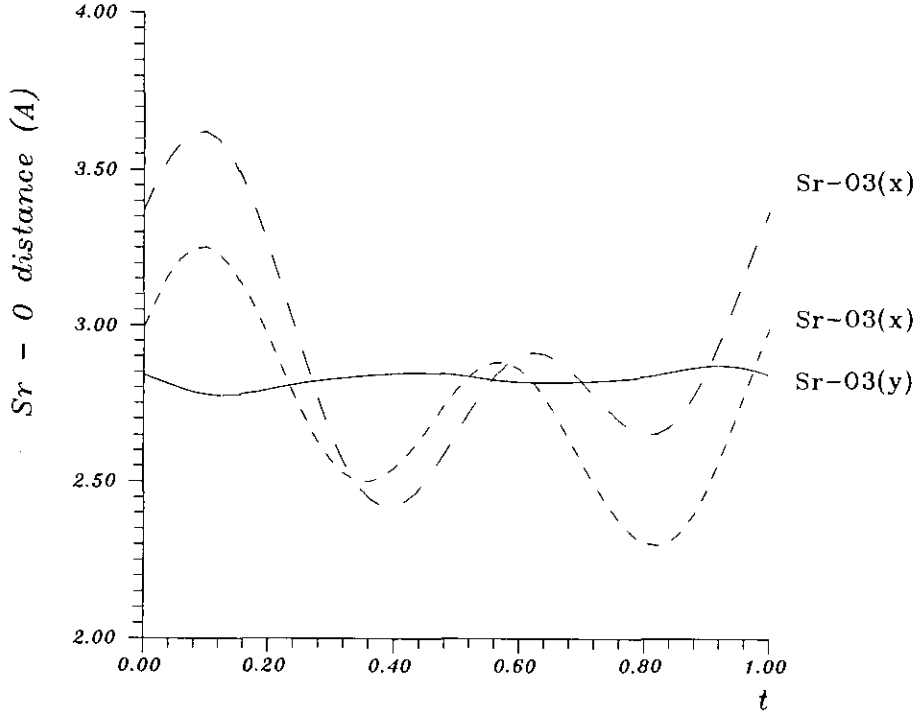

FIG. 5. The (Sr/Nd)–O distances as a function of t. Sr–O(x) distances are to oxygen atoms at a distance $\approx \pm 0.5$ in the x-axis direction; Sr–O(y) distances are to oxygen at a distance ≈ 0.5 in the y-axis direction.

