

## A STRUCTURAL DISTORTION IN THE 123-SUPERCONDUCTOR ISOMORPH $\text{LaBa}_2(\text{Cu}_2\text{Nb})\text{O}_8$

M.-J. REY<sup>a</sup>, Ph. DEHAUDT<sup>a</sup>, J. JOUBERT<sup>b</sup> and A.W. HEWAT<sup>c</sup>

<sup>a</sup> Centre d'Etudes Nucleaires de Grenoble, 85X, F-38042 Grenoble, Cedex, France

<sup>b</sup> Laboratoire des Materiaux et du Génie Physique de l'ENSPG, domaine Universitaire, F-38400 Saint Martin d'Hères, France

<sup>c</sup> Institut Laue-Langevin, 156X, F-38042 Grenoble, Cedex, France

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A low temperature structural transition in the 123-superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  has been proposed involving zig-zag folding of the CuO-chains, but it has not been possible to demonstrate the resulting superlattice reflections because the CuO-chains are broken after relatively short distances unless  $\delta=0$ . In the 123-isomorph  $\text{LaBa}_2(\text{Cu}_2\text{Nb})\text{O}_8$ , which is not a superconductor, Y is replaced by La, and the CuO-chains by planes of NbO-octahedra. We find by direct observation of superlattice reflections that zig-zag folding of the NbO-octahedra can indeed occur in this structure type. The tilt pattern is similar to that of the low temperature phase of  $\text{SrTiO}_3$ , with the same I4/mcm space group.

### 1. Introduction

The earliest low temperature measurements of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  structure [1] showed that it was well ordered except that the oxygen along the CuO-chains was "disordered" perpendicular to the chain axis, even at 5 K. François et al. [2] suggested the possibility of a low temperature structural transition, where the chain oxygen would order to either side of the chain axis, to producing zig-zag chains. Such a transition would be similar to transitions in other perovskite-based structures, such as  $\text{La}_2\text{CuO}_4$ , where complete octahedra tilt against each other. In  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  the CuO-chains are of course incomplete octahedra, being joined by oxygen along the *b*-axis, but with oxygen missing along the *a*-axis.

Unfortunately the coherence length for such zig-zag chains might be rather short, since the chains would be broken by missing oxygen; for example chains would be broken every 10 cells even for very good samples with  $\delta=0.1$ . This makes it very difficult to observe the expected superlattice reflections associated with the doubling of the cell due to the zig-zag chains. François et al. [2] used short wavelength neutrons in an attempt to resolve a double-well po-

sition for O(4), but were unable to demonstrate superlattice reflections.

Murayama [3] has shown that the CuO-chains in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  can be replaced by planes of TaO-octahedra to produce the nonsuperconducting isomorphous compound  $\text{LaBa}_2(\text{Cu}_2\text{Ta})\text{O}_8$ . There is apparently no missing oxygen within these planes of octahedra, which extend indefinitely (fig. 1).  $\text{LaBa}_2(\text{Cu}_2\text{Nb})\text{O}_8$  also exists, and recently Greaves and Slater [4] have studied the room temperature structure of  $\text{La}_{1.1}\text{Ba}_{1.9}\text{Cu}_{2.1}\text{M}_{0.9}\text{O}_8$  (where M=Ta, Nb) using pulsed neutron diffraction, and concluded that the oxygen joining the NbO- or TaO-octahedra is disordered.

Since this structure is otherwise well ordered and oxygen stoichiometric, we decided that it offered a good chance of demonstrating the type of structural instability and superstructure that had been proposed for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  [2]. We therefore examined  $\text{LaBa}_2(\text{Cu}_2\text{Nb})\text{O}_8$  at 5 K and 300 K, using the D1A diffractometer at ILL Grenoble, which has much higher resolution than the pulsed neutron machine used by Greaves et al. We have been able to observe the superlattice reflections directly, and hence obtain the correct space group. In this new model, all oxygen atoms appear ordered, and the distortion

