Physica C 165 (1990) 499-504
North-Holland

A STRUCTURAL STUDY OF Ni-SUBSTITUTED $Pb_2Sr_2YCu_3O_{8+\delta}$

U. AMADOR, F. GARCÍA-ALVARADO, E. MORÁN and M.A. ALARIO-FRANCO
Depto. de Quimica Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid. Madrid 28040, Spain

J. RODRIGUEZ-CARJAVAL
Institute Laue-Langevin, Grenoble Cedex, France

Received 30 November 1989
Revised manuscript received 26 December 1989

Novel $Pb_2Sr_2YCu_{3-x}Ni_xO_8$ materials have been obtained. By means of powder neutron diffraction a structural study of a sample with $x \cong 0.8$ was performed. Ni cation substitutes approximately 27% of copper ions scattering entering the Cu(2) positions and forming $(Cu_{0.6}Ni_{0.4})O_2$ planes. The crystal structure is described in the space group Cmmm.

1. Introduction

Cava et al. [1] and Subramanian et al. [2] have reported the discovery of a new family of "layered" copper oxides showing a superconducting transition at about 70 K and general formulae $Pb_2Sr_2A_{1-x}Ca_xCu_3O_{8+\delta}$ (A: rare-earth, $0 \leq x \leq 0.5$). Superconductivity is acquired in $Pb_2Sr_2ACu_3O_{8+\delta}$ by partial substitution of a divalent ion (Ca or Sr) on the rare-earth site.

These compounds have a great interest due to the wide range of possible metal substitution and oxygen stoichiometry which is similar to that observed in the YBaCuO family. Moreover the presence of a lone pair on the Pb ion originates structural distortions.

The structure has been analyzed by both X-ray single crystal data and neutron powder diffraction. Cava et al. [1,3] have refined the structure on the C-centered group Cmmm and unit cell $\sqrt{2}a_p \times \sqrt{2}a_p \times c$; however, the non-centered tetragonal group P4/mmm and the unit cell $a_p \times a_p \times c$ (obtained by rotating 45° around c) was used by Subramanian et al. [2].

Although these refinements yield essentially the same structure, the origin of the orthorhombic distortion is not yet clear. Cava et al. [3] propose as an explanation the irregular coordination of the Pb(II) cation due to the lone pair. However on such a basis it is not obvious why the ***a***- and ***b***-axes are not equal.

More recently electron diffraction and high resolution electron microscopy studies on $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$ samples [4,5,6] have shown both a complex microstructure (intergrowth, stacking faults, antiphase boundaries, etc.) and a systematic violation of the C-centering (very weak but well defined ($hk0$) spots with $h+k=\text{odd}$); this suggests that regular, well ordered, atomic displacements could be the origin of the orthorhombic distortion.

In order to understand more deeply the structural features of this material, we have started a systematic study of metal substitutions. In this connection, nickel appears as an interesting first choice since in, for example, $Ba_2YCu_3O_7$, it appears to be one of the cations whose substitution is less damaging for the superconducting properties [7].

We report in this paper the results of a neutron diffraction refinement for the composition $Pb_2Sr_2YCu_{2.2}Ni_{0.8}O_{8.0}$. This was the composition having the maximum amount of nickel under the synthesis conditions employed.

2. Experimental

Samples with nominal compositions $Pb_2Sr_2YCu_{3-x}Ni_xO_8$ ($0 \leq x \leq 1$) were prepared using the two-step procedure described by Cava et al. [1]. The appropriate quantities of $Sr(CH_3COO)_2 \cdot 1/2H_2O$, PbO, CuO, $NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$ (Merck a.r.) and Y_2O_3 (Research Chemicals) were fired at 890°C in flowing pure N_2 or O_2/N_2 (1% O_2) gas stream.

Magnetic susceptibility down to 4.2 K was measured using an ASMI magnetometer at minimum magnetic field 14 kG, $HdH/dz = 29$ kG^2/cm.

X-ray powder diffraction was performed on a Siemens D-500 apparatus, using Cu Kα radiation.

