Effect of physical and chemical pressure on the superconductivity of high-temperature oxide superconductors

A. A. R. Fernandes,* J. Santamaria,† S. L. Bud'ko,‡ O. Nakamura,§ J. Guimpel,** and Ivan K. Schuller
Physics Department 0319, University of California-San Diego, La Jolla, California 92093-0319
(Received 22 April 1991)

We have compared the changes in the structure and superconductivity of the $Gd_{1-x}Y_xBa_2Cu_3O_{7-\delta}$ system produced by rare-earth-ion substitution (chemical pressure) and by hydrostatic pressure. Although the application of both chemical and physical pressure result in an overall compression of the unit cell, the effect on T_c is of opposite sign. A detailed comparison of the evolution of the structure under both kinds of pressure shows that the origin of this qualitatively different behavior in T_c is correlated with the apical oxygen to CuO_2-plane distance which also presents opposite trends. The origin of this difference is found in the extremely inhomogeneous character of the chemical pressure which, in spite of inducing an overall compression of the structure, produces an expansion of certain regions of the unit cell.

One problem satisfactorily solved for the 1:2:3 cuprates was the existence of a single superconducting compound with a layered perovskite crystalline structure. This well-known structure including oxygen ordering was resolved by Rietveld refinement of neutron-diffraction data.[1] However the relation between this structure and the origin of superconductivity has not been elucidated. Various structural distances have been claimed to be crucial for the superconductivity of high-T_c oxides. Kamimura[2] has claimed within the framework of a spin-polaron model that the Cu(2)-O(4) (Ref. 3) overlap affects the Cu site Hund's coupling between the Cu $d_{x^2-y^2}$ and Cu d_{z^2} levels affecting in turn the effective spin-spin interaction. Cava[4] has related the critical temperature with the charge transfer to the CuO_2 planes whose changes are mainly due to the Cu(2)-O(4) bond-length changes. The same Cu(2)-O(4) distance is important within the anharmonic phonon model proposed by Müller.[5] Hirsch[6] has introduced a BCS model in which the charge carriers are holes moving through the oxygen-anion lattice in the CuO_2 planes with hopping rate dependent on the O(2)-O(3) distance. Hamiltonians which take account of the site Coulomb interaction have been proposed[7,8] in order to model the behavior of the CuO_2 planes with an obvious dependence of the hopping rates on the interatomic distances.

With this background the experimental study of the effect of pressure on the structure and superconducting properties of the high-T_c cuprates is of great importance. Determination of the crystalline structure under pressure using diffraction methods is not an easy experimental task. A possible alternative is the use of "chemical pressure," i.e., the substitution of ions of different sizes to induce changes in the crystalline lattice. For this purpose the $R Ba_2Cu_3O_{7-\delta}$ systems—where R is Y or a rare earth with the exception of Pr, Ce, and Tb—provide the interesting advantage that the superconducting critical temperature is only slightly affected by the substitution of the trivalent ion on the R site.[9] In this way it is possible

to induce changes in the material structure without completely suppressing the superconductivity. Moreover, recently it was shown[10] that hydrostatic and chemical pressures have opposite effects in the superconducting and magnetic properties of the $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system.

The main goal of this paper is to determine which structural parameter is mainly responsible for the pressure dependence of T_c. For this purpose we chose $Gd_{1-x}Y_xBa_2Cu_3O_{7-\delta}$ as a model system[11] to induce chemical pressure without modifying other physical properties of the system. We studied the evolution of the crystalline structure and the superconductivity of $Gd_{1-x}Y_xBa_2Cu_3O_{7-\delta}$ as a function of Y concentration, x. The structure was determined by Rietveld refinement[12] of powder x-ray-diffraction spectra (XRD) and the critical temperature and its pressure dependence were determined from electrical resistivity measurements. The results show that chemical and physical pressures have opposite effect on the superconducting properties of high-temperature oxides. A comparison of the evolution of the structure in both cases shows that there is a direct correlation between the changes in T_c and the Cu(2)-O(4) distance. Moreover, the data indicates that the changes in all other distances are not correlated with the changes in T_c. This may provide an important clue in determining possible mechanisms responsible for the superconductivity in high-temperature oxide superconductors.