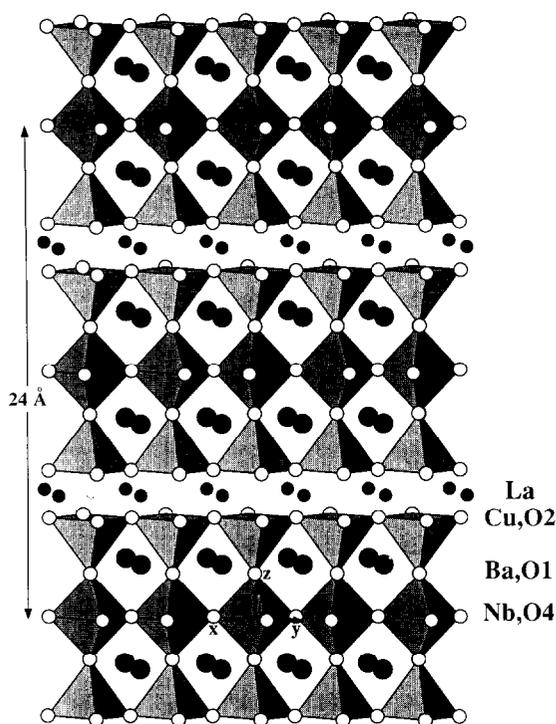


Fig. 1. Crystal structure of  $\text{LaBa}_2(\text{Cu}_2\text{Nb})\text{O}_8$  showing that it is ideally the same as that of tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , with Y replaced by La and the CuO-chains by planes of corner connected NbO-octahedra. These octahedra twist around the  $c$ -axis, with alternate planes twisted in opposite directions. In  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  the CuO-squares forming the chains, which can be regarded as incomplete octahedra, may twist in the same way.

from the ideal 123-type structure is similar to that which occurs at low temperature in perovskite  $\text{SrTiO}_3$ . A similar structural distortion may responsible for the oxygen "disorder" observed in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .

## 2. Sample preparation

The sample was prepared by solid state reaction of  $\text{BaCO}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{CuO}$  in atomic proportions appropriate for a nominal composition of  $\text{Ba}_2\text{LaCu}_2\text{NbO}_8$ . This mixture was pressed into pellets at 200 MPa, and heated twice in air at  $1000^\circ\text{C}$  for 24 hours, with regrinding after each heat treatment.

## 3. Neutron diffraction

All measurements were made in vanadium tubes to avoid extraneous lines in the diffraction patterns, which indicate a single phase sample with only a few weak impurity lines. Data was collected at ambient temperature, and later at 5 K in a He-flow cryostat. The diffraction patterns were refined (fig. 2) using an early version of the Rietveld program [5]. In this program the background is subtracted; the  $R$ -factors are then larger than obtained with programs that also fit the background, but the goodness of fit is independent of the background level.

The P4/mmm model of Murayama [3] was used for the initial structure refinement, except that the oxygen atoms were relabelled to correspond with the labelling of Capponi et al. [1] for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . Figure 1 shows how oxygen O(4) connects the infinite planes of NbO-octahedra which replace the CuO-planes; it was this oxygen that was found to be disordered by Greaves and Slater [4]. Table I shows that the structural parameters obtained with this P4/mmm model are unremarkable except for the large B11 factor for O(4), which indicates strong disorder along the  $x$ -axis, perpendicular to the Nb-O(4) bond. As Greaves and Slater remarked, this is similar to the disorder found in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  [1] and also in  $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14+x}$  [16], and could indicate a rotation of the NbO-octahedra around the  $c$ -axis.

The occupancies of the different sites were also refined to check for possible oxygen deficiency, and for disorder of the cations over the different metal sites. For example, one of the first questions addressed by Murayama [3] was whether Ta completely replaced the 123-chain copper, or whether some replaced the 123-plane copper. Greaves et al. [4] were concerned whether La occupied some of the Ba-sites. Our measurements showed no evidence for cation occupancy disorder, and also no evidence for oxygen deficiency. The occupancies and scattering powers of all sites were therefore fixed at their nominal values for the final refinements reported here.

## 4. P4/mbm and I4/mcm models for $\text{LaBa}_2(\text{Cu}_2\text{Nb})\text{O}_8$

Since by definition  $B = 8\pi^2 \langle u^2 \rangle$  where  $\langle u^2 \rangle$  is the

