

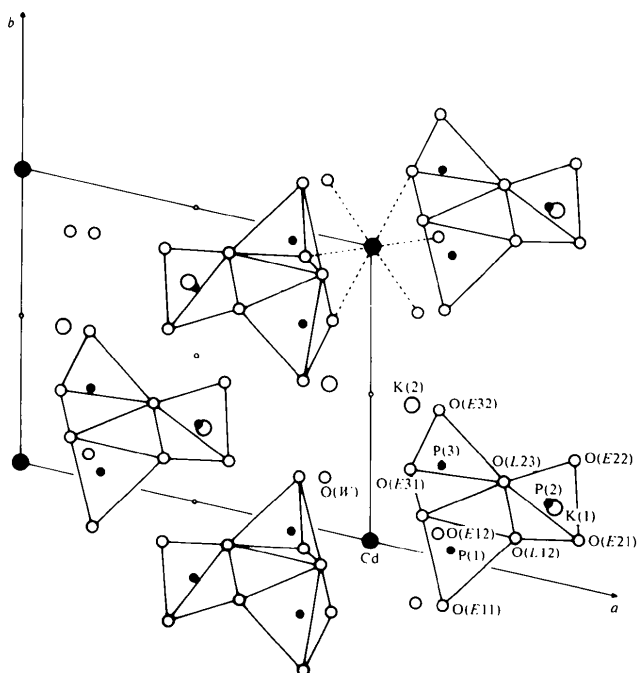
Tableau 4 (suite)

Environnements des atomes de potassium

K(1)—O(E12)	3,070 (3)	K(2)—O(E11)	2,733 (3)
K(1)—O(E21)	2,895 (4)	K(2)—O(E31)	2,865 (3)
K(1)—O(E21)	3,149 (4)	K(2)—O(E31)	3,157 (3)
K(1)—O(E11)	2,954 (3)	K(2)—O(E22)	2,698 (4)
K(1)—O(L23)	2,924 (3)	K(2)—O(E32)	2,765 (3)
K(1)—O(L12)	2,859 (3)	K(2)—O(E32)	3,068 (4)
K(1)—O(E22)	3,182 (4)	K(2)—O(W)	2,854 (2)
K(1)—O(E22)	2,736 (4)		
K(1)—O(E32)	2,920 (3)		

Environnements des atomes de phosphore

P(1)	O(E11)	O(E12)	O(L12)	O(L13)
O(E11)	<u>1,475 (3)</u>	2,574 (4)	2,492 (4)	2,481 (4)
O(E12)	121,2 (2)	<u>1,480 (3)</u>	2,456 (4)	2,516 (4)
O(L12)	108,4 (2)	105,9 (2)	<u>1,596 (3)</u>	2,492 (4)
O(L13)	107,6 (2)	109,6 (2)	102,6 (2)	<u>1,598 (3)</u>
P(2)	O(E21)	O(E22)	O(L12)	O(L23)
O(E21)	<u>1,471 (4)</u>	2,552 (6)	2,482 (4)	2,457 (5)
O(E22)	120,8 (2)	<u>1,464 (4)</u>	2,471 (4)	2,546 (5)
O(L12)	107,8 (2)	107,5 (2)	<u>1,598 (3)</u>	2,495 (4)
O(L23)	105,5 (2)	111,6 (2)	101,9 (2)	<u>1,613 (3)</u>
P(3)	O(E31)	O(E32)	O(L13)	O(L23)
O(E31)	<u>1,490 (3)</u>	2,557 (4)	2,473 (4)	2,508 (4)
O(E32)	119,7 (2)	<u>1,468 (3)</u>	2,525 (4)	2,532 (4)
O(L13)	106,0 (1)	110,5 (2)	<u>1,604 (2)</u>	2,473 (3)
O(L23)	107,9 (1)	110,5 (2)	100,5 (1)	<u>1,612 (3)</u>

Fig. 1. Projection de l'arrangement atomique sur le plan ab .

