# $Sr_9Ni_{6.64}O_{21}$: A New Member ($n = 2$) of the Perovskite-Related $A_{3n+3}A'_nB_{3+n}O_{9+6n}$ Family

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Crystals of a new phase $Sr_9Ni_{6.64}O_{21}$ were grown. This compound is the $n = 2$ member of the $A_{3n+3}A'_nB_{3+n}O_{6n+9}$ series. The composition and the crystal structure have been established from X-ray single crystal diffraction data. The structure contains face-shared chains of $NiO_6$ polyhedra parallel to the c axis and is related with the hexagonal 2H polytype perovskite. $Sr_9Ni_{6.64}O_{21}$ crystallizes in the space group $R\bar{3}c$ (No. 167) with $a = 9.467(2)$ Å, $c = 35.87(5)$ Å, $V = 2784.(4)$ Å$^3$, and $Z = 6$. A comparison is made between the structure of the title compound and the other members of the series. © 1996 Academic Press, Inc.

## INTRODUCTION

Compounds whose structures are built up by the stacking of layers derived from $ABO_3$ perovskites have been largely studied and structural relationships between them have been recently reported (1, 2). One series belonging to this large family of compounds is the one that results from the stacking of mixed $[A_3O_9]$ and $[A_3A'O_6]$ layers, generically formulated as $A_{3n+3}A'_nB_{n+3}O_{6n+9}$.

A good number of oxides containing 4d and 5d elements crystallize in structures included in this series (3, 4). To our knowledge not many compounds in which $A'$ and $B$ positions are occupied by the same 3d cation have been studied. $Sr_{12}Ni_{7.5}O_{27}$ (5) is the $n = 3$ member of the series, and $Ba_6Ni_5O_{15}$, reported by (6), corresponds to $n = 1$. The aim of this work is to present the synthesis and the crystal structure of $Sr_9Ni_{6.64}O_{21}$, the $n = 2$ member of this series.

## EXPERIMENTAL

*Synthesis and crystal growth.* Crystals of $Sr_9Ni_{6.64}O_{21}$ were grown in Ni crucibles ($\phi = 30$ mm, $h = 32$ mm) from analytical grade reagents, mixing 1 g of $Sr(OH)_2 \cdot 8H_2O$, 0.5 g of NiO, and 3 g of KOH. After this mixture was heated to 880°C and soaked for 2 h, the power to the furnace was turned off. The crystals were then washed with distilled cold water and dried.

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*X-ray structure determination.* A black prismatic crystal was mounted in a kappa diffractometer. A summary of the fundamental crystal data is given in Table 1. The cell dimensions were refined by least-squares fitting the $\theta$ values of 25 reflections. Systematic extinctions are not very clear in this kind of compound whose structures are all of them $ABO_3$ superstructures. Extinctions can even vary from one crystal to another within the same phase. After

**TABLE 1**
**Crystallographic Parameters for $Sr_9Ni_{6.64}O_{21}$**

| Crystal data | |
|---|---|
| Formula | $Sr_9Ni_{6.64}O_{21}$ |
| Formula weight, g mol$^{-1}$ | 1514.3 |
| Crystal system | Trigonal |
| Space group | $R\bar{3}c$ (No. 167) |
| Cell dimensions | |
| $a$, Å | 9.467(2) |
| $c$, Å | 35.87(5) |
| $Z$ | 6 |
| $V$, Å$^3$ | 2784.(4) |
| $\rho_{calcd}$, g cm$^{-3}$ | 5.5 |
| Crystal dimensions, mm$^3$ | $0.05 \times 0.05 \times 0.25$ |
| | |
| Data collection | |
| Radiation | $MoK\alpha$ ($\lambda = 0.71069$ Å) |
| Temperature, °K | 295 |
| Scan technique | $\omega/2\theta$ |
| $2\theta$ range, ° | 1–50 |
| Data collected | (0, 0, 0) to (11, 11, 42) |
| Unique data | 650 |
| Observed reflections $I > 2\sigma(I)$ | 189 |
| $R_{int}$, % | 4.2 |
| $F(000)$ | 4236 |
| $\mu(MoK\alpha)$, cm$^{-1}$ | 319 |
| | |
| Structure solution and refinement | |
| $R(F)^a$ | $R = 0.069$ |
| $R_w(F)^b$ | $R_w = 0.068$ |
| Weighting scheme | unit |
| Maximum shift/error | 0.076 |
| Absorption correction range | 0.86–1.11 |