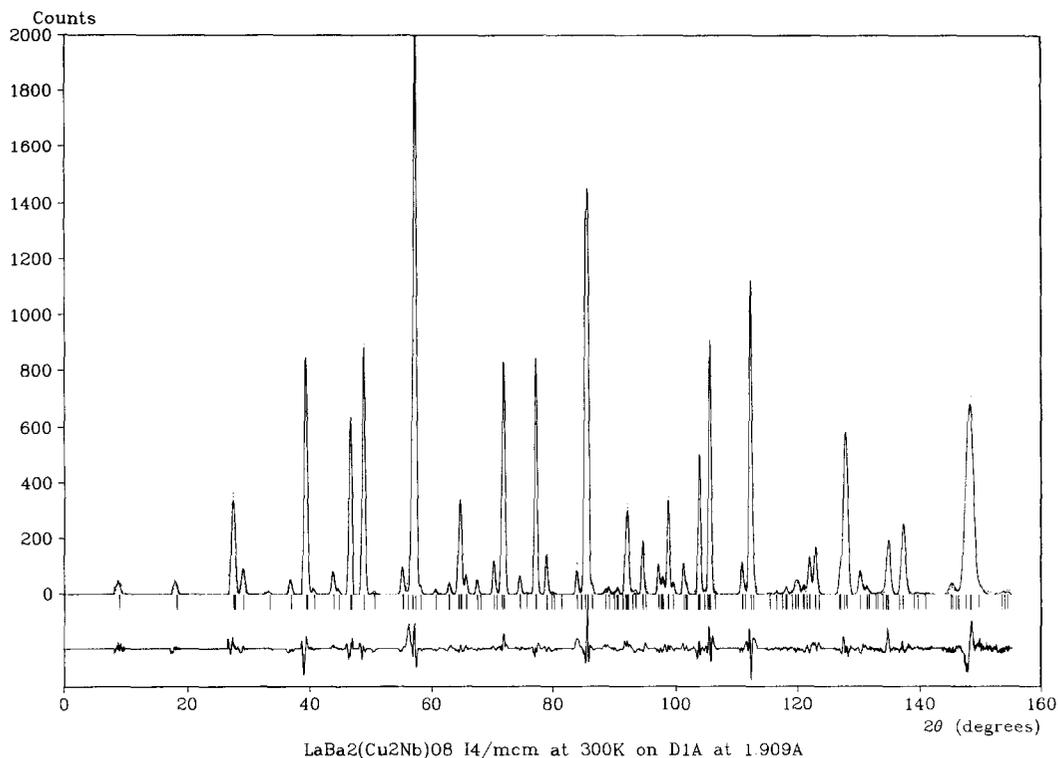


Fig. 2. Observed, calculated and difference neutron diffraction patterns for  $I4/mcm$   $\text{LaBa}_2(\text{Cu}_2\text{Nb})\text{O}_8$  at ambient temperature.

mean square atomic displacement in  $\text{\AA}^2$ , a value of  $B11 = 7.5$  implies large displacements of  $\sim 0.3 \text{\AA}$  for the  $\text{O}(4)$  oxygen atoms. If there is no oxygen deficiency, the connection between the  $\text{NbO}$ -octahedra will be unbroken for large distances. These two conditions mean that it should be possible to observe the superstructure in  $\text{LaBa}_2(\text{Nu}_2\text{Nb})\text{O}_8$ , something that is much more difficult in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .

First, the possible models for this superstructure must be considered. Glazer [7] has classified the many different distorted perovskite structures, and deduced their symmetry and space groups. The two simplest models involve a tilt around one axis of the octahedra; if in successive layers the octahedra tilt in the same direction, the space group is shown to be  $C4/mmb$  i.e.  $P4/mbm$  (No. 127) in the standard coordinate system that we are using. An example is the T2-phase of  $\text{NaNbO}_3$ . If instead the alternate layers tilt in opposite directions, the space group is  $F4/mmc$  i.e.  $I4/mcm$  (No. 140) on our axes. An example is the low temperature phase of  $\text{SrTiO}_3$ . In both

cases, the  $(x, y)$ -axes for the new cell are at  $45^\circ$  to the  $(x, y)$ -axes of the  $P4/mmm$  cell, and the  $(a, b)$  cell dimensions are multiplied by  $\sqrt{2}$ . For  $I4/mcm$ , the  $c$ -axis is also multiplied by 2, since alternate layers of  $\text{NbO}$ -octahedra rotate in opposite directions (fig. 1).

Both these models fit the diffraction pattern well. The structural parameters are very similar to those obtained with  $P4/mmm$  (table I), except of course that the fractional  $z$ -ordinate is halved when the  $c$ -axis is doubled for  $I4/mcm$ . The only real difference between the models is for  $\text{O}(4)$ . Instead of being at  $(-\frac{1}{4}, \frac{1}{4}, 0)$  on the new axes, it is displaced in a direction perpendicular to the  $\text{Nb}-\text{O}(4)$  bond, to  $(-0.23, 0.27, 0)$ . The  $B11 = 22$  factor for  $\text{O}(4)$  is then much more normal, though still higher than for the other atoms. Both these new models, which permit rotations of rigid  $\text{NbO}$ -octahedra, give more physically reasonable parameters than does the original  $P4/mmm$  model. It is not possible to decide between these models on the basis of  $R$ -factors alone.