Référence

BOULLÉ, A. (1938). *C.R. Acad. Sci.* **206**, 517–518.*Acta Cryst.* (1978). **B34**, 22–26The Crystal Structure of Paramelaconite, $\text{Cu}_{12}^{2+}\text{Cu}_4^+\text{O}_{14}^*$

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(Received 28 July 1975; accepted 6 July 1977)

Paramelaconite is an oxygen-deficient tetragonal copper oxide, space group $I4_1/amd$, with unit-cell dimensions $a = 5.817$, $c = 9.893$ Å and contents $\text{Cu}_{16-2x}^{2+}\text{Cu}_{2x}^+\text{O}_{16-x}$ where $x = 1.85$. Its structure has been obtained by Patterson synthesis and least-squares refinement of three-dimensional intensity data ($R = 8.3\%$) collected from spherical crystals using an integrating Weissenberg camera. The atomic arrangement is similar to that in tenorite, a cupric oxide. The relationship between the two structures is discussed. The appearance of a few weak satellite reflections is suggestive of ordering of oxygen vacancies.

Introduction

The rare mineral paramelaconite, an oxide of copper, was exhaustively investigated by Frondel (1941). He

showed, from chemical analysis, density, cell size and space-group considerations that its ideal composition is approximately $\text{Cu}_{16}\text{O}_{16}$ and the real chemical composition is approximately $\text{Cu}_{16}\text{O}_{14}$. The observed cell contents are represented by a general formula $\text{Cu}_{16-2x}^{2+}\text{Cu}_{2x}^+\text{O}_{16-x}$ where $x = 1.85$. The mineral is therefore a cupric oxide (CuO) with an oxygen defect structure in which the omission of O atoms is compensated by the appearance of cuprous ions in place of

* Dr Naryan Datta's illness and untimely death have delayed the amendments to the original draft of this paper. Part of this paper is condensed from a section of his thesis accepted by London University for the degree of PhD (Datta, 1970).

some of the cupric copper. It crystallizes in the tetragonal system and its space group is $I4_1/amd$. Frondel discussed the structural implications, especially of the marked pseudo-cell with halved a and c axes, but did not attempt a structure determination.

The mineral tenorite, CuO , which contains Cu^{2+} only, crystallizes in the monoclinic space group $C2/c$ (Tunell, Posanjak & Kasanda, 1935; Åsbrink & Norrby, 1970).

The formation of paramelaconite may be due to the replacement of some Cu^{2+} ions in the tenorite structure by Cu^+ with the omission of half the number of O^{2-} ions allowing the original tenorite structure to be distorted and to take a symmetry higher than monoclinic. Hence there may be a structural relationship between tenorite (CuO) and paramelaconite. In order to investigate this relationship and the positions of the substitutions and vacant sites, the structure determination was undertaken.

Experimental

The naturally occurring specimen of paramelaconite was obtained by courtesy of Professor Clifford Frondel of Harvard University, Massachusetts, USA. Only two specimens of paramelaconite are known. These were obtained by Dr A. E. Foote, about 1890, at Copper Queen Mine, Bisbee, Arizona.

The crystal of paramelaconite was examined optically using a two-circle goniometer. It was tetragonal in development with forms $\{001\}$, $\{101\}$ and $\{100\}$.

Small, approximately equidimensional, fragments cut from the specimen were ground into spheres (Bond, 1951) and then washed in methanol containing 0.25% HNO_3 to remove adherent powder.

Since paramelaconite is opaque an X-ray method was used to orientate the spherical crystals [essentially that described by Henry, Lipson & Wooster (1961)]. The ground crystals were mounted at the tips of hollow fibres of borosilicate glass. The mean radius of each crystal and its standard deviation were determined from shadowgraphs (Jeffery, 1971). Accurate cell parameters were determined by a back-reflection technique similar to the method described by Farquhar & Lipson (1946). The density was determined by a modified flotation method (Taylor & Doyle, 1968).

The space group of the crystal was reinvestigated using oscillation, Laue and Weissenberg methods. Paramelaconite showed a distinct pseudo-halving for both a and c axes. Weissenberg photographs of even layers about both the axes showed that reflections hkl indexed on the real cell were very strong when $h + k + l = 4n$ and much weaker for $h + k + l = 4n + 2$.

Three-dimensional data were collected about a and c on a Nonius integrating Weissenberg camera (Wiebenga & Smits, 1950). The integrating Weissenberg camera was aligned photographically (Whitaker,

1965). The precautions and considerations described by Whitaker, concerning crystal size, collimator diameter, selection of X-ray tube, *etc.*, for collection of X-ray intensity data were followed in this case (Whitaker, 1965; Jeffery & Whitaker, 1965). In order to eliminate the occurrence of multiple reflections the camera inclination angle μ was mis-set by 0.5° (Jeffery, 1969). The integrated diffraction spots were measured with a special photometer designed by Jeffery (1963).

