

A Series of Oxygen-Defect Perovskites Containing Cu^{II} and Cu^{III}: The Oxides $\text{La}_{3-x}\text{Ln}_x\text{Ba}_3 [\text{Cu}_{5-2y}^{\text{II}} \text{Cu}_{1+2y}^{\text{III}}] \text{O}_{14+y}$

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A series of oxygen-defect perovskites, containing Cu^{II} and Cu^{III}, $\text{La}_3\text{Ba}_3 [\text{Cu}_{5-2y}^{\text{II}} \text{Cu}_{1+2y}^{\text{III}}] \text{O}_{14+y}$, has been synthesized at 1000°C, for $0.05 \leq y \leq 0.43$. The substitution of lanthanum for yttrium and lanthanides has been studied. These oxides are tetragonal: $a = a_p 2^{1/2}$ and $c = 3a_p$. The structural study of $\text{La}_3\text{Ba}_3 \text{Cu}_6\text{O}_{14.10}$ shows that oxygen vacancies are ordered, involving for copper three sorts of coordination: square, pyramidal (4 + 1), and distorted octahedral (4 + 2). The distribution of Cu^{III}, as well as the lanthanide ions on the different sites, is discussed.

Introduction

The number of oxygen-defect perovskites ABO_{3-x} known at the present time is limited. This is probably related to the nature of the *B* atoms forming the octahedral framework: the anion deficiency should be stabilized if the *B* atom is going to be able to present, in addition to the octahedral coordination, an environment derived from the latter but characterized by a smaller number of coordination. In this respect, copper is a potential candidate due to its ability to take octahedral, square planar, or pyramidal coordination. Moreover, the oxygen nonstoichiometry in the copper oxides can be influenced by the possibility of formation of trivalent copper, depending on the experimental conditions. Ternary oxides $\text{A}_m\text{Cu}_n\text{O}_t$ containing Cu^{III} can indeed be prepared under 1 atm oxygen pressure (1-4) or under high oxygen pressure (5, 6) according to the nature of the A

element. Some A elements like barium allow the formation of Cu^{III} in air (7, 8). The present paper deals with a series of defect perovskites $\text{La}_{3-x}\text{Ln}_x\text{Ba}_3\text{Cu}_6\text{O}_{14+y}$ which have been synthesized in air and in which copper takes two oxidation states: +2 and +3.

Synthesis and Characterization

The Oxides $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14+y}$

La_2O_3 and CuO oxides and BaCO_3 were mixed and heated in air, in platinum crucibles, first for 12 hr at 900°C, then for 24 hr at 1000°C, and finally quenched at room temperature. From the different compositions which were investigated a pure compound was isolated with the atomic ratios: $\text{La}/\text{Ba} = (\text{La} + \text{Ba})/\text{Cu} = 1$. The observed weight loss was smaller than that deduced from the departure of CO_2 . The partial oxidation of Cu(II) to Cu(III) was thus considered, leading to the formula La_3Ba_3

$[\text{Cu}_{5-2y}^{\text{II}} \text{Cu}_{1+2y}^{\text{III}}] \text{O}_{14+y}$. The y value obtained from the weight loss during the synthesis, $y = 0.10$, was in agreement with this hypothesis. This was confirmed by the microthermogravimetric study of the reduction of the quenched product under hydrogen.

The variation of y as a function of temperature and especially oxygen pressure was then examined. Annealing the quenched compound in air gave a maximum value of y (0.37) at 400°C. The quenched compound ($y = 0.10$) was then annealed at this temperature under different oxygen pressures, ranging from $5 \cdot 10^{-3}$ to 1 atm. The y value and thus the Cu(III) amount, deduced from microthermogravimetric measurements, increased regularly with the oxygen pressure, as shown in Table I.

All these oxides were obtained in the form of a black powder, whose X-ray patterns show strong reflections similar to those of the stoichiometric perovskites. They have been indexed in a tetragonal cell whose parameters are related to that of the cubic perovskite a_p , in the following way: $a = b = a_p \cdot 2^{1/2}$; $c = 3a_p$. These parameters do not vary appreciably with the oxygen amount: $a = 5.5253(4)$ Å and $c = 11.721(1)$ Å for the air-quenched sample ($y = 0.10$), while $a = 5.5291(8)$ Å and $c = 11.729(2)$ Å for the sample annealed under 1 atm oxygen ($y = 0.43$).