Neutron powder diffraction measurements were made at 255 K and at 1.5 K with the high resolution D2B Diffractometer at the Institute Laue-Langevin (Grenoble). Neutrons of wavelength 1.5945 Å were selected for the experiments. The sample container was a vanadium can of about 1 cm in diameter and 5 cm length, and the data were collected in the angular range 3°–140° (2θ angles) in steps of 0.05°. The structure was refined using the Rietveld method [8] with a modified version of the DBW 3.2 Wiles and Young program [9], which allows simultaneous refinement (and quantitative phase analysis [10]) of eight structures and the background. Neutron scattering amplitudes employed were [11]:

$b(\mathrm{Pb}) = 0.9400 \times 10^{-12}$ cm $b(\mathrm{Sr}) = 0.7020 \times 10^{-12}$ cm

$b(\mathrm{Y}) = 0.7750 \times 10^{-12}$ cm $b(\mathrm{Ni}) = 1.0300 \times 10^{-12}$ cm

$b(\mathrm{Cu}) = 0.7718 \times 10^{-12}$ cm $b(\mathrm{O}) = 0.5805 \times 10^{-12}$ cm

The peak shape function used was a pseudo-Voigt one with an asymmetry correction for 2θ angles below 50°. In the final step of the refinement, all structural and profile parameters were refined simultaneously. Refinement was terminated when the shifts for all parameters were less than 0.3σ.

3. Results and discussion

The purest sample containing a significant amount of Ni, with nominal composition $Pb_2Sr_2YCu_2NiO_{8+\delta}$, was chosen for the neutron experiment. Powder X-ray diffraction showed that this sample contained a small amount of unreacted NiO. Magnetic susceptibility measurements of the same sample did not show any superconducting transition down to 4.2 K. The lattice parameters obtained from X-ray diffraction experiments are $a = 5.404(5)$ Å, $b = 5.436(4)$ Å and $c = 15.697(7)$ Å. As the orthorhombic distortion is very small $(200(a-b)/(a+b) = 0.59)$ the tetragonal group P4/mmm with the unit cell $a_p \times a_p \times c$ was attempted. The starting structural parameters used in the neutron diffraction refinement were those reported by Cava et al. [3]. In three successive refinements the Ni atoms were located in the Cu(2), in the Cu(1) planes and randomly distributed among them (see fig. 1), respectively. The results of this refinement suggest that Ni replaces the Cu(2) ions, i.e. it is located in the Cu–O_2 planes.

On the other hand, the thermal parameter for the oxygen in the Pb–O plane is rather high (7.2 Å^2): this could indicate disorder of these atoms. Nevertheless, if the refinement is made with the oxygen atoms split, although the thermal parameter gets lower, the R-factors are not better. Moreover the peaks are abnormally wide suggesting that the symmetry may be lower than tetragonal. Therefore the Cmmm group with O(2) in the (00Z) special site was attempted. With this model, the O(2) thermal parameter is still high, but it decreases (0.42 Å^2) when oxygen atoms are split. Hence, the displacements of O(2) atoms from the ideal positions appear to be an essential feature of this material, yet the Pb-ions are located in their ideal positions.

Figure 2 shows the experimental and calculated

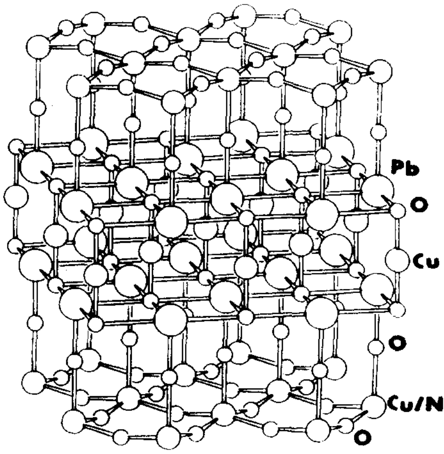

Fig. 1. Schematic representation of the structure of $Pb_2Sr_2YCu_3O_{8+\delta}$. Ytrium and strontium ions have been omitted for clarity.