$^a R = \Sigma|\Delta F|/\Sigma|F_o|$.
$^b R_w = (\Sigma w(|F_o| |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

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### TABLE 2
### Atomic Coordinates and Thermal Parameters for $Sr_9Ni_{6.64}O_{21}$

| Atom | $W^a$ | $x/a$ | $y/b$ | $z/c$ | $U_{eq}^b$ |
|------|------|-------|-------|-------|--------|
| Sr1 | 36f | 0.647(1) | 0.005(1) | 0.1417(2) | 11(1) |
| Sr2 | 18e | 0.321(1) | 0.0 | 0.75 | 7(1) |
| Ni1 | 6b | 0.0 | 0.0 | 0.0 | 10(13) |
| Ni2 | 12c | 0.0 | 0.0 | 0.069(1) | 18(6) |
| Ni3 | 12c | 0.0 | 0.0 | 0.2154(6) | 3(7) |
| Ni4$^c$ | 12c | 0.0 | 0.0 | 0.360(2) | 64(13) |
| O1 | 36f | 0.521(8) | 0.198(6) | 0.369(2) | 25(25) |
| O2 | 36f | 0.834(5) | −0.002(5) | 0.315(1) | 5(10) |
| O3 | 18e | −0.166(7) | −0.166(0) | 0.25 | 12(25) |
| O4 | 36f | 0.525(12) | 0.327(16) | 0.439(3) | 118(47) |

$^a$ Wyckoff letter.
$^b$ $U_{eq} = \frac{1}{3}(\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j) 10^3$.
$^c$ Fractional site occupancy.

checking a good number of crystals, absences in $hkl$ when $\bar{h} + k + l = 3n + 1$ and $h\,\bar{h}0l$ when $l = 2n + 1$ were assumed. The data collection was performed at 295 K. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni and Sr were taken from the "International Tables for X-Ray Crystallography" (8). The structure was solved by Patterson and Fourier methods.

### TABLE 3
### Selected Interatomic Distances (Å), Angles (deg), and Polyhedral Edge Lengths (Å) for Sr in $Sr_9Ni_{6.64}O_{21}$

| Sr1 | $O1^1$ | $O1^2$ | $O1^3$ | $O2^2$ | $O2^4$ | $O2^5$ | $O3^6$ | $O4^7$ |
|------|------|------|------|------|------|------|------|------|
| $O1^1$ | 2.79 | 63 | 63 | 73 | 121 | 90 | 151 | 129 |
| $O1^2$ | 2.87 | 2.71 | 51 | 132 | 133 | 71 | 92 | 124 |
| $O1^3$ | 2.87 | 2.31 | 2.71 | 95 | 176 | 121 | 114 | 84 |
| $O2^2$ | 3.08 | 4.66 | 3.77 | 2.39 | 84 | 126 | 135 | 73 |
| $O2^4$ | 4.77 | 4.94 | 5.40 | 3.41 | 2.69 | 61 | 64 | 91 |
| $O2^5$ | 3.77 | 3.08 | 4.61 | 4.40 | 2.69 | 2.56 | 67 | 142 |
| $O3^6$ | 5.16 | 3.77 | 4.41 | 4.57 | 2.80 | 2.82 | 2.79 | 77 |
| $O4^7$ | 4.71 | 4.54 | 3.46 | 2.86 | 3.68 | 4.72 | 3.11 | 2.44 |