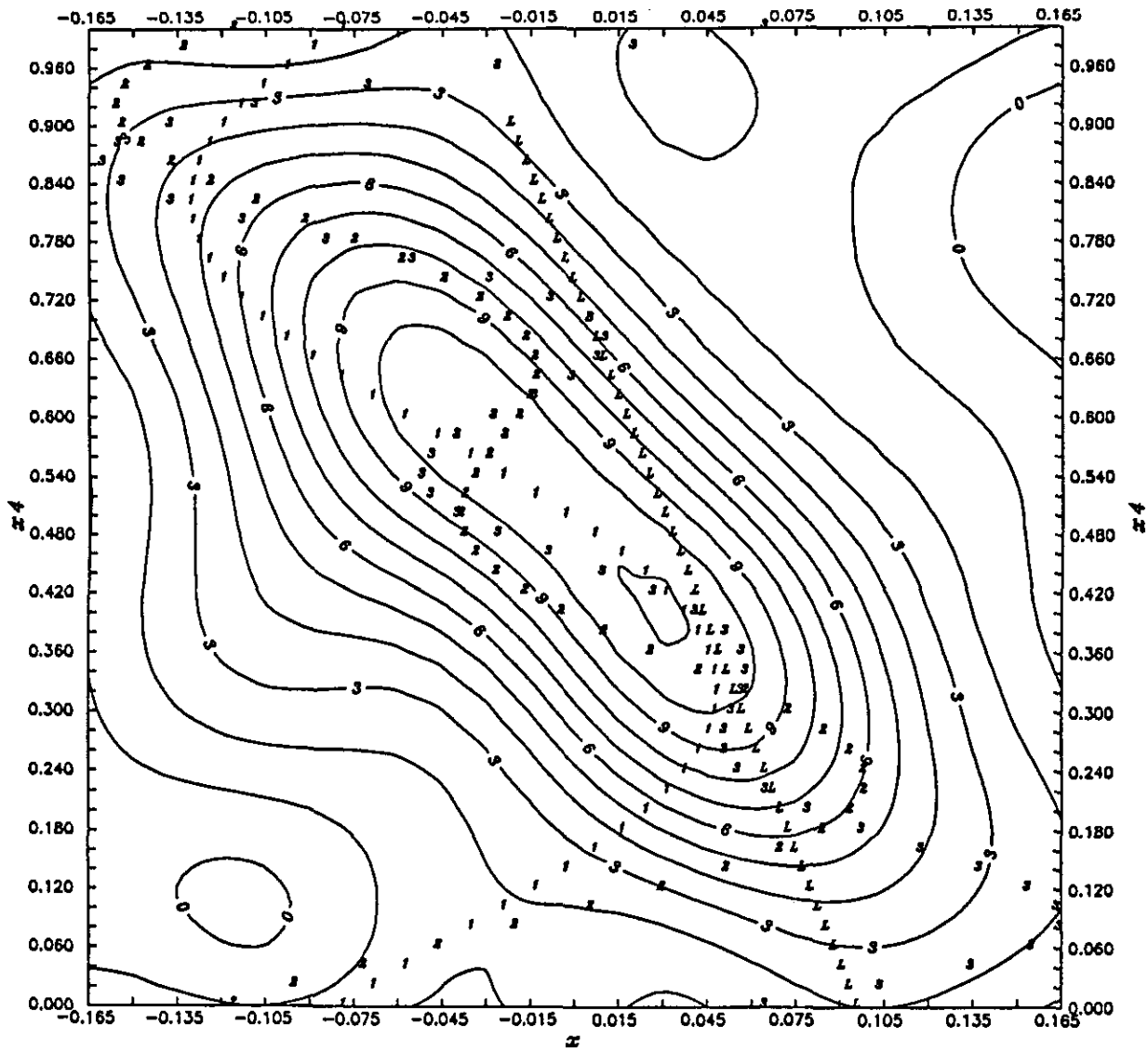

FIG. 6. x–t section of the four-dimensional difference Fourier map showing the modulation of the oxygen atom O(3) at $y = 0.25$, $z = 0.149$, and least-squares refined modulation functions with different number of harmonic terms and a linear function. 1, 2, and 3 correspond to the number of harmonics, and L corresponds to the linear function. Contours at intervals of 1.0 $e/Å^{-3}$.

The dependence of the Sr/Nd thermal parameter U_{11} and the Sr occupancy on x_4 in the two alternate refinements are related, preferred occupancy by the heavier atom (Nd) corresponding to a lower value of the thermal parameter (Fig. 4). As the R factors are similar, no definitive conclusion can be drawn, but it is clear that either a thermal-parameter or an occupancy modulation is present. The dependence of Sr/Nd–O distances on t is shown in Fig. 5. For t sections within the −0.06–+0.24 interval some of Sr/Nd–O3 distances become too large even for the Sr atom, so the coordination number in this region appears to be 7 rather than 9. As the maximum neodymium probability occurs at $t = 0.15$–0.25, the occupancy modulation may be related to the shift of the oxygen atoms and the decrease of the cation coordination number.

A related problem is the description of O3 modulation by the harmonic function (Eq. [1]). The shape of the O3 peak in the $x - x_4$ section of the Fourier map (Fig. 6) somewhat resembles a distorted sin function with a very large linear part. We refined the displacement with one, two, and three harmonic terms, and with a linear function. None of these describes the shape of the peak well in t sections quite close to 0 (±0.10). Because of this, the Sr/Nd–O distances may differ from those calculated from the refinement parameters by up to 0.2–0.4 Å. Even

after taking this difference into account at least one of the Sr/Nd–O distances remains too large for Nd, and the coordination number is not more than 8 for the sections with the maximum neodymium content.

V. SUMMARY OF CONCLUSIONS

1. The modulation in the Nd-containing Bi-2222 phase and the Bi-2212 phase are very similar.

2. The linear oxygen displacement model first applied in the analysis of the 2212 phase also describes the modulation of the Bi–O plane oxygen atoms in the 2222 phase. The excess of oxygen in the 2222 phase is located in the BiO layers.

3. The modulation of the Sr/Nd site can be refined with either thermal-parameter or occupancy modulation. The two models cannot be distinguished from diffraction data, but the stoichiometry and the modulation of the Sr/Nd–O distances provide some support for the occupancy modulation model.

VI. ACKNOWLEDGMENTS

Support of this work by the National Science Foundation (CHE9021069), the New York State Institute on Superconductivity (NYSIS90F030), and the Russian Scientific Council on Superconductivity (Poisk) is gratefully acknowledged. We thank Dr. K. Kalmikov for help in EDX analysis of the crystal on which this refinement is based.

REFERENCES

1. V. Petricek, Y. Gao, P. Lee, and P. Coppens, *Phys. Rev. B* **42,** 387 (1990).
2. Y. Gao, P. Coppens, D. E. Cox, and A. R. Moodenbaugh, *Acta Crystallogr., Sect. A* **49,** 141 (1993).
3. Y. Tokura, T. Arima, H. Takagi, S. Uchida, T. Ishigaki, H. Asano, R. Beyers, A. I. Nassal, P. Lacorre, and J. B. Torrance, *Nature* **342,** 890 (1989).
4. I. Nakai, K. Imai, T. Arima, Y. Tokura, H. Asano, H. Takagi, S. Uchida, R. Beyers, and J. B. Torrance, *Jpn. J. Appl. Phys.* **29,** L572 (1990).
5. ZAF-correction, Copyright CAMECA, 1978.
6. P. M. de Wolff, T. Janssen, and A. Janner, *Acta Crystallogr., Sect. A* **37,** 625 (1981).
7. V. Petricek, *Acta Crystallogr., Sect. A* **45,** 61 (1989).
8. V. Petricek and P. Coppens, *Acta Crystallogr., Sect. A* **44,** 1051 (1988).
9. J.-M. Tarascon, Y. Le Page, and W. R. McKinnon, *Eur. J. Solid State Inorg. Chem.* **27,** 81 (1990).
10. Y. Le Page, W. R. McKinnon, J.-M. Tarascon, and P. Barboux, *Phys. Rev. B* **40,** 6810 (1989).
11. N. R. Khasanova, A. L. Kharlanov, E. V. Antipov, L. M. Kovba, A. A. Gippius, and V. V. Moshchalkov, *Physica C* **190,** 522 (1992).