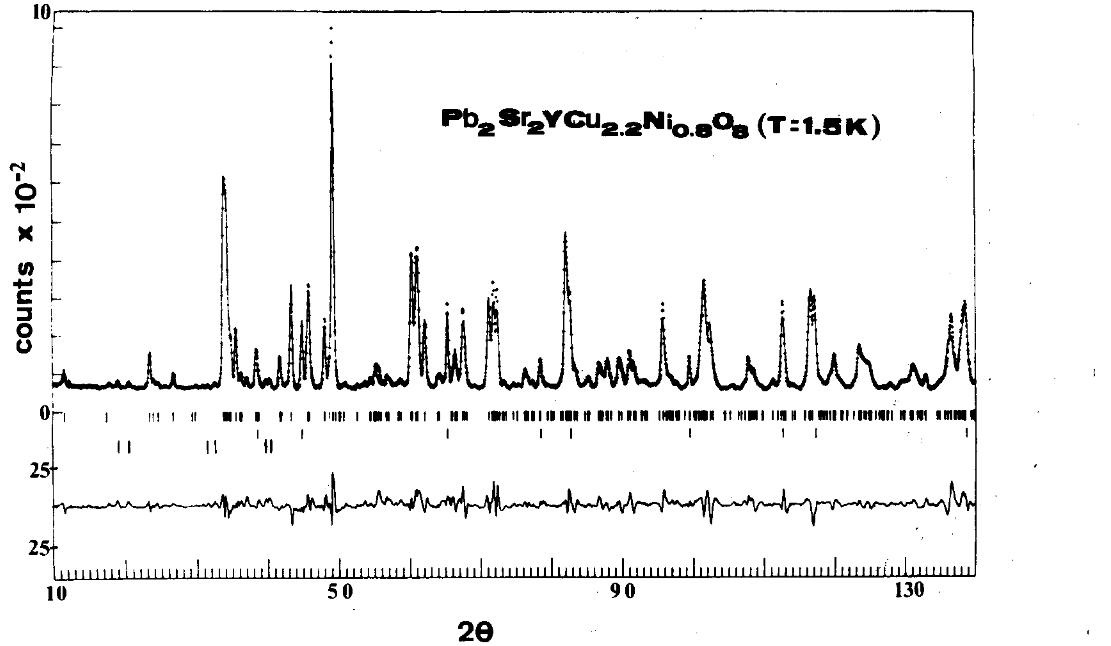

Fig. 2. Experimental and calculated neutron diffraction patterns of $Pb_2Sr_2YCu_{2.2}Ni_{0.8}O_{8.0}$ at 1.5 K. Peaks corresponding to NiO and unknown impurities are also indicated.

Table I
Structure parameters for $Pb_2Sr_2YNi_{0.8}Cu_{2.2}O_8$ at 1.5 K and 255 K.

(a) $T=1.5$ K, SG: Cmmm, $Z=2$, $a=5.3956(2)$ Å, $b=5.4310(2)$ Å, $c=15.6573(7)$ Å.

Atom	Site	x/a	y/b	z/c	B(Å^2)	occ.
Pb	4l	1/2	0.0	0.3881(3)	0.67(6)	1/4
Sr	4k	0.0	0.0	0.2199(2)	0.31(8)	1/4
Y	2a	0.0	0.0	0.0	0.14(7)	1/8
Cu(1)	2d	0.0	0.0	1/2	0.60(6)	1/8
Cu(2)	4l	1/2	0.0	0.1072(3)	0.41(5)	0.15(1)
Ni	4l	1/2	0.0	0.1072(3)	0.41(5)	0.10(1)
O(1)	4l	1/2	0.0	0.2489(6)	1.11(8)	1/4
O(2)	16r	0.050(2)	0.064(2)	0.3816(6)	0.13(6)	1/4
O(3)	8m	1/4	1/4	0.0924(3)	0.60(7)	1/2

$R_p=7.22$, $R_{wp}=9.18$, $R_B=10.6$, $R_{exp}=2.61$, $\chi^2=12.3$.

(b) $T=255$ K, SG: Cmmm, $Z=2$, $a=5.4035(3)$ Å, $b=5.4386(3)$ Å, $c=15.6965(8)$ Å.