Table I

Structural parameters for  $\text{LaBa}_2(\text{Cu}_2\text{Nb})\text{O}_8$  for the different models at 300 K. In P4/mmm, the structure is similar to tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with Nb(O(1), O(4))-octahedra replacing the CuO-chains; note the apparent disorder (B22) of O(4). In P4/mbm and I4/mcm, the octahedra twist around [001], and all atoms appear ordered (no large B-factors). At 5 K the *R*-factors are a little larger simply because the count time was shorter.

		P4/mmm (Å)	P4/mbm (Å)	I4/mcm (Å)	I4/mcm-5 K (Å)
<i>a</i>		3.9673(1)	5.6107(2)	5.6107(2)	5.5988(3)
<i>b</i>		3.9673(1)	5.6107(2)	5.6107(2)	5.5988(3)
<i>c</i>		11.9933(5)	11.9933(5)	23.9863(9)	23.9347(12)
Ba	(z)	0.1923(2)	0.1919(2)	0.0960(1)	0.0963(1)
	(B)	0.59(5)	0.61(5)	0.59(5)	0.15(6)
La	(z)	0.5	0.5	0.25	0.25
	(B)	0.69(5)	0.73(5)	0.79(4)	0.50(5)
Nb	(B)	0.50(6)	0.51(6)	0.45(6)	0.14(7)
Cu	(z)	0.3528(1)	0.3531(2)	0.1766(1)	0.1767(1)
	(B)	0.48(3)	0.51(3)	0.50(3)	0.36(4)
O(1)	(z)	0.1615(2)	0.1610(2)	0.0807(1)	0.0813(1)
	(B11)	1.37	1.55	1.55	0.79
	(B22)	1.37	1.55	1.55	0.79
	(B33)	1.38	1.22	0.97	0.66
O(2)	(x)	0.	-0.2490(4)	-0.2510(3)	-0.2506(4)
	(y)	0.5	0.2510(4)	0.2491(3)	0.2494(4)
	(z)	0.3689(1)	0.3688(1)	0.1842(1)	0.1841(1)
	(B11)	0.32	0.25	0.30	0.10
	(B22)	0.32	0.25	0.30	0.10
	(B33)	1.88	1.90	1.86	1.49
O(4)	(x)	0.	-0.2305(7)	-0.2253(5)	-0.2180(5)
	(y)	0.5	0.2695(7)	0.2747(5)	0.2820(5)
	(B11)	7.44	2.71	2.22	2.28
	(B22)	1.22	2.71	2.22	2.28
	(B33)	0.62	1.33	1.36	0.57
<i>R</i> <sub>I</sub>		4.07	5.22	4.78	5.80
<i>R</i> <sub>P</sub>		8.76	9.90	9.39	10.97

since they all fit the strong peaks very well.

For this is necessary to search for the very weak superstructure peaks that must be produced if the (*a*, *b*)-axes are multiplied by  $\sqrt{2}$ , and the *c*-axis by 2. This was not possible with the neutron data of Greaves and Slater [4], but should be possible with the higher resolution D1A data.

Figure 3 shows a portion of the diffraction pattern for scattering near  $2\theta=90^\circ$ , where the strong peaks are indexed as (*h*, *k*, *l*) with *h*+*k*=even and *l*=even on the enlarged I4/mcm cell. Peaks for which *h*+*k*=odd or *l*=odd must of course be zero for the smaller P4/mmm cell. Figure 3 shows that these superstructure peaks are however clearly visible in the neutron diffraction pattern, so the structure cannot be P4/mmm. Since these superlattice peaks corre-

spond to *l*=odd, neither can the structure be P4/mbm, where the *c*-axis is not doubled. Only the I4/mcm cells fits the observed superlattice peaks. The fit is really very good, considering that the I4/mcm model has the same number of parameters as the P4/mbm model, and that the stacking of layers of NbO-octahedra with opposite tilts will not be perfect because of the large distance between these layers. (Occasionally, adjacent layers might have the same tilts.)