$Gd_{1-x}Y_xBa_2Cu_3O_{7-\delta}$ ceramics were prepared from high purity Gd_2O_3, Y_2O_3, $BaCO_3$, and CuO. After the oxides were mixed and ground the resulting powder was calcined 2 h in air at 930 °C and cooled to room temperature at a rate of 10 °C/min. This procedure was repeated three times. The powder was then pressed into a pellet, heat treated in a flow of O_2 at 950 °C for 6 h, and cooled to 400 °C at a rate of 2 °C/min. This temperature was maintained for 6 h and then the pellet was cooled down to room temperature at 2 °C/min. Iodometric titration[13] on representative samples showed the oxygen content to be $7.00\pm.05$.
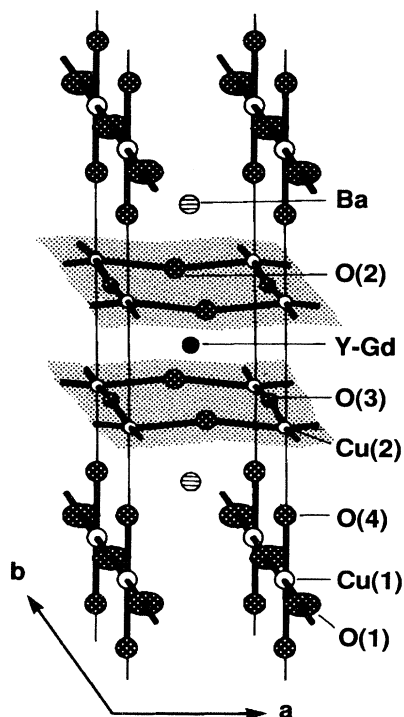
FIG. 1. Unit cell structure and nomenclature of ions for $Gd_{1-x}Y_xBa_2Cu_3O_{7-\delta}$. Drawing of structure and nomenclature of ions after Ref. 1.

XRD measurements were performed on a rotating-anode Rigaku diffractometer (model D/Max-B) equipped with a graphite monochromator. All the samples studied showed a single-phase XRD spectrum. The structural parameters were refined using the RIETAN program[14] for the Rietveld refinement of powder XRD spectra. The orthorhombic $RBa_2Cu_3O_{7-\delta}$ system has the *Pmmm* (No. 47) space symmetry group.[1] Figure 1 shows the structure of the unit cell and ion nomenclature adopted.[3] Table I defines the refined and fixed parameters. It was found that the noise level of our data provided enough sensitivity to refine the positions of the O ions but not their occu-

pation or Debye-Waller factors. Changes of more than 10% did not show any significant difference within the experimental error bars. Because of this fact the oxygen occupancies were fixed at one atom per site in accordance to titration experiments and the Debye-Waller coefficients were fixed at the values reported by Beno *et al.*[1] Refinements were carried out modeling the sample as a mixture of $GdBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_3O_{7-\delta}$ phases. This hypothesis does not fit the experimental data which indicates that these samples consist of $Gd_{1-x}Y_xBa_2Cu_3O_{7-\delta}$ solid solutions. For these, the R position in the center of the unit cell, is occupied by both Y and Gd. Several methods were used to refine this position; (a) the occupancies of Y and Gd were refined independently, (b) the occupancies of Y and Gd were refined with the constraint that they should add up to 1, (c) the occupancies of Y and Gd were fixed at the nominal composition. All these methods gave the same results within statistical deviation and for cases (a) and (b) the refined composition coincided with the nominal composition within 10%. As a test for the uniqueness of the results we used both pure $YBa_2Cu_3O_{7-\delta}$ and the pure $GdBa_2Cu_3O_{7-\delta}$ structures as starting point for the refinement procedure. In both cases convergence occurred to the same set of structural parameters.