The Oxides $\text{La}_{3-x}\text{Ln}_x\text{Ba}_3\text{Cu}_6\text{O}_{14+y}$ ($\text{Ln} = \text{Y, Pr, Nd, Sm, Eu, Gd, Er, Yb}$)

These compounds were prepared in the

TABLE I

THE OXIDES $\text{La}_{3-x}\text{Ln}_x\text{Ba}_3\text{Cu}_6\text{O}_{14+y}$: EVOLUTION OF y AS A FUNCTION OF OXYGEN PRESSURE^a

| P_{O_2} (atm) | $5 \cdot 10^{-3}$ | 10^{-2} | $2 \cdot 10^{-2}$ | $5 \cdot 10^{-2}$ | 0.1 | 0.2 | 1 |
|---------------------------|-------------------|-----------|-------------------|-------------------|------|------|------|
| y | 0.05 | 0.19 | 0.25 | 0.31 | 0.34 | 0.37 | 0.43 |

^a After annealing the quenched oxide ($y = 0.10$) at 400°C.

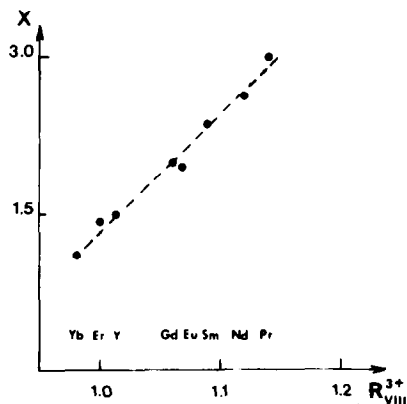


FIG. 1. Substitution of La^{3+} for Ln^{3+} in $\text{La}_{3-x}\text{Ln}_x\text{Ba}_3\text{Cu}_6\text{O}_{14+y}$: evolution of x as a function of the ionic radii of Ln^{3+} (13).

same way as the oxide $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14.10}$, quenching the sample from 1000°C to room temperature in air. In the case of yttrium and europium, the oxides were heated for periods greater than 24 hr, in order to obtain better crystallization. The possibility of substitution of lanthanum for another lanthanide or for yttrium decreases regularly with the size of Ln^{3+} (Fig. 1): a total substitution ($x = 3$) was obtained for praseodymium, while less than 50% of lanthanum could be replaced by ytterbium. The evolution of the oxygen amount y , was not investigated in an exhaustive manner. It can be stated that for the same experimental conditions as those used for $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14.10}$, the variation of the Cu(III) amount remains weak. It seems, however, that y decreases with the size of the Ln^{3+} ion: the y values observed for the three richest compounds in Ln^{3+} , $\text{Ln} = \text{Pr, Nd, and Sm}$ are respectively 0.10, 0.04, and 0.01.

All these oxides are black and are isostructural of $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14.10}$ the c/a ratio remains equal to $3/2^{1/2}$ independently of the composition. The corresponding a_p parameter decreases regularly with the size of Ln^{3+} in agreement with the lanthanidic contraction (Fig. 2).

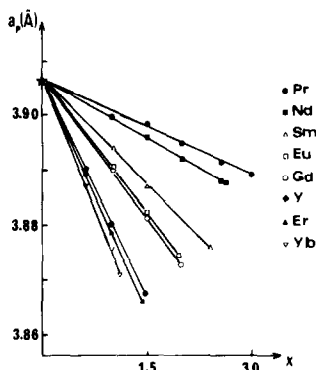


FIG. 2. Evolution of the a_{11} parameter of the oxides $\text{La}_{3-x}\text{Ln}_x\text{Ba}_3\text{Cu}_6\text{O}_{14+y}$.