| Sr2 | $O1^8$ | $O1^9$ | $O2^{10}$ | $O2^{11}$ | $O3^{12}$ | $O3^{13}$ | $O4^8$ | $O4^9$ | $O4^{14}$ | $O4^{15}$ |
|------|------|------|------|------|------|------|------|------|------|------|
| $O1^8$ | 2.56 | 129 | 71 | 143 | 133 | 93 | 61 | 78 | 63 | 109 |
| $O1^9$ | 4.61 | 2.56 | 143 | 71 | 93 | 133 | 78 | 61 | 109 | 63 |
| $O2^{10}$ | 3.08 | 5.04 | 2.76 | 115 | 62 | 63 | 131 | 101 | 108 | 81 |
| $O2^{11}$ | 5.04 | 3.08 | 4.67 | 2.76 | 63 | 62 | 101 | 131 | 81 | 108 |
| $O3^{12}$ | 4.75 | 3.78 | 2.80 | 2.82 | 2.63 | 62 | 164 | 114 | 127 | 68 |
| $O3^{13}$ | 3.78 | 4.75 | 2.82 | 2.80 | 2.72 | 2.63 | 114 | 164 | 68 | 127 |
| $O4^8$ | 2.79 | 3.46 | 5.16 | 4.37 | 5.48 | 4.63 | 2.90 | 75 | 46 | 119 |
| $O4^9$ | 3.46 | 2.79 | 4.37 | 5.16 | 4.63 | 5.48 | 3.53 | 2.90 | 119 | 46 |
| $O4^{14}$ | 2.90 | 4.48 | 4.60 | 3.68 | 4.98 | 3.11 | 2.26 | 5.02 | 2.92 | 165 |
| $O4^{15}$ | 4.48 | 2.90 | 3.68 | 4.60 | 3.11 | 4.98 | 5.02 | 2.26 | 5.79 | 2.92 |

*Note.* Standard deviation involving Sr is 0.08 Å and 2.7°. Symmetry code: 1. $(-y) + \frac{2}{3}, (-x) + \frac{1}{3}, (z + \frac{1}{2}) + \frac{1}{3} - 1$; 2. $(x - y), (-y), (-z + \frac{1}{2})$; 3. $(-x) + 1, (-x + y), (-z + \frac{1}{2})$; 4. $(-x + y) + \frac{2}{3} + 1, (y) + \frac{1}{3}, (z + \frac{1}{2}) + \frac{1}{3} - 1$; 5. $(x) - \frac{1}{3}, (x - y) - \frac{2}{3}, (z + \frac{1}{2}) - \frac{2}{3}$; 6. $(x - y) + \frac{2}{3}, (x) + \frac{1}{3}, (-z) + \frac{1}{3}$; 7. $(x) + \frac{1}{3}, (y) + \frac{2}{3} - 1, (z) + \frac{2}{3} - 1$; 8. $(-x + y) + \frac{2}{3}, (-x) + \frac{1}{3}, (z) + \frac{1}{3}$; 9. $(y) + \frac{1}{3}, (x) + \frac{2}{3} - 1, (-z + \frac{1}{2}) + \frac{2}{3} + 1$; 10. $(-x) + 1, (-y), (-z) + 1$; 11. $(-x + y) + 1, (y), (z + \frac{1}{2})$; 12. $(-x), (-y), (-z) + 1$; 13. $(x - y); (x), (-z) + 1$; 14. $(x) + \frac{2}{3} - 1, (y) + \frac{1}{3} - 1, (z) + \frac{1}{3}$; 15. $(x - y) + \frac{1}{3}, (-y) + \frac{2}{3}, (-z + \frac{1}{2}) + \frac{2}{3}$.

### TABLE 4
### Selected Interatomic Distances (Å), Angles (deg), and Polyhedral Edge Lengths (Å) for Ni in $Sr_9Ni_{6.64}O_{21}$

| Ni1 | $O1^1$ | $O1^2$ | $O1^3$ | $O1^4$ | $O1^5$ | $O1^6$ |
|---|---|---|---|---|---|---|
| $O1^1$ | <u>1.84</u> | 180 | 78 | 102 | 78 | 102 |
| $O1^2$ | 3.68 | <u>1.84</u> | 102 | 78 | 102 | 78 |
| $O1^3$ | 2.31 | 2.87 | <u>1.84</u> | 180 | 78 | 102 |
| $O1^4$ | 2.87 | 2.31 | 3.68 | <u>1.84</u> | 102 | 77 |
| $O1^5$ | 2.31 | 2.87 | 2.31 | 2.87 | <u>1.84</u> | 180 |
| $O1^6$ | 2.87 | 2.31 | 2.87 | 2.31 | 3.68 | <u>1.84</u> |