The temperature dependence of the resistivity was measured in the 8–290 K range with a four-probe dc method on slabs of size $1\times1\times7$ mm^3. The pressure dependence of the resistivity was measured in the 0.5–16-kbar range by a four-probe ac setup and current densities smaller than 3 Å/cm^2. Measurements under pressure were performed in a piston-cylinder hydrostatic-pressure cell similar to that used in Ref. 15 with a 40:60 mineral oil:pentane mixture as pressure medium. The temperature was measured using a SiO_2 diode in thermal contact with the exterior of the cell. At the typical temperature sweep rate of 0.1 K/min used in the experiments there was no thermal lag between sample and thermometer and the resistance data was the same both in cooling down and warming up. In the pressure range under consideration both the transition width and the normal state resistivity at the onset of the transition remained constant. Because of this fact within experimental accuracy the pressure derivative, dT_c/dP, was in-

TABLE I. Fixed and refinable parameters for the XRD Rietveld refinement in $Gd_{1-x}Y_xBa_2Cu_3O_{7-\delta}$. Relative ion position in the unit cell, x, y, z, in units of lattice parameters a, b, c, respectively, occupancy, g, of the site, isotropic thermal parameters, B, in Å^2. Numerical values indicate fixed parameters.

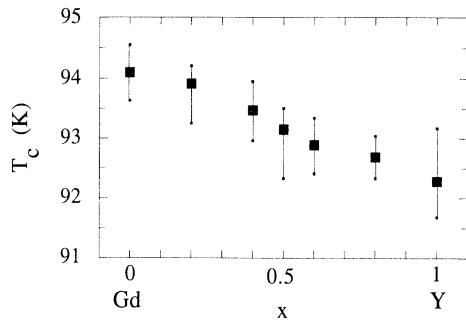|	x	y	z	g	B
Y	0.5	0.5	0.5	g_Y	B_Y
Gd	0.5	0.5	0.5	g_{Gd}	B_{Gd}
Ba	0.5	0.5	z_{Ba}	1	B_{Ba}
Cu(1)	0	0	0	1	$B_{Cu(1)}$
Cu(2)	0	0	$z_{Cu(2)}$	1	$B_{Cu(2)}$
O(1)	0	0.5	0	1	1.12
O(2)	0.5	0	$z_{O(2)}$	1	0.62
O(3)	0	0.5	$z_{O(3)}$	1	0.64
O(4)	0	0	$z_{O(4)}$	1	0.75

FIG. 2. Transition temperature, T_c, as a function of yttrium concentration, x, in the system $Gd_{1-x}Y_xBa_2Cu_3O_{7-\delta}$. Bars indicate the 10–90 % transition width.

FIG. 4. Lattice parameters a, b, and c as a function of yttrium concentration, x, in the system $Gd_{1-x}Y_xBa_2Cu_3O_{7-\delta}$. Lines show linear fit to the data.

dependent of the specific definition of T_c. The extrapolation of T_c to $P=0$ coincided with the independent dc resistivity measurements.

Figure 2 shows the critical temperature T_c as a function of x was defined at 50% of the resistive transition and the bars indicate the 10–90 % transition width. The monotonic *decrease* in T_c is clearly independent of the criterion used for the definition of T_c. Figure 3 shows the pressure dependence of T_c for several values of x. It is clear that in the studied pressure range T_c *increases* linearly with pressure for all compositions. The limiting values of dT_c/dP for $x=0$ and $x=1$ are in good agreement with the literature[16] and dT_c/dP decreases linearly with x, as shown in the inset of Fig. 3.