The raw intensity data were corrected for Lorentz, polarization and absorption factors and weights were calculated according to the method described by Rose & Jeffery (1964). The layer correction factors were derived by the method developed by Rollett & Sparks (1960). The correlated equivalent reflections and their weights were averaged with a computer program. Some 650 reflections were measured and reduced to 83 symmetry-independent reflections. Within one-sixteenth of reciprocal space (for the $Cu K\alpha$ sphere) there were about 50 reflections with zero intensity.

Crystal data

$a = 5.817$ (1), $c = 9.893$ (2) Å, $c/a = 1.701$ (1), $V = 334.75$ (13) Å³, $D_m = 6.114$ (38), $D_x = 6.312$ g cm⁻³ (for content $Cu_{16}O_{16}$), $D_x = 6.164$ g cm⁻³ (for $Cu_{16}O_{14.15}$). Absorption coefficient for $Cu K\alpha$: $\mu = 270$ cm⁻¹. Crystal radius: (1) mounted on a : 0.074 (2) mm, (2) mounted on c : 0.098 (4) mm. Laue symmetry: $4/mmm$; reflections present only for $h + k + l = 2n$, $00l$ when $l = 4n$, $hk0$ when $h, k = 2n$ and hhl when $l = 2n$, $2h + l = 4n$. Space group: $I4_1/amd$ (second setting chosen with origin at $2/m$). Pseudo-cell space group: $I4/mmm$.

Patterson synthesis

Two-dimensional (Ok) and three-dimensional sharpened Patterson syntheses were evaluated. On the projection vector map (Fig. 1) the following two sets of peaks appeared at $(-vw)$, together with those related by the cm symmetry of the Patterson projection. (1) $(0, 0; \frac{1}{2}, 0)$ of peak height 712 and (2) $(0, \frac{1}{8}; \frac{1}{4}, \frac{1}{8})$ of peak height 93. The calculated peak height for the superimposed $Cu-O$ vectors was approximately 91, so (2) were attributed to $Cu-O$ vectors.

From the Patterson peak positions and space-group considerations, assuming there were 16 Cu and 16 O atoms per unit cell, the atoms were located as follows (first trial structure):

- $Cu(1)$ in (c) 0,0,0 (8)
- $Cu(2)$ in (d) $0, 0, \frac{1}{2}$ (8)
- $O(1)$ in (e) $0, \frac{1}{2}, z$ (8) where $z = 0.09$
- $O(2)$ in (b) $0, \frac{1}{4}, \frac{3}{8}$ (4)
- $O(3)$ in (a) $0, \frac{1}{4}, \frac{7}{8}$ (4).

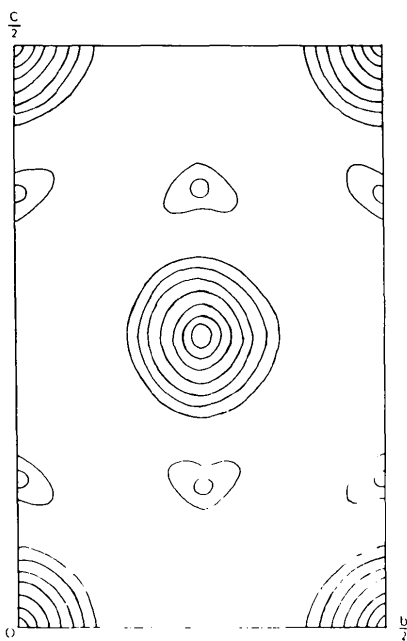


Fig. 1. Paramelaconite: *a* axis sharpened Patterson projection.

With the same Cu atom positions there was another possibility of 16 O positions at $x, \frac{1}{4} + x, \frac{7}{8}$ on twofold axes where $x = 0.25$ (second trial structure). No further information could be obtained from the three-dimensional Patterson map.