| Ni2 | $O1^1$ | $O1^3$ | $O1^5$ | $O4^1$ | $O4^3$ | $O4^5$ |
|---|---|---|---|---|---|---|
| $O1^1$ | <u>1.79</u> | 81 | 81 | 100 | 105 | 174 |
| $O1^3$ | 2.31 | <u>1.79</u> | 81 | 174 | 100 | 105 |
| $O1^5$ | 2.31 | 2.31 | <u>1.79</u> | 105 | 174 | 100 |
| $O4^1$ | 2.79 | 3.65 | 2.90 | <u>1.86</u> | 75 | 75 |
| $O4^3$ | 2.90 | 2.79 | 3.65 | 2.26 | <u>1.86</u> | 75 |
| $O4^5$ | 3.65 | 2.89 | 2.79 | 2.26 | 2.26 | <u>1.86</u> |

| Ni3 | $O2^7$ | $O2^8$ | $O2^9$ | O3 | $O3^{10}$ | $O3^{11}$ |
|---|---|---|---|---|---|---|
| $O2^7$ | <u>1.90</u> | 89 | 90 | 92 | 92 | 177 |
| $O2^8$ | 2.66 | <u>1.90</u> | 90 | 92 | 177 | 93 |
| $O2^9$ | 2.70 | 2.70 | <u>1.90</u> | 177 | 92 | 92 |
| O3 | 2.80 | 2.79 | 3.90 | <u>2.00</u> | 86 | 86 |
| $O3^{10}$ | 2.82 | 3.88 | 2.80 | 2.72 | <u>2.00</u> | 86 |
| $O3^{11}$ | 3.90 | 2.81 | 2.82 | 2.72 | 2.72 | <u>2.00</u> |

| Ni4 | $O2^{12}$ | $O2^{13}$ | $O2^{14}$ | $O4^{15}$ | $O4^{16}$ | $O4^{17}$ |
|---|---|---|---|---|---|---|
| $O2^{12}$ | <u>2.25</u> | 74 | 74 | 136 | 89 | 140 |
| $O2^{13}$ | 2.71 | <u>2.25</u> | 74 | 89 | 140 | 136 |
| $O2^{14}$ | 2.71 | 2.71 | <u>2.25</u> | 140 | 137 | 89 |
| $O4^{15}$ | 3.75 | 2.86 | 3.80 | <u>1.79</u> | 78 | 78 |
| $O4^{16}$ | 2.86 | 3.82 | 3.77 | 2.26 | <u>1.79</u> | 78 |
| $O4^{17}$ | 3.80 | 3.77 | 2.86 | 2.26 | 2.26 | <u>1.79</u> |

*Note.* Standard deviation involving Ni atoms is 0.08 Å and 2.4°. Symmetry code: 1. $(x) + \frac{1}{3} - 1, (y) + \frac{2}{3} - 1, (z) + \frac{2}{3} - 1$; 2. $(-x) + \frac{2}{3}, (-y) + \frac{1}{3}, (-z) + \frac{1}{3}$; 3. $(-y) + \frac{1}{3}, (x - y) + \frac{2}{3} - 1, (z) + \frac{2}{3} - 1$; 4. $(y) + \frac{2}{3} - 1, (-x + y) + \frac{1}{3}, (-z) + \frac{1}{3}$; 5. $(-x + y) + \frac{1}{3}, (-x) + \frac{2}{3}, (z) + \frac{2}{3} - 1$; 6. $(x - y) + \frac{2}{3} - 1, (y) + \frac{1}{3} - 1, (-z) + \frac{1}{3}$; 7. $(y), (x) - 1, (-z + \frac{1}{2})$; 8. $(x - y) - 1, (-y), (-z + \frac{1}{2})$; 9. $(-x) + 1, (-x + y) + 1, (z + \frac{1}{2})$; 10. $(-y), (x - y), (z)$; 11. $(-x + y), (-y), (z)$; 12. $(x) - 1, (y), (z)$; 13. $(-y), (x - y) - 1, (z)$; 14. $(-x + y) + 1, (-x) + 1, (z)$; 15. $(y) + \frac{2}{3} - 1, (x) + \frac{1}{3} - 1, (-z + \frac{1}{2}) + \frac{1}{3}$; 16. $(x - y) + \frac{2}{3} - 1, (-y) + \frac{1}{3}, (-z + \frac{1}{2}) + \frac{1}{3}$; 17. $(-x) + \frac{2}{3}, (-x + y) + \frac{1}{3}, (-z + \frac{1}{2}) + \frac{1}{3}$.