Table II shows the structural parameters obtained from the Rietveld refinement of XRD as a function of yttrium concentration, x. It should be stressed that, as explained previously, these parameters have been obtained by a variety of different methods to assure us that they
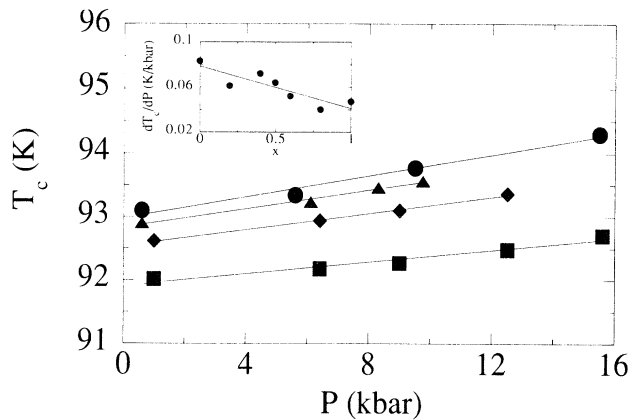
are not spurious results caused by the numerical refinement procedure.

Figure 4 shows the relationship between the lattice parameters and x. The lattice parameters decrease linearly as a function of composition x; the decrease in a being larger than in b or c. From the figure it is obvious that the lattice undergoes a monotonic compression when Gd is substituted by Y. The orthorhombic lattice strain defined as $e=2(b-a)/(b+a)$ increases monotonically from 1.44×10^{-2} to 1.64×10^{-2}. This result and the above results for the pressure derivative of T_c are in agreement with the trends[17,18] observed in oxygen-deficient (1:2:3), (2:4:7), (1:2:4), and $YBa_2(Cu_{1-x}M_x)O_{7-\delta}$ compounds for which dT_c/dP increases with decreasing orthorombicity.

At this point the naive overall conclusion from the *structural* point of view is that the application of chemical pressure is equivalent to the application of hydrostatic pressure since both lead to an overall compression of the unit cell. This is in agreement with expectations based on the relative ionic sizes of Gd and Y, i.e., the substitution

FIG. 3. Critical temperature, T_c, as a function of pressure, P, in the system $Gd_{1-x}Y_xBa_2Cu_3O_{7-\delta}$ for $x=0$ (solid circles); $x=0.4$ (solid triangles); $x=0.5$ (solid diamonds); $x=1$ (solid squares). Lines show linear fits to the data. The inset shows the pressure derivative dT_c/dP as a function of x.
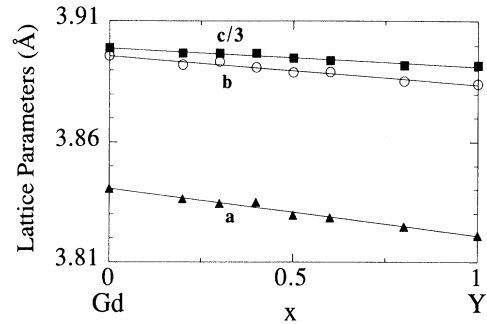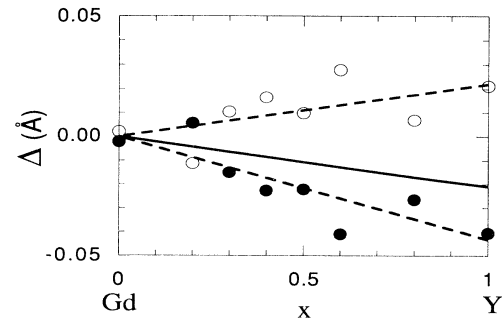

FIG. 5. Composition, x, induced changes, Δ, in the lattice parameter c (solid line), the distance between the CuO_2 planes (solid circles) and difference between them, i.e., height of the rest of the unit cell (empty circles). Dashed lines are linear fits to the data. Solid line for lattice parameter c is a linear fit to the data in Fig. 4.