Least-squares refinement

A full-matrix structure-factor least-squares program written by Dr G. S. Shearing was used. The scattering factors for Cu^{2+} and O^{2-} were taken from Cromer & Waber (1965). The initial scale and temperature factors of the atoms used were previously determined from a Wilson (1942) plot. The value of the overall temperature factor obtained was $B = 0.53 \text{ \AA}^2$. High parameter interaction was avoided by not refining the interacting parameters together.

The first trial structure was subjected to least-squares refinement and from the very first cycle the isotropic temperature factor for O(2) at $0, \frac{1}{4}, \frac{3}{8}$ turned negative and became increasingly negative (-1.55 \AA^2 finally) while the structure was refining. After six cycles of refinement the residual was $R = 10.1\%$ and $z = 0.100$. Attempts were made to refine the postulated structure for O

atoms only using weak reflections of the type $h + k + l = 4n + 2$ (to which Cu makes no contribution). After six cycles of refinement the residual was $R = 36.5\%$. The B value of O(2) was -0.226 \AA^2 . The occupancy for each of the three atoms O(1), O(2) and O(3), with a fixed $B = 2.5 \text{ \AA}^2$, was refined in turn. The refined values for O(1) and O(3) did not show any appreciable deficiency of O atoms and that for O(2) showed a higher occupancy.

For the second trial structure the isotropic refinement residual was $R = 8.7\%$, with $x = 0.277$ (5). The B values are given in Table 1. Six cycles of refinement were carried out for O atoms only, using the weak reflections ($h + k + l = 4n + 2$) and the final value of the residual was $R = 26.0\%$, while the parameters for the O atom were $x = 0.274$ (5) and $B = 0.52$ (3) \AA^2 .

The first trial structure was rejected because of the negative temperature factor of O(2) and the higher values of $R = 36.5\%$ for the weak reflections and $R = 10.1\%$ for all reflections.

The occupancy for the O atom positions of the second trial structure was refined and its final value was 0.47 instead of 0.50 (for $\text{Cu}_{16}\text{O}_{16}$) which showed a deficiency of approximately one O atom. The value obtained may well be in error for the reason that weak reflections of the type $h + k + l = 4n + 2$, which are due to the contribution of O atoms only, are subject to greater proportional errors.

Two cycles of anisotropic refinement were carried out and the temperature factor results are shown in Table 1. There was no significant change in x or $\sigma(x)$. The final residual was $R = 8.3\%$.* A Fourier synthesis was calculated from the final observed structure factors. A difference Fourier synthesis did not show any significant peaks.

Attempts were made to refine the structure of paramelaconite using a trial structure derived by analogy with the structures of tetragonal monoxides of palladium or platinum (Moore & Pauling, 1941). For the observed space group $I4_1/amd$ of paramelaconite it was not possible to build up a trial structural model where only one type of Cu—O distance could exist, because of the fixed positions of the Cu atoms. It was possible to make up a trial model of paramelaconite

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32899 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Positional parameters, anisotropic temperature factors ($B_{ij} \times 10^4$) and B_{iso} from previous refinement

	Coordinates	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{iso}
Cu(1)	0,0,0	44 (15)	45 (17)	10 (4)	0 (0)	0 (0)	1 (16)	0.53 (7)
Cu(2)	$0,0,\frac{1}{2}$	38 (14)	36 (6)	9 (4)	0 (0)	0 (0)	8 (0)	0.47 (7)
O	$\left\{ \begin{array}{l} x, \frac{1}{4} + x, \frac{7}{8} \\ x = 0.277 (5) \end{array} \right.$	34 (69)	34 (69)	16 (13)	11 (111)	-31 (90)	31 (90)	0.55 (3)

consisting of 16 Cu and 16 O atoms analogous to PdO and PtO structures in the space group $I\bar{4}m2$. The postulated structure was subjected to least-squares refinement. It was found that the shifts for Cu atoms were very small but two O atoms with refinable 'z' parameters moved by approximately 8.0 Å which was obviously meaningless.

General description

The interatomic distances and angles are shown in Table 2. The projection of the structure down $[001]$ is shown in Fig. 2. The Cu atoms are surrounded by four O atoms in a distorted square-planar arrangement and O atoms are surrounded by Cu atoms in a distorted tetrahedral arrangement.

The O^{2-} ions are slightly displaced from the 4_1 axis and spiral round it to give columns parallel to c . The $O \cdots O$ distances in these columns are very short (2.49 Å) and the vacant oxygen sites are probably required to relieve strain in these columns, as well as that produced by the very short Cu—O bond of 1.80 Å.