An empirical absorption correction was applied at the end of the isotropic refinements (9). The maximum and minimum absorption factors were 1.11 and 0.86. The centrosymmetric $R\bar{3}c$ space group was obtained during the course of the refinement. Due to the high values of the Ni4 and O4 thermal parameters, population factors of these atoms were refined. After several cycles of refinement this factor fell to 0.82(7) and remained unchanged for Ni4. In the case of O4 it remains around the unit, no matter the number of cycles or the fixed value of the isotropic temperature factor introduced. A final isotropic refinement was undertaken with unit weights. No trend in $\Delta F$ vs $F_o$ or $\sin\theta/\lambda$ was observed. Final difference synthesis showed no significant electron density.

Most of the calculations were carried out with the "XRay80 System" (10).

## RESULTS AND DISCUSSION

Atomic position coordinates and temperature factors as well as main interatomic distances and angles for $Sr_9Ni_{6.64}O_{21}$ are included in Tables 2, 3, and 4.
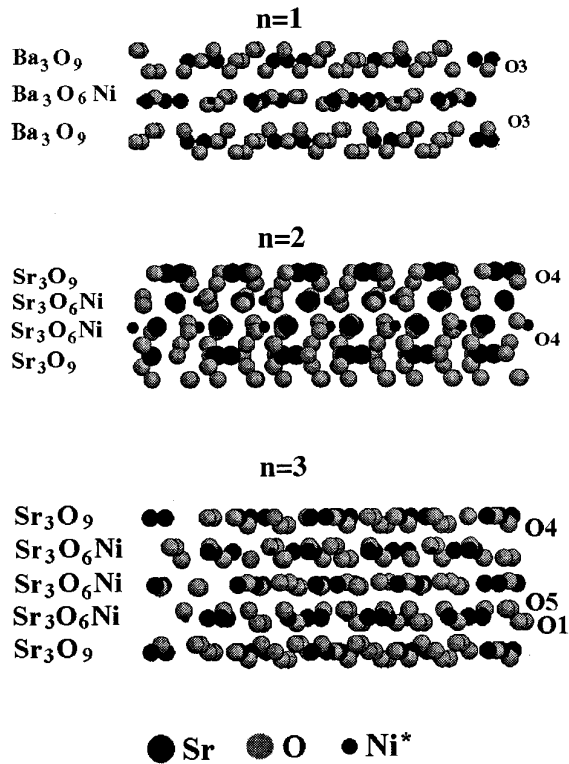
FIG. 1. View of the layer stackings in $A_{3n+3}A'_nB_{n+3}O_{6n+9}$, for $Ba_6Ni_5O_{15}$, $n = 1$; $Sr_9Ni_{6.64}O_{21}$, $n = 2$; and $Sr_{12}Ni_{7.5}O_{27}$, $n = 3$.

$Sr_9Ni_{6.64}O_{21}$ is a new trigonal phase with mixed $[A_3O_6]$ and $[A_3A'O_6]$ layers in which $A = Sr$, and $A' = Ni$. Thus the parameters of the unit cell are $a = a' \cdot \sqrt{3} = 9.467(2)$ Å, $a'$ being the cell parameter of the hexagonal perovskite (11) and $c = 35.87(5)$ Å as consequence of the octahedral sites created between the stacked layers.

As mentioned before, this family of compounds has been represented by the general formula $A_{3n+3}A'_nB_{n+3}O_{6n+9}$, where $n$ is the number of consecutive $[A_3A'O_6]$ layers in the sequence. $Sr_9Ni_{6.64}O_{21}$ is the new member of the series that corresponds to $n = 2$. Thus, the structure is conceived as the result of stacking infinite layers perpendicular to the $c$ axis in the sequence one $[Sr_3O_9]$ layer + two $[Sr_3NiO_6]$ layers. Figure 1 shows the stacking of the layers in the three Ni phases, $n = 1$, 2, and 3, known until now.