TABLE II. Results of the Rietveld refinement of the powder XRD. Lattice parameters a, b, and c are expressed in Ångstroms, fractional positions of the ions, z, are expressed in units of c. Thermal parameters B are expressed in Å^2. R_e and R_{up} are statistical indicators of the model defined as

$$R_e = \left[\frac{N_p - N_r - N_c}{\sum_i w_i [y_i(0)]^2} \right]^{1/2},$$

$$R_{up} = \left\{ \frac{\sum_i w_i [y_i(0) - y_i(c)]^2}{\sum_i w_i [y_i(0)]^2} \right\}^{1/2},$$

where N_p is the number of experimental data, N_r is the number of refinable parameters, N_c is the number of constraints, $y_i(0)$ and $y_i(c)$ are the observed and calculated data points and w_i is the statistical weight of the data point. The values in parentheses indicate the calculated error in the last significant figure.

x	1	0.8	0.6	0.5	0.4	0.3	0.2	0
a	3.820 9(1)	3.824 6(1)	3.828 4(1)	3.829 4(1)	3.834 9(1)	3.834 4(1)	3.836 3(1)	3.840 5(1)
b	3.884 3(1)	3.885 4(1)	3.889 3(1)	3.889 1(1)	3.891 2(1)	3.893 6(1)	3.892 3(1)	3.895 9(1)
c	11.676 7(3)	11.676 3(2)	11.682 8(2)	11.683 7(2)	11.689 7(3)	11.691 4(2)	11.690 5(2)	11.695 9(2)
z_{Ba}	0.183 4(3)	0.183 6(3)	0.183 6(2)	0.183 2(3)	0.183(3)	0.183 4(2)	0.183 4(3)	0.183 3(3)
$z_{Cu(2)}$	0.354 6(7)	0.354(8)	0.354 7(8)	0.353 9(9)	0.354(8)	0.353 7(6)	0.352 8(9)	0.353 2(8)
$z_{O(2)}$	0.378(3)	0.377(3)	0.376(3)	0.374(3)	0.372(3)	0.372(2)	0.372(3)	0.369(2)
$z_{O(3)}$	0.378(3)	0.376(3)	0.376(3)	0.376(3)	0.379(3)	0.374(2)	0.381(3)	0.377(3)
$z_{O(4)}$	0.161(3)	0.163(3)	0.162(2)	0.165(2)	0.161(3)	0.166(3)	0.162(4)	0.164(3)
B_Y	0.5(15)	1.4(70)	1.0(12)	1.1(14)	1.02	0.75	1.02	—
B_{Gd}	—	2(28)	1.3(15)	1.1(18)	1.3(3)	1.02	1.3(4)	0.7(2)
B_{Ba}	1.0(1)	1.6(1)	1.2(1)	1.2(1)	0.85(1)	0.4(1)	0.8(2)	0.6(1)
$B_{Cu(1)}$	1.1(4)	2.4(4)	1.7(4)	1.5(4)	1.3(4)	0.2(3)	1.9(6)	1.1(4)
$B_{Cu(2)}$	0.8(2)	1.2(3)	1.2(2)	1.2(3)	0.8(2)	0.3(2)	0.8(2)	0.4(2)
R_e	1.79	1.97	2.27	2.19	2.18	2.34	2.19	2.47
R_{up}	4.62	7.5	7.4	7.78	6.7	6.63	7.92	7.14