Atom	Site	x/a	y/b	z/c	B(Å^2)	occ.
Pb	4l	1/2	0.0	0.3868(3)	1.14(8)	1/4
Sr	4k	0.0	0.0	0.2193(3)	0.39(9)	1/4
Y	2a	0.0	0.0	0.0	0.40(9)	1/8
Cu(1)	2d	0.0	0.0	1/2	1.10(8)	1/8
Cu(2)	4l	1/2	0.0	0.1092(3)	0.74(7)	0.15(1)
Ni	4l	1/2	0.0	0.1092(3)	0.74(7)	0.10(1)
O(1)	4l	1/2	0.0	0.2504(6)	1.11(8)	1/4
O(2)	16r	0.047(2)	0.071(2)	0.3846(6)	0.42(6)	1/4
O(3)	8m	1/4	1/4	0.0937(2)	0.82(5)	1/2

$R_p=7.64$, $R_{wp}=9.74$, $R_B=9.68$, $R_{exp}=5.27$, $\chi^2=3.41$.

neutron diffraction patterns at 1.5 K and 255 K. Both "$Pb_2Sr_2YCu_2NiO_{8+\delta}$" and small amounts of NiO are present. Magnetic ordering has not been observed. The only effect of the temperature is that the thermal expansion is more important along the *c*-axes than on the *ab*-plane, as expected in view of the "lamellar" nature of this structure.

Structural parameters are collected in table I. The calculated composition is $Pb_2Sr_2YCu_{2.2}Ni_{0.8}O_{8.0}$. Neither cationic nor anionic vacancies are detected. On the other hand, no extra oxygen has been detected in the ($\frac{1}{2}$, 0, 0) sites, so that the Ni atoms do not appear to be in octahedral coordination as is the case in, for example, La_2NiO_4. There is no extra oxygen in the Cu(1) planes either, so that the oxygen content is close to eight. The Ni content is in agreement with the quantitative phase analysis, 20% of the initial NiO remaining unreacted. If we consider the formal valences Y^{3+}, $Cu(1)^+$, $Cu(2)^{2+}$, Pb^{2+} and O^{2-}, the oxidation state of Ni becomes (+2). This is in agreement with the calculation of the effective valence of the Ni ion from the Ni–O distances. Using the Brown and Altermatt method [12] the value found is 2.07. In the Pb site the corresponding value is 1.96, but for Cu(1) and Cu(2) the calculated values are higher than 1 and 2, respectively, 1.19 and 2.21; whether this is the reason for the material not being a superconductor remains to be seen. These values are similar to those reported by Cava et al. [3] which are in fact not consistent with the oxygen content obtained in the structural refinement. Obviously, the effective valence calculation is often not more than a crude approximation.

Table II shows the main interatomic distances and angles. It can be deduced that the yttrium ions are surrounded by eight oxygen atoms located at the corners of a tetragonal prism. Both Cu(2) and Ni are located in elongated, square-based pyramids. These coordination polyhedra are a common feature of most copper oxide based superconductors. Sr atoms are coordinated to nine oxygen atoms forming a distorted polyhedron. The displacement of O(2) in the *ab*-plane from the ideal position (00*Z*) produces a strong distortion on the local neighborhood. In the coordination polyhedron of Pb there are three shorter distances. Cava et al. have suggested that the lone pair of Pb^{2+} pointing towards the plane defined by the three nearest oxygens is responsible for the distorted coordination. The displacements of the oxygen atoms in the Pb-O planes could produce an average linear or angular coordination on Cu(1). However, a probably linear randomly oriented coordination appears more likely since an angular oxygen di-coordinated copper seems to be unusual [13], while linearly coordinated copper has previously been observed in other related materials (e.g. $YBa_2Cu_3O_6$ [14], $Ba_4Y_2Cu_6O_{13}$ [15]).

Table II
Bond length (in Å units) and angles for $Sr_2Pb_2YCu_{2.2}Ni_{0.83}O_8$ at 1.5 K and 255 K.

T=1.5 K		T=255 K	
Pb–O(1)	2.18(1)×1	Pb–O(1)	2.14(1)
–O(2)	2.46(1)×1	–O(2)	2.48(1)
–O(2)	2.99(1)×1	–O(2)	2.98(1)
–O(2)	2.384(8)×1	–O(2)	2.365(9)
–O(2)	3.078(8)×1	–O(2)	3.138(9)
Sr–O(1)	2.736(2)×2	Sr–O(1)	2.746(2)
–O(1)	2.753(2)×2	–O(1)	2.783(2)
–O(2)	2.57(1)×1	–O(2)	2.636(1)
–O(3)	2.766(8)×4	–O(3)	2.755(8)
Y–O(3)	2.399(6)×8	Y–O(3)	2.422(6)
Cu(1)–O(2)	1.905(9)×2	Cu(1)–O(1)	1.87(1)
Cu(2)–O(1)	2.22(2)×1	Cu(2)–O(1)	2.216(1)
–O(3)	1.928(2)×4	–O(3)	1.939(2)
Angle O(2)–Cu(1)–O(2)	153.3(2)		151.4(4)
	158.9(4)		156.1(4)
	163.9(3)		164.5(4)
	180.0(1)		180.0(1)