In the unit cell there are two crystallographically independent Sr atoms with different environments depending on the kind of layer in which they are situated. Sr1 atoms at the $36f$ position are in the $Sr_3NiO_6$ layers; as a consequence of the less oxygen contents in them, Sr1 is coordinated to eight oxygen atoms, with a mean bond distance of 2.64 Å. (This layer is formed by substitution of one Ni atom in place of three oxygen atoms.) Sr2 which is involved in the minority but richest in the oxygen group of layers, $[Sr_3O_9]$, is thus situated at the $18e$ position and its coordination number is ten, the mean Sr2–O distance being 2.75 Å. Both averages agree with those found in the literature
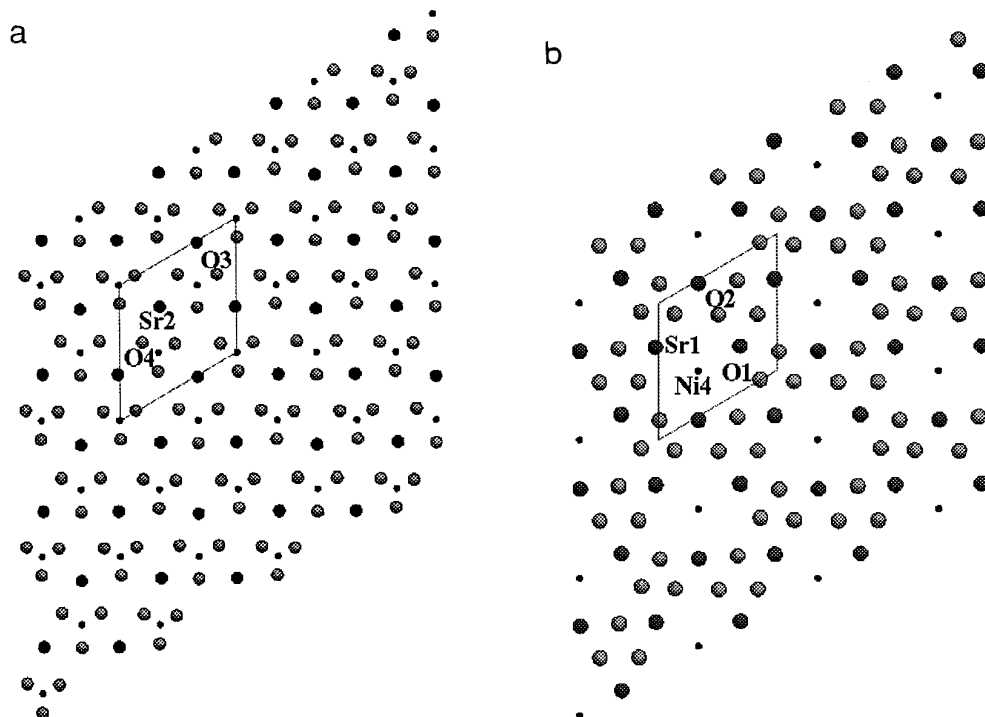


FIG. 2. View of the two kinds of hexagonal layers perpendicular to the $c$ direction. (a) $[Sr_3O_9]$ and (b) $[Sr_3NiO_6]$.
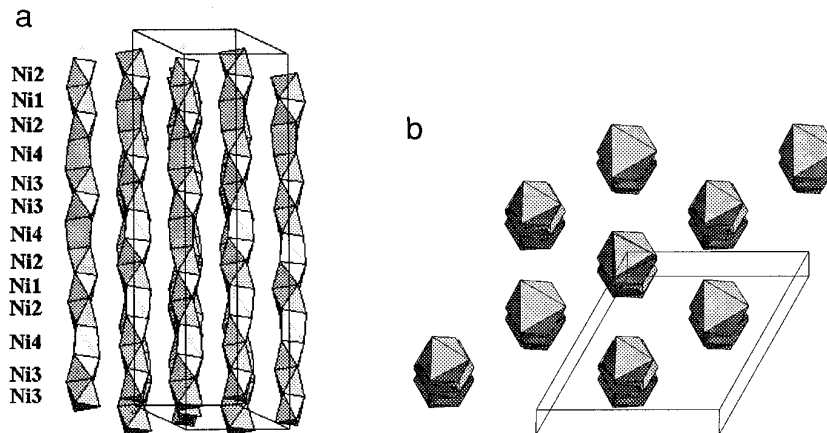
**FIG. 3.** Chains of $NiO_6$ polyhedra (a) parallel and (b) perpendicular to the **c** direction.

for eightfold and tenfold coordinated Sr in these compounds (5). Figure 2 shows both types of layers.