The measurement was later repeated at 5 K, where the superlattice peaks are a little stronger, indicating increased rotation of the NbO-octahedra (fig. 3). This is confirmed by the larger displacement obtained for O(4) (table I). It is to be expected that at some higher temperature a structural transition will occur in  $\text{LaBa}_2(\text{Cu}_2\text{Nb})\text{O}_8$ , as in other perov-

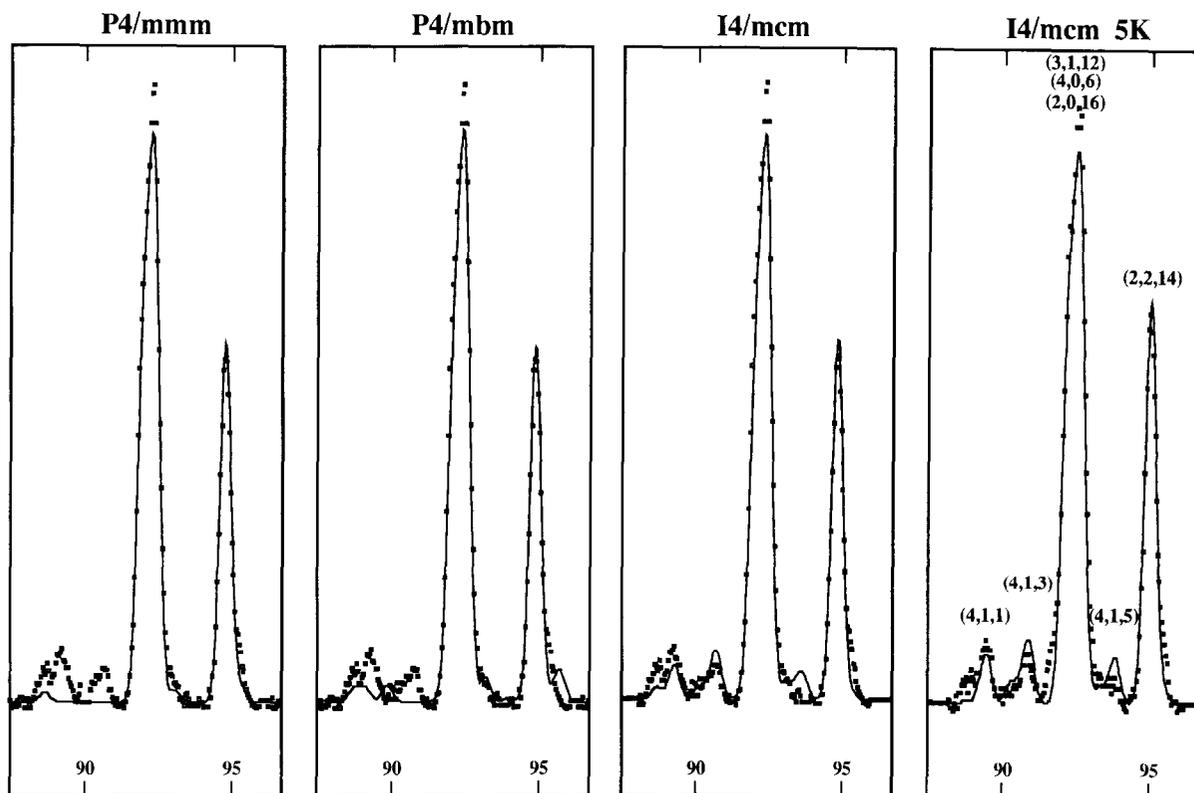


Fig. 3. A small section of fig. 2 showing the  $h+k=\text{odd}$  or  $l=\text{odd}$  superlattice reflections for the enlarged  $I4/mcm$  cell. These reflections are absent in the simple  $P4/mmm$  model, but are introduced when the octahedra twist around the  $c$ -axis in the models  $P4/mbm$  ( $l=\text{even}$ ) and  $I4/mcm$  ( $l=\text{odd}$ ). Clearly the  $I4/mcm$  model is correct since  $l=\text{odd}$  reflections occur.

skite-like structures, with the superstructure disappearing to produce the higher symmetry  $P4/mmm$  structure.

### 5. Metal–oxygen distances and valences in $\text{LaBa}_2(\text{Cu}_2\text{Nb})\text{O}_8$

Table II lists the metal–oxygen distances and Brown–Shannon [8,9] valences calculated for the three different models for  $\text{LaBa}_2\text{Cu}_2\text{NbO}_8$ . It is immediately clear that the material cannot be a superconductor, since all of the copper is  $\text{Cu}^{2+}$  (the calculated  $V$  is even smaller than 2). These are only empirical values, but in all other copper superconductors serve as a good indication of the presence of the electron hole concentration believed necessary for superconductivity (c.f. Cava et al. [10]). The in-plane  $\text{Cu–O}(2)$  distances of  $1.99 \text{ \AA}$  are significantly

longer than the  $1.94 \text{ \AA}$  for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  though the  $2.30 \text{ \AA}$  distance to the “bridging” oxygen  $\text{O}(1)$  is similar.