In order to clarify the coordination of Cu(1) and to explain the C-centering violation (closely related to the orthorhombic distortion), we have also tested the models proposed by Zandbergen et al. [5]:

i) Tilt of the CuO_5 pyramids. Two space groups (Pmam(standard Pmma) and Pman(standard Pmna)) can be used for describing the structure originated by the tilt (fig. 3). The refinement on both space groups using the unit cell ($\sqrt{2}a_p \times \sqrt{2}a_p \times c$) yields too high values of *R*-factors. Oxygen thermal parameters for the CuO_5 pyramid are also abnormally high. This indicates that the CuO_5 pyramids are not tilted, so that this cannot be the origin of the orthorhombic distortion.

ii) Shift of the oxygen atoms in the Pb–O layer.

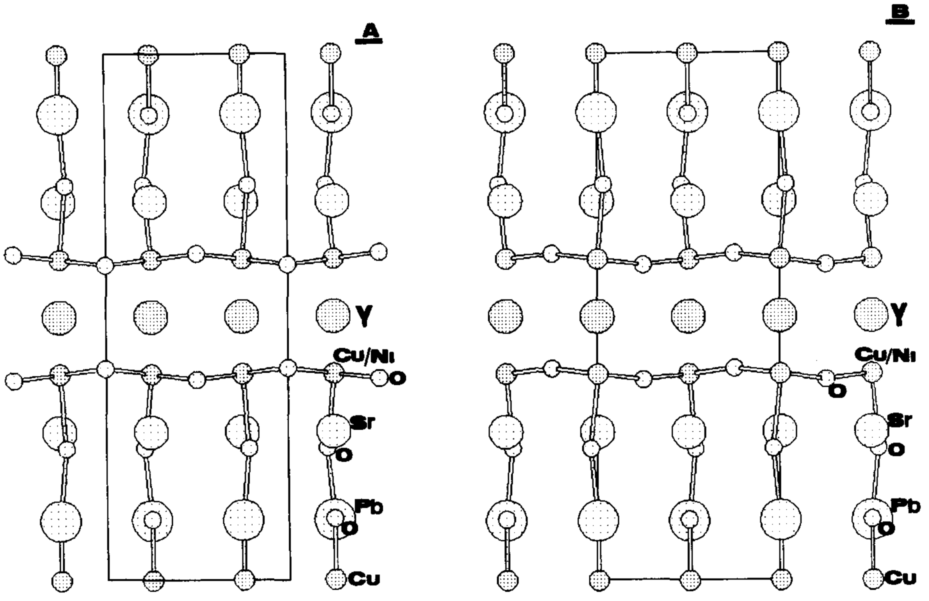

Fig. 3. Structural models originated by tilting of CuO_5 pyramid. (a) Space group Pmma, (b) space group Pmna.

The ordered displacement of the oxygen in the Pb–O layer and the structural model proposed by Zandbergen et al. ($\sqrt{2}a_p \times \sqrt{2}a_p \times c$) are shown in fig. 4. The structural refinements of this model on the Pmam(Pmma) and Pman(Pmna) groups with the oxygen displacements restricted to the ($\frac{1}{4}$ Y Z) and (0 Y Z) planes, respectively, are not better than the ones obtained using the Cava et al. model. The same oxygen displacements can be described with a C-centered unit cell ($2a_p \times 2a_p \times c$), see fig. 4) and Cmmm and Cmma space groups. Using these space groups does not improve the refinement.

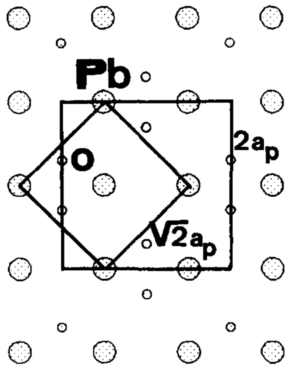

Fig. 4. Structural models originated by oxygen ordered displacements in the Pb–O layer.