FIG. 7. Cu(2)-O(4) distance as a function of chemical, x (empty circles) and hydrostatic, P (solid circles) pressure. Data for hydrostatic pressure after Jorgensen et al. (Ref. 19).
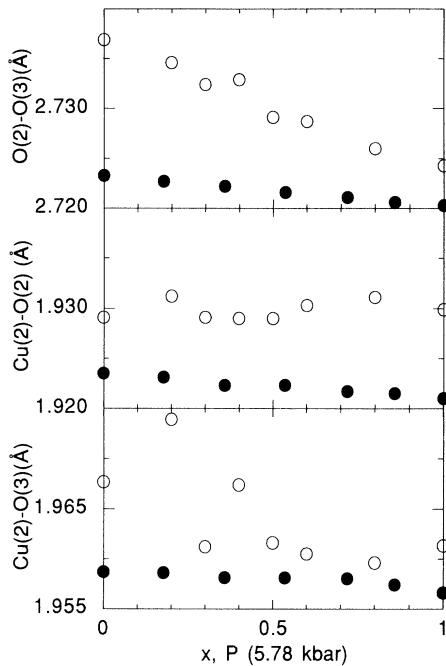

FIG. 6. Intra-CuO$_2$-plane distances as a function of chemical, x (empty circles) and hydrostatic, P (solid circles) pressure. Data for hydrostatic pressure after Jorgensen et al. (Ref. 19).

of a smaller ion is equivalent to applying pressure. However from the *superconducting* point of view the trends are opposite. The substitution of a smaller ion results in a depression of T_c, whereas the application of hydrostatic pressure results in an increase in T_c. The possible cause for this difference is shown in Fig. 5 where we plot the chemical pressure dependence of the lattice parameter c, the distance between CuO$_2$ planes and the difference between them, i.e., the height of the rest of the unit cell. The data indicate that since the distance between CuO$_2$ planes undergoes a higher compression than the whole unit cell in the c direction, the rest of the unit cell undergoes expansion at the same time. It is clear then that the chemical pressure has a highly inhomogeneous character and its equivalence to a compressive or expansive stress depends on the particular interatomic distance which is examined.

The remaining task is to identify which distance is the one that correlates with changes in T_c. A comparison of trends in the structural data as obtained from Rietveld refinement of powder neutron diffraction data and the results presented here may shed some clue to the relevant structural parameter. Figures 6 and 7 show the behavior of the intra-CuO$_2$-plane interatomic distances and of the Cu(2)-O(4) distance both in the case of chemical and hydrostatic pressures.[19] Although, as expected from the lower sensitivity of XRD to the O ions and specially to the O(4) position, the O positions have higher scatter
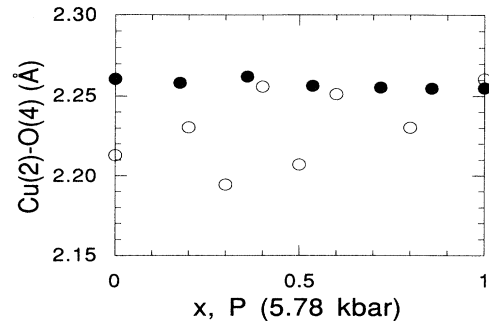
than in the neutron diffraction case some trends can be recognized. From Fig. 6 it is clear that of the intraplane distances only the Cu(2)-O(2) distance has a qualitatively different behavior for chemical and hydrostatic pressures. Under hydrostatic pressure it is reduced while under chemical pressure it either remains constant or increases. However the change in T_c induced by this range of chemical pressure (2 K) is one order of magnitude larger than the one induced by hydrostatic pressure (0.2 K). This is in quantitative disagreement with the data in Fig. 6 and so we must disregard any of the in-plane interatomic distances as the main origin of the pressure dependence of T_c. Within the scatter of our data in Fig. 7 the Cu(2)-O(4) distance changes are the only ones in qualitative and quantitative agreement with the experimental chemical and hydrostatic pressure dependences of T_c.

In conclusion, we found in the Gd$_{1-x}$Y$_x$Ba$_2$Cu$_3$O$_{7-\delta}$ solid solutions a qualitatively different behavior in the chemical and hydrostatic pressure dependences of the critical temperature. This behavior is only correlated with the Cu(2)-O(4) distance indicating that this distance may play an important role in the mechanism controlling the pressure dependence of T_c. The qualitatively different behavior of this distance under chemical or physical pressure is due to the highly inhomogeneous character of the chemical pressure which induces an expansion of the Cu(2)-O(4) distance in spite of the overall compression of the unit cell.