Ni atoms are all six coordinated. Ni1, Ni2, and Ni3 are octahedral but Ni4, that is that situated in the $[Sr_3NiO_6]$ layer, is at the prismatic site.

As a consequence of the stacking sequence octahedral sharing of opposite faces $[Ni_3O_{12}]$ trimeric and $[Ni_2O_9]$ dimeric groups are formed, which are connected through trigonal prisms, giving rise to chains parallel to the **c** axis with the sequences shown in Fig. 3. Distances Ni–Ni between the octahedral ones are quite similar, Ni2–Ni1 = 2.46(2) Å in the Ni2–Ni1–Ni2 trimeric group and Ni3–Ni3 = 2.48(3) Å in the dimeric group, practically the same as that in Ni metal (2.49 Å). In the joining with the prismatic Ni the differences are larger, Ni2–Ni4 = 2.55(6) Å and Ni4–Ni3 = 2.71(6) Å. This sort of packing gives rise to differences among nickel distances within the chain, but not to such an extent as in $Ba_6Ni_5O_{15}$, where the shortest is 2.34 Å and the longest is 2.81 Å.

Prismatic sites are not completely occupied. As indicated in the Experimental the population factor of Ni4 is 0.82(7). In this way, the content of Ni in the $A'$ site per formula equals 1.64 instead of 2.

O4 has a higher temperature factor than the other oxygen atoms. After checking that its site is fully occupied, the explanation could be found in its position. This oxygen atom, that should be in the $Sr_3O_9$ layer in the ideal compact hexagonal packing, is shifted out of the layer toward the Ni3 atom, remaining nearly in a interlayer position. This fact allows a higher thermal vibration of this atom and agrees with the largest standard deviation in its **x** and **y** coordinates. In Fig. 1 the oxygen atoms out of the layer are labeled.

Several models have been proposed in order to establish the Ni valence in these compounds. According to formal ideas on chemical valence and the values of Ni–O distances, an ordered distribution of $Ni^{4+}$ (low-spin), $Ni^{3+}$ (low-spin), and $Ni^{2+}$ was suggested for (6) $Ba_6Ni_5O_{15}$. Later an alternative valence distribution in which the Ni is present as $Ni^{2+}$ and low-spin $Ni^{4+}$ in an also ordered structure has been proposed (1).

For $Sr_{12}Ni_{7.5}O_{27}$ the nickel oxidation state was studied by calculations of the Coulomb terms of the lattice energy, concluding that the best model for this compound is the one in which the whole amount of Ni is formally $Ni^{4+}$ (5, 12).

Taking into account the chemical formula obtained after refining the population factors of Ni(4) and the oxygen atoms –$Sr_9Ni_{6.64}O_{21}$–, with a mean oxidation state for Ni of 3.61, none of these models fits perfectly. One reasonable way to maintain the electrical neutrality is by assuming a total occupation of $Ni^{4+}$ at octahedral sites (Ni1, Ni2, and Ni3) and thus a formal charge of $2.5^+$ in the prismatic sites. This $2.5^+$ can be reached by either a 50–50% occupation of $Ni^{2+}Ni^{3+}$ or a 25% of $Ni^{4+}$ and 75% in the partially occupied (pp = 0.82) prismatic sites (Ni4).

This model could imply a small disorder around Ni4 that would justify the twice standard deviation for the **z** coordinate of this atom with respect to the remaining Ni atoms, as well as the high thermal parameter of Ni4, even after refining its population factor.

Depending on the Ni occupation in trigonal sites, different formulas can be obtained for the $n = 2$ structural type, from $Sr_9Ni_5O_{21}$ in which all the trigonal sites are vacant to $Sr_9Ni_7O_{21}$ in which all the prismatic sites are occupied and chains are not broken in any place. $Sr_9Ni_{6.64}O_{21}$ is an intermediate compound within the $n = 2$ range composition.

## ACKNOWLEDGMENTS

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