4. Conclusions

The introduction of Ni ions substituting copper cations in $Pb_2Sr_2YCu_3O_{8+\delta}$ takes place in the Cu(2) positions. No ordering between Ni and Cu ions in these planes has been observed. The oxidation state of Ni appears to be (+2); correspondingly, the oxygen content is not altered by such a substitution. The only way for changing the oxygen content using Ni introduction would be to achieve a substitution degree higher than 60%, since then the Ni(II) ions would have to be introduced in the Cu(1) positions and this may force a higher oxygen content. Alternatively, an oxidation in flowing oxygen could be done, but the treatment conditions have to be well defined to avoid the oxidation of lead.

Although the displacement of oxygen atoms in the Pb–O planes could be ordered, this ordering is probably short range. The size of the domains is, however, large enough to be observed by transmission electron microscopy like a violation of the C-centering. Disordering of these domains forces the structure to be described in the Cmmm group with the O(2) split among the (XYZ) site.

This new Ni-doped material does not show a superconducting transition; yet this compound appears to be worth further study for a number of reasons. The $Pb_2Sr_2YCu_{3-x}Ni_xO_{8+\delta}$ family has indeed good qualities for studying both differences and similarities between Cu and Ni compounds. Introduction of oxygen in the Cu(1) planes, oxidation of Ni^{+2} to Ni^{+3}, Cu^{+2} to Cu^{+3}, ..., would be an interesting test of the capabilities of this system. Studies in this way are in progress.

Acknowledgements

We thank Dr. R.J. Cava for a preprint of ref. [1]. We also thank C.I.C.Y.T. for financial support. U.A. also thanks the M.E.C. for a grant to go to I.L.L..

References

[1] R.J. Cava, B. Batlogg, J.J. Krajewski, L.W. Rupp, L.F. Schneemeyer, T. Siegrist, R.B. van Dover, P. Marsh, W.F. Peck, P.K. Gallagher, S.H. Glarum, J.H. Marshall, R.C. Farrow, J.V. Waszczak, R. Hull and P. Trevor, Nature 336 (1988) 211.

[2] M.A. Subramanian, J. Gopalakrishnan, C.C. Torardi, P.L. Gai, E.D. Boyes, T.R. Asken, R.B. Flippen, W.E. Farneth and A.W. Sleight, Physica C 157 (1989) 124.

[3] R.J. Cava, M. Marezio, J.J. Krajewski, J.J. Peck Jr., A. Santoro and F. Beech, Physica C 157 (1989) 272.

[4] E.A. Hewat, J.J. Capponi, R.J. Cava, C. Chaillout, M. Marezio, J.L. Tholence, Physica C 157 (1989) 509.

[5] H.W. Zandbergen, K. Kadowaki, M.J.V. Menken, G. Van Tendeloo and S. Amelinckx, Physica C 158 (1989) 155.

[6] P. Goodman, D.G. Jensen and T.J. White, Physica C 158 (1989) 173.

[7] S. Oseroff, D.C. Vier, J.F. Smyth, C. Salling, S. Schultz, Y. Dalichaouch, B.W. Lee, M.B. Maple, Z. Fisk, J.D. Thompson, J.L. Smith and E. Zirngiebl, Solid State Commun. 64(2) (1987) 241.

[8] H.M. Rietveld, J. Appl. Crystall. 2, (1969) 65.

[9] D.B. Wiles and R.A. Young, J. Appl. Cryst 14 (1981) 149.

[10] D. Bish and L. Howard, J. Appl. Cryst. 21 (1988) 86.

[11] V.F. Sears, Chalk River Nuclear Lab., Int. Report AECL-8490 (1984).

[12] I.D. Brown and D. Altermatt, Acta Crystallogr. B41 (1985) 244.

[13] Structural Inorganic Chemistry, 4th ed., ed. A.F. Wells (Clarendon Press, Oxford, 1975) p. 875.

[14] J. Jorgensen, M.A. Beno, D.G. Hinks, L. Sondelhorn, K. Volin, R.L. Hiterman, J.D. Graco, I.K. Schuller, C.V. Segre and Z. Zhang, Phys. Rev. B36 (1987) 5731.

[15] C. Chaillout, M.A. Alario-Franco, J.J. Capponi, J. Chenavas, P. Strobel and M. Marezio, Solid State Commun. 65 (1988) 283.