*On leave from Instituto Militar de Engenharia, Brazil.

†On leave from Universidad Complutense de Madrid, Spain.

‡On leave from Institute for High Pressure Physics, Troitsk, Moscow Region, 142092, U.S.S.R.

§On leave from the Tonen Corporation, Tokyo, Japan.

**On leave from Centro Atómico Bariloche, 8400 Bariloche, Argentina.

[1]For structural determination see, for instance, M. A. Beno, L. Soderholm, D. W. Capone II, D. G. Hinks, J. D. Jorgensen, J. D. Grace, I. K. Schuller, C. U. Segrè, and K. Zhang, Appl. Phys. Lett. **51**, 57 (1987).

[2]H. Kamimura, S. Matsuno, and K. Ishida, Physica C **162-164**, 781 (1989).

[3]Throughout this paper we adopt the ion notation defined in Ref. 1.

[4]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 C **165**, 419 (1990).

[5]K. A. Müller, Z. Phys. B **80**, 193 (1990).

[6]J. E. Hirsch, Phys. Lett. A **134**, 451 (1989); F. Marsiglio and J. E. Hirsch. Phys. Rev. B **41**, 6435 (1990).

[7]P. W. Anderson, Science **235**, 1196 (1987).

[8]F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).

[9]R. M. Hazen, in *Physical Properties of High Temperature Superconductors II* edited by D. M. Ginsberg (World Scientific, Singapore, 1990), p. 121, and references therein.

[10]G. Nieva, S. Ghamaty, B. W. Lee, M. B. Maple, and Ivan K. Schuller, Phys. Rev. B **44**, 6999 (1991).

[11]A. Tominaga, F. Nakamura, and Y. Narahara, Jpn. J. Appl. Phys. **26**, L1351 (1987); E. W. Collings, P. J. Melling, S. L. Swartz, R. D. Smith, J. J. Rayment, M. J. Pechan, and M. Pardavi-Horvath, Adv. Cryog. Eng. Matter. **34**, 633 (1988); C. Lin, G. Lu, C.-D. Wei, Z.-X. Liu, Y.-X. Sun, J. Lan, X. Zhu, G.-Z. Li, S.-Q. Feng, Y.-D. Dai, and Z.-Z. Gan, Physica C **153-155**, 190 (1988).

[12]H. M. Rietveld, J. Appl. Crystallogr. **2**, 65 (1969).

[13]A. I. Nazzal, V. Y. Lee, E. M. Engler, R. D. Jacowitz, Y. Tokura, and J. B. Torrance, Physica C **153-155**, 1367 (1988).

[14]F. Izumi, Rigaku J. **6**, 10 (1989); in *Advances in the Rietveld Method,* edited by R. A. Young (Oxford University Press, England, in press).

[15]S. L. Bud'ko, A. G. Gapotchenko, and E. S. Itskevich, Solid State Commun. **69**, 387 (1989).

[16]R. J. Wijngaarden and R. Griessen, in *Studies of High Temperature Superconductors,* edited by A. Narlikar (Nova Science, New York, 1989), Vol. 2, p. 29.

[17]B. Bucher, J. Karpinski, E. Kaldis, and P. Wachter, J. Less-Common Met. **164-165**, 20 (1990).

[18]M. Kurisu, K. Kumagai, Y. Maeno, and T. Fujita, Physica C **152**, 339 (1988).

[19]Data for hydrostatic pressure dependence of the structure was taken from J. D. Jorgensen, S. Pei, P. Lightfoot, D. G. Hinks, B. W. Veal, B. Dabrowski, A. P. Paulikas, R. Kleb, and I. D. Brown, Physica C **171**, 93 (1990).