Relationship with the tenorite structure

The unit cell of tenorite has the following dimensions: $a = 4.653$, $b = 3.410$ and $c = 5.108$ Å, all ± 0.01 Å, and

Table 2. Interatomic distances (Å) and angles ($^\circ$)

Standard deviations are given in parentheses.			
Cu(1)—O(3)	2.035 (21)	O(1)'—Cu(1)—O(3)	95.2 (7)
Cu(2)—O(3)	1.801 (19)	O(1)'—Cu(1)—O(2)'	84.8 (7)
		O(1)—Cu(2)—O(3)	87.4 (6)
O(1)—O(3)	2.599 (37)	O(1)—Cu(2)—O(2)	92.6 (7)
O(1)'—O(3)	3.217 (37)		
O(3)—O(4)	2.492 (34)		

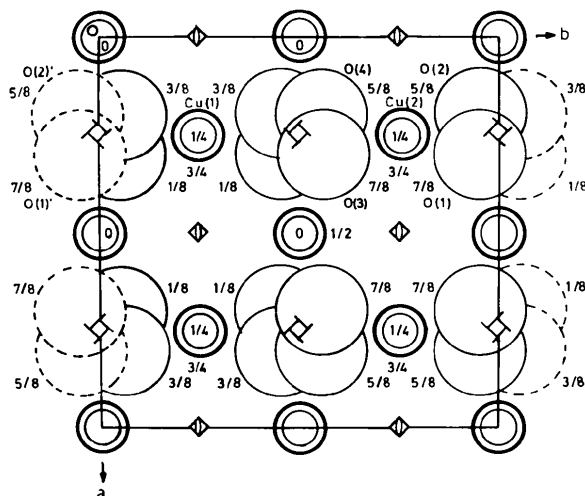


Fig. 2. Paramelaconite structure viewed down $[001]$.

$\beta = 99^\circ 29' \pm 20'$. The unit cell contains four chemical units of CuO and its space group is $C2/c$. The four Cu atoms occupy the positions: $\frac{1}{4}, \frac{1}{4}, 0$; $\frac{3}{4}, \frac{1}{4}, \frac{1}{2}$; $\frac{1}{4}, \frac{3}{4}, \frac{1}{2}$; $\frac{3}{4}, \frac{3}{4}, 0$ and the four O atoms are at $0, n, \frac{3}{4}$; $0, \bar{n}, \frac{1}{4}$; $\frac{1}{2}, n + \frac{1}{2}, \frac{3}{4}$; $\frac{1}{2}, \frac{1}{2} - n, \frac{1}{4}$ where $n = 0.584$ or 0.916 (these two values for n lead to the same structure with a shift of origin). Each Cu atom is surrounded by four O atoms in a planar arrangement at the corners of a rectangle (Cu—O = 1.95, $O \cdots O = 2.61$ and 2.88 Å) and each O atom is surrounded by four Cu atoms on the corners of a non-equilateral tetrahedron (Tunell, Posanjak & Kasanda, 1935; Åsbrink & Norrby, 1970). A distorted structure of tenorite ($\beta = 90^\circ$) projected on to the ab plane is shown in Fig. 3.

A comparison of the structures of tenorite and paramelaconite shows that the Cu—O atomic arrangements are similar in the two cases. In the tenorite structure it is possible to outline a multiple cell taking the Cu atom at $\frac{1}{4}, \frac{1}{4}, 0$ or $\frac{3}{4}, \frac{3}{4}, 0$ as the origin. The proposed cell is built up from four distorted (β made equal to 90°) cells of tenorite, with $a' = b' = 5.76$ Å and $c' = 2c \sin(180^\circ - \beta) = 10.02$ Å and angles $\alpha' = \beta' = 90^\circ$ and $\gamma' = 72^\circ$. In paramelaconite $a = b = 5.81$ Å and $c = 9.89$ Å; $\alpha = \beta = \gamma = 90^\circ$. The proposed cell is shown in Fig. 3. The upper atoms at $\frac{1}{4}, \frac{3}{4}, \frac{1}{2}$ and $\frac{3}{4}, \frac{1}{4}, \frac{1}{2}$ in the sheared tenorite structure are at the body-centred positions of each of the eight sub-units of the proposed cell which is similar to that of paramelaconite.