The  $\text{Ba–O}(4)$  distances of  $3.04 \text{ \AA}$  in the  $P4/mmm$  model are rather large, and suggest an explanation for the rotation of the  $\text{NbO}$ -octahedra. Such rotations reduce two of the  $\text{Ba–O}(4)$  distances to  $2.88 \text{ \AA}$  in the  $I4/mcm$  model, similar to the  $\text{Ba–O}(2)$  distances. Structural transitions in perovskite-like materials are known to be associated with a mismatch between the sizes of the cations and the their sites in the oxygen lattice, and a rotation of the  $\text{NbO}$ -octahedra is to be expected if the  $\text{Ba}$  ion is too far from the  $\text{O}(4)$  oxygens in  $P4/mmm$ .

The Brown–Shannon [8,9] valence sum for  $\text{Ba}$  at 2.2 is very similar to that in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , and is close to the ideal values of 3 for  $\text{La}$  and 5 for  $\text{Nb}$ . These values provide additional evidence that the difference cations are completely ordered on their respec-

Table II  
Bond lengths (Å) and valence charges  $V$  for  $\text{LaBa}_2(\text{Cu}_2\text{Nb})\text{O}_8$ .

		P4/mmm (Å)	P4/mbm (Å)	I4/mcm (Å)	I4/mcm – 5 K (Å)
Ba	–O(1)×4	2.829(0)	2.830(0)	2.829(0)	2.823(0)
	–O(4)×2	3.042(2)	2.939(3)	2.915(3)	2.881(3)
	–O(4)×2	3.042(2)	3.141(3)	3.170(3)	3.210(3)
	–O(2)×2	2.902(2)	2.900(2)	2.906(3)	2.890(3)
	–O(2)×2	2.902(2)	2.910(2)	2.896(3)	2.883(3)
	– $V$	2.191(6)	2.205(8)	2.224(10)	2.285(10)
La	–O(2)×4	2.531(1)	2.526(2)	2.541(2)	2.534(2)
	–O(2)×4	2.531(1)	2.526(2)	2.529(2)	2.527(2)
	– $V$	3.032(8)	3.024(16)	3.000(16)	3.036(16)
Nb	–O(1)×2	1.937(2)	1.931(2)	1.935(2)	1.946(2)
	–O(4)×4	1.984(0)	1.990(4)	1.993(3)	1.996(3)
	– $V$	5.148(10)	5.126(45)	5.079(36)	4.998(35)
Cu	–O(1)	2.294(3)	2.304(3)	2.302(3)	2.283(3)
	–O(2)×4	1.993(0)	1.993(2)	1.992(2)	1.987(2)
	– $V$	1.902(10)	1.897(10)	1.902(10)	1.935(10)

tive sites. The NbO-octahedra are very regular, and rotate as rigid units.

## 6. Implications for $\text{YBa}_2\text{Cu}_3\text{O}_7$

The present work supports the idea of François et al. [2] that the structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  itself is potentially unstable to folding of the CuO-chains, and that this is the reason for the observed disorder of the O(4) chain oxygen. Of course such rotations of CuO-squares, or of CuO-octahedra in  $\text{La}_2\text{CuO}_4$ , do not couple strongly to the electronic states of copper or oxygen. For this, changes in the Cu–O distances are needed. Cava et al. [10] have demonstrated that superconductivity in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is indeed very sensitive to changes in the Cu(2)–O(1) distance of O(1) bridging the CuO-plane to the CuO-chain. Kaldis et al. [11] have shown that the strong pressure dependence of  $T_c$  in  $\text{YBa}_2\text{Cu}_4\text{O}_8$  is associated with similar changes in the Cu(2)–O(1) distance to the bridging oxygen.

Rotations of octahedra responsible for the so-called “antiferroelectric” structural transitions in perovskite do of course change the bond lengths to second order. In fact, Glazer [7] showed how the resulting characteristic changes in lattice constants could be used to determine the rotations. For example, folding of the CuO-chain in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  would shorten

the  $b$ -axis, and François et al. [2] attributed the anomaly in the slope of the orthorhombic distortion to just such a folding. The very high electronic polarizability of oxygen could mean that even small changes in Cu–O distances might be important for coupling such structural instabilities to charge fluctuations.

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