Structural Study of the Oxide

$\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14.10}$

No single crystal could be obtained due to the decomposition of the compounds at temperatures greater than 1000°C . The structure of this oxide was thus studied from its X-ray powder pattern registered with a Philips goniometer for the $\text{CuK}\alpha$ radiation. The intensities of the peaks corresponding to 74 reflections were measured. The observed density ($d_{\text{exp}} = 6.70$) corresponds to one group $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14.10}$ per cell ($d_{\text{calc}} = 6.67$). The existence of the $1\ 0\ 0$ reflection, though weak, involves the absence of reflection conditions. From the eight possible space groups, we have chosen the most symmetrical space group, $P\ 4/mmm$, in order to limit the number of variable parameters. Because of the similarity of this phase to the perovskite, the metallic atoms were placed in analogous positions: the barium and lanthanum ions were statistically distributed in $4(i)$ ($0\ \frac{1}{2}\ z$; $z \approx \frac{1}{6}$) and $2(f)$ ($0\ \frac{1}{2}\ \frac{1}{2}$), while the copper atoms were placed in $1(a)$ ($0\ 0\ 0$), $1(c)$ ($\frac{1}{2}\ \frac{1}{2}\ 0$), $2(g)$ ($0\ 0\ z$; $z \approx \frac{1}{3}$), and $2(h)$ ($\frac{1}{2}\ \frac{1}{2}\ z$; $z \approx \frac{1}{3}$). The great anionic deficiency with respect to the stoichiometric perovskites set the problem of the distribution of the 14.1 oxygen atoms over the 18 possible sites of the structure. Starting from the ideal formula

$\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14}$, we have assumed that the structure was built up from CuO_2 sheets parallel to (001) as in $\text{La}_{2-x}\text{A}_{1+x}\text{Cu}_2\text{O}_{6-x/2}$ (9) involving, for copper at least, the square planar coordination. Twelve oxygen atoms O_1 and O_2 were thus respectively distributed on $4(j)$ ($x\ x\ 0$; $x \approx \frac{1}{4}$) and $8(r)$ ($x\ x\ z$; $x \approx \frac{1}{4}$ and $z \approx \frac{1}{3}$). For the two remaining oxygen atoms O_3 , located between the CuO_2 layers at about the same level as the barium and the lanthanum atoms, different distributions over four sets of sites— $1(b)$ ($0\ 0\ \frac{1}{2}$); $1(d)$ ($\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$); $2(h)$ ($\frac{1}{2}\ \frac{1}{2}\ z$; $z \approx \frac{1}{6}$); $2(g)$ ($0\ 0\ z$; $z \approx \frac{1}{6}$)—were considered. After successive refinement of the atomic coordinates of the metallic atoms, of the oxygen atoms O_1 and O_2 , and of the isotropic thermal parameters it was found that the O_3 atoms were located principally in $2(h)$. The minimum discrepancy factor $R = \sum |I_{\text{obs}} - I_{\text{calc}}| / \sum I_{\text{obs}}$, $R = 0.039$, was obtained for the thermal and positional parameters given in Table II. Table III shows the agreement between the calculated and observed intensities.

Description of the Structure and Discussion

This structure can be described from that of perovskite by formation of ordered oxygen vacancies in the "A-O" planes. The result is that the plane stacking sequence

TABLE II
FINAL POSITIONAL AND THERMAL PARAMETERS OF
 $\text{Ba}_3\text{La}_3\text{Cu}_6\text{O}_{14.1}$

| Atom | Site | x | y | z | B (\AA^2) |
|---------------|--------|---------------|---------------|---------------|-------------------------|
| A_1 | $4(i)$ | 0 | $\frac{1}{2}$ | 0.1798(3) | 0.43(4) |
| A_2 | $2(f)$ | 0 | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.35(7) |
| Cu_1 | $1(a)$ | 0 | 0 | 0 | 0.1(3) |
| Cu_2 | $1(c)$ | $\frac{1}{2}$ | $\frac{1}{2}$ | 0 | 0.2(3) |
| Cu_3 | $2(g)$ | 0 | 0 | 0.348(2) | 0.8(2) |
| Cu_4 | $2(h)$ | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.346(2) | 0.9(2) |
| O_1 | $4(j)$ | $\frac{1}{4}$ | $\frac{1}{4}$ | 0 | 0.1(1) |
| O_2 | $8(r)$ | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.358(2) | 1.8(5) |
| O_3 | $2(h)$ | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.147(5) | 0.1(1) |