If in the tenorite structure (CuO) some of the Cu^{2+} ions are replaced by Cu^+ and vacant oxygen sites

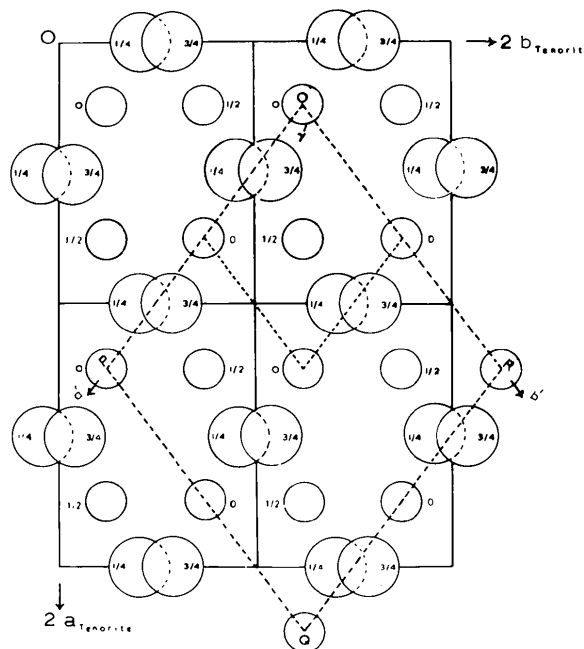


Fig. 3. The proposed cell showing four distorted unit cells of tenorite (in which $\beta = 90^\circ$) projected on to the ab plane. Small circles represent Cu, large circles, O atoms. $OPQR$ is the proposed cell.

produced, then the Cu—O packing could alter slightly so that the structure crystallizes with the monoclinic angle β changed to 90° and the γ' angle increased from 72° to 90° , $a' = b'$ remaining unchanged. Hence the tenorite structure could rearrange in a symmetry higher than monoclinic without altering the general character of the bonding. The main difference is that two of the four equal Cu—O bonds in tenorite are lengthened and two shortened in paramelaconite. The volume of the modified tenorite cell will be $V' = 332.4 \text{ \AA}^3$, approximately equal to that of paramelaconite ($V = 334.7 \text{ \AA}^3$) and slightly greater than four times the volume of the tenorite cell (320 \AA^3).

The Cu—O bond in cuprite (Cu_2O) is 1.84 \AA compared with 1.95 \AA in tenorite (CuO). If the formation of paramelaconite is due to the omission of some O^{2-} ions with the replacement of twice the number of Cu^{2+} ions by Cu^+ in the tenorite structure, then it would be expected that the observed (average) Cu—O bond distance in paramelaconite would be somewhat smaller than that in tenorite. The average Cu—O distance for tenorite is $1.956(3) \text{ \AA}$ and for paramelaconite $1.92(3) \text{ \AA}$, but the difference, although in the right direction, is hardly significant.

Comparison with other structures

The shortest $\text{O}\cdots\text{O}$ distance, 2.49 \AA in paramelaconite, is significantly shorter than the sum of the van der Waals radii (2.8 \AA , Pauling, 1960) and the corresponding distances in similar structures. In palladium oxide, PdO , and platinumous oxide, PtO , (Moore and Pauling, 1941) the shortest $\text{O}\cdots\text{O}$ distances are 2.63 and 2.65 \AA respectively. In silver monoxide, AgO , (Scatturin, Bellon & Zannetti, 1958; Scatturin, Bellon & Salkind, 1961) the $\text{O}\cdots\text{O}$ distances of the O atoms in square-planar configuration round $\text{Ag}(2)$ are 2.83 and 2.91 \AA . In the accurately refined CuO (tenorite) structure (Åsbrink & Norrby, 1970) the shortest $\text{O}\cdots\text{O}$ distance is 2.61 \AA .

The vacant sites and substitutions

There are some very faint satellite reflections on heavily overexposed photographs of the $hk0$ reciprocal lattice

layer. Since these reflections repeat after 90° rotation it is reasonable to suppose that they arise from some ordering of the oxygen vacancies on a scale at least ten times that of the main pseudo-repeat distance. These satellite reflections were too few and weak to allow detailed analysis.

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