TABLE III
X-RAY DIFFRACTION DATA OF $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14.10}$

| <i>hkl</i> | <i>d</i> _{obs} | <i>d</i> _{calc} | <i>I</i> _{obs} | <i>I</i> _{calc} | <i>hkl</i> | <i>d</i> _{obs} | <i>d</i> _{calc} | <i>I</i> _{obs} | <i>I</i> _{calc} |
|------------|-------------------------|--------------------------|-------------------------|--------------------------|------------|-------------------------|--------------------------|-------------------------|--------------------------|
| 001 | 11.67 | 11.72 | 0.6 | 1.0 | 119 | 1.2358 | 1.2354 | 13.6 | 3.6 |
| 100 | — | 5.525 | vw | 0.3 | 333 | | | | |
| 003 | 3.907 | 3.907 | 12.9 | 1.9 | 420 | | | | |
| 110 | | | | | 10.3 | 317 | — | 1.2089 | 0.4 |
| 111 | 3.705 | 3.706 | 0.6 | 0.3 | 405 | — | 1.1900 | 0.2 | 0.4 |
| 112 | 3.249 | 3.251 | 1.1 | 0.9 | 334 | | | | |
| 113 | 2.7630 | 2.7626 | 100 | 71.3 | 209 | 1.1782 | 1.1780 | 3.0 | 0.8 |
| 200 | | | | | 28.1 | | | | |
| 202 | — | 2.4988 | 0.3 | 0.3 | 406 | 1.1276 | 1.1278 | 5.1 | 4.0 |
| 005 | 2.3432 | 2.3442 | 4.5 | 1.2 | 1110 | — | 1.1227 | 5.1 | 0.9 |
| 114 | | | | | 2.3 | | | | |
| 203 | 2.2553 | 2.2556 | 12.9 | 12.7 | 229 | — | 1.0836 | 1.7 | 0.4 |
| 115 | 2.0097 | 2.0101 | 0.8 | 0.1 | 336 | | | | |
| 204 | | | | | 0.3 | | | | |
| 006 | 1.9536 | 1.9535 | 27.1 | 7.7 | 2010 | — | 1.0790 | 0.3 | 0.3 |
| 220 | | | | | 19.4 | | | | |
| 205 | 1.7875 | 1.7874 | 0.5 | 0.4 | 407 | — | 1.0655 | 0.2 | 0.3 |
| 116 | 1.7473 | 1.7472 | 6.0 | 2.0 | 512 | | | | |
| 223 | | | | | 1.4 | 319 | 4.3 | | |
| 310 | | | | | 2.3 | 426 | 4.8 | | |
| 007 | 1.6734 | 1.6744 | 0.5 | 0.5 | 513 | 1.0443 | 1.0441 | 15.5 | 5.9 |
| 312 | | | | | 0.3 | | | | |
| 206 | 1.5948 | 1.5949 | 33.8 | 9.6 | 427 | — | 0.9941 | 0.9 | 0.5 |
| 313 | | | | | 25.0 | | | | |
| 117 | 1.5383 | 1.5390 | 0.5 | 0.5 | 440 | — | 0.9767 | 3.7 | 1.8 |
| 225 | 1.5012 | 1.5006 | 2.1 | 0.9 | 3110 | | | | |
| 314 | | | | | 0.9 | 338 | 0.3 | | |
| 207 | — | 1.4319 | 0.6 | 0.7 | 1112 | — | 0.9475 | 2.3 | 0.3 |
| 226 | 1.3814 | 1.3813 | 14.7 | 8.5 | 409 | | | | |
| 400 | | | | | 5.2 | | | | |
| 118 | — | 1.3718 | 0.9 | 0.9 | 443 | — | 0.9445 | 0.5 | 0.6 |
| 009 | 1.3025 | 1.3023 | 3.1 | 0.1 | 530 | | | | |
| 316 | | | | | 1.7 | 428 | 0.1 | | |
| 403 | 1.3025 | 1.3023 | 3.1 | 0.7 | 2012 | — | 0.9445 | 9.0 | 1.3 |
| 330 | | | | | 0.5 | | | | |
| 227 | — | 1.2712 | 1.0 | 0.6 | 533 | 0.9210 | 0.9208 | 9.0 | 5.2 |
| 332 | | | | | 0.1 | | | | |

$|\text{AO} - \text{CuO}_2|_\infty$ along *a* in the cubic perovskite is replaced by the sequence $|\text{Cu}_2\text{O}_4 - \text{A}_2\text{O}\square - \text{Cu}_2\text{O}_4 - \text{A}_2\square_2 - \text{Cu}_2\text{O}_4 - \text{A}_2\text{O}\square|_\infty$ along *c* in $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14.10}$ (Fig. 3). Three sorts of coordination are thus observed for copper in this structure: square planar for Cu_1 and Cu_3 , pyramidal (4 + 1) for Cu_4 , and distorted octahedral (4 + 2) for Cu_2 (Table IV).

Whatever the nature of the copper coor-

dination may be, we always observed for this atom a basal plane characterized by four Cu–O distances close to 1.95–1.96 Å. The great distance (2.33 Å) observed for Cu_4 is close to that obtained for copper with a similar coordination in $\text{La}_{2-x}\text{A}_{1+x}\text{Cu}_2\text{O}_{8-x/2}$ (9) (2.26–2.36 Å). On the other hand, Cu_2 has four long Cu–O distances in the (*x* 0 *y*) plane and two short distances along *c*, contrary to the usually

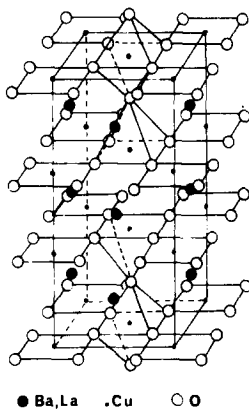


FIG. 3. Structure of $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14.10}$.

observed Jahn–Teller distortion. Such an environment has, however, already been observed in K_2CuF_4 (10) Pr_2CuO_4 (11). The very short $\text{Cu}_2\text{--O}$ distances (1.72 Å), smaller than those observed for copper in 4 + 1 coordination in BaCuO_2 (1.80 Å) (12) made us think that the oxidation state of this element may be +3, in agreement with the very short distances observed in LaSrCuO_4 (6). This environment suggests for Cu^{III} a $d^2_x2-y2 - d_{z^2}$ configuration (11).

The distribution of lanthanum and barium over the A_1 and A_2 sites could not be studied due to the similar values of the scattering factors of La^{3+} and Ba^{2+} which are isoelectronic. The $A_1\text{--O}$ distances are much greater than the $A_2\text{--O}$ distances; these let us deduce that the barium atoms are located only on the A_1 sites. In order to verify this hypothesis, the yttrium compound $\text{La}_2\text{YBa}_3\text{Cu}_6\text{O}_{14+y}$ was examined, the scattering factor of yttrium being smaller than that of lanthanum or barium. The intensities ratio of the 1 1 2 and 2 0 3 reflections of this compound was thus compared to that of $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14.10}$. The I_{112}/I_{203} ratio varies appreciably indeed with the electronic distribution on the A_1 and A_2 sites, since the contributions of the A_1 sites to the structure factors F_{112} and F_{203} have opposite signs, while the contribu-

tions of A_2 sites have the same sign. The experimental value $(I_{112}/I_{203})_{\text{Y}} = 0.20$ observed for the $\text{La}_2\text{YBa}_3\text{Cu}_6\text{O}_{14+y}$, much greater than that of $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14.1}$, $(I_{112}/I_{203}) = 0.085$, shows that the smallest ion, yttrium, is located on the A_2 site, leading to the probable distribution: (3Ba + 1La) on A_1 and (1La + 1Y), on A_2 , in agreement with our hypothesis.

The very large oxygen deviation from stoichiometry is an important feature of these compounds. The ordered distribution of the oxygen vacancies with regard to the ideal perovskite must be emphasized; it is worth noting that the distribution of the O_3 atoms on the 1(b) and 1(d) sites appreciably increases the R factor. In the same manner, a statistical distribution of these atoms over the 2(g) and 2(h) sites, which would involve the disappearance of the superstructure in the (0 0 1) plane, is not possible. A partial occupation of the 2(g) sites cannot, however, be eliminated. The 0.1 supplementary oxygen atoms, which have not been considered for these calculations, could be located, if we consider Cu^{3+} ions with an octahedral coordination, either on the 2(g) or on the 1(d) sites. The second hypothesis agrees with the fact that the introduction of one supplementary oxygen atom induces the presence of two Cu^{3+} ions. However, calculations made on a richer oxygen compound do not allow us to choose between these sites. The presence of copper in these compounds, simulta-

TABLE IV
INTERATOMIC DISTANCES OF $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14.10}$

| $M\text{--O}$ | Distance (Å) | $M\text{--O}$ | Distance (Å) |
|---------------------------|----------------------|---------------------------|----------------------|
| $A_1\text{--O}_1$ | $2.874(3) \times 4$ | $\text{Cu}_2\text{--O}_1$ | $1.954(0) \times 4$ |
| $A_1\text{--O}_2$ | $2.860(17) \times 4$ | $\text{Cu}_2\text{--O}_3$ | $1.723(59) \times 1$ |
| $A_1\text{--O}_3$ | $2.790(8) \times 2$ | $\text{Cu}_3\text{--O}_2$ | $1.957(2) \times 4$ |
| $A_2\text{--O}_2$ | $2.567(15) \times 8$ | $\text{Cu}_4\text{--O}_1$ | $1.959(2) \times 4$ |
| $\text{Cu}_1\text{--O}_1$ | $1.954(0) \times 4$ | $\text{Cu}_4\text{--O}_3$ | $2.333(63) \times 1$ |

neously with two oxidation states, Cu(II) and Cu(III), suggests interesting electrical properties, which will be investigated as a function of oxygen amounts.

References

1. W. KLEMM, G. WEHRMEYER, AND H. BADE, *Z. Elektrochem. Ber. Bunsenges. Phys. Chem.* **63**, 56 (1959).
2. K. HESTERMANN AND R. HOPPE, *Z. Anorg. Allg. Chem.* **367**, 249 (1969).
3. K. HESTERMANN AND R. HOPPE, *Z. Anorg. Allg. Chem.* **367**, 261 (1969).
4. K. HESTERMANN AND R. HOPPE, *Z. Anorg. Allg. Chem.* **367**, 270 (1969).
5. G. DEMAZEAU, C. PARENT, M. POUCHARD, AND P. HAGENMULLER, *Mater. Res. Bull.* **7**, 913 (1972).
6. J. B. GOODENOUGH, G. DEMAZEAU, M. POUCHARD, AND P. HAGENMULLER, *J. Solid State Chem.* **8**, 325 (1973).
7. M. ARJOMAND AND D. MACHIN, *J. Chem. Soc. Dalton Trans.*, 1061 (1975).
8. H. N. MIGEON, F. JEANNOT, M. ZANNE, AND J. AUBRY, *Rev. Chim. Miner.* **13**, 440 (1976).
9. N. NGUYEN, L. ER-RAKHO, C. MICHEL, J. CHOISNET, AND B. RAVEAU, *Mater Res. Bull.* **15**, 891 (1980).
10. K. KNOX, *J. Chem. Phys.* **30**, 991 (1959).
11. J. M. LONGO AND P. M. RACCAH, *J. Solid State Chem.* **6**, 526 (1973).
12. R. KIPKA AND H. MULLER-BUSCHBAUM, *Z. Naturforsch. A* **326**, 121 (1977).
13. R. D. SHANNON AND C. T. PREWITT, *Acta Crystallogr.* **25**, 925 (1969).