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Neutron Diffraction Refinement of Pyroelectric Lithium Perchlorate Trihydrate

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Abstract

The crystal structure of pyroelectric lithium perchlorate trihydrate has been refined from neutron diffraction data, corrected for thermal diffuse scattering. $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$, FW 160.436, hexagonal, $P6_3mc$, $a = 7.7192(4)$, $c = 5.4531(5)$ Å, $V = 281.40$ Å³, $Z = 2$ [Chomnilpan, Liminga & Tellgren (1977). *Acta Cryst.* **B33**, 3954–3957]; $D_x = 1.89$, $D_m = 1.89$ Mg m⁻³, $\mu(\text{measured}) = 0.23$ mm⁻¹, $\lambda = 1.210$ Å. Refinement based on 1284 data recorded at 294 K from a spherical

crystal gave a final $R_w(F^2)$ value of 0.048. The intensity data were severely affected by extinction. Refinements using several extinction models showed that significant differences in the thermal parameters were obtained in all refinements. The changes in the positional parameters were not significant. The ClO_4^- ion was found to be slightly asymmetric: the Cl–O bond directed along the polar c axis is 1.428 (1) Å compared to the value 1.439 (1) Å for the other three Cl–O bonds, which are equivalent by symmetry.

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Introduction

Several X-ray and neutron diffraction studies of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ have been published (Sequeira, Bernal, Brown & Faggiani, 1975, and references therein). The absolute configuration of a crystal of the compound was determined by means of anomalous scattering (Chomnilpan, Liminga & Tellgren, 1977) and the sense of some piezo- and pyroelectric coefficients was related to the absolute polarity and atomic arrangement (Liminga, Chomnilpan & Abrahams, 1978). The possible asymmetry of the ClO_4^- ion may be important for the polar properties of the compound as one of the Cl—O bonds is directed along the polar c axis; the remaining three bonds are related by a threefold axis. A slight asymmetry of the perchlorate ion was found in the X-ray study by Chomnilpan *et al.* (1977) where the Cl—O bond along the polar axis was 0.012 (4) Å shorter than the other bonds. However, Sequeira *et al.* (1975) report a completely regular perchlorate ion [Cl—O: 1.441 (2) and 3×1.440 (2) Å]. These bond lengths were then calculated from a set of 'best' parameter values obtained by averaging parameters from three independent (two X-ray and one neutron) diffraction experiments. Recent X-ray refinements of NH_4ClO_4 and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$, including deformation-density functions in the least-squares calculations, have shown that significant changes in molecular geometry can result from a deformation refinement as compared to a conventional refinement (Lundgren, 1979*a*, 1980). We therefore decided to refine the present structure further, introducing deformation-density functions. The present neutron data refinement was made in order to obtain an accurate set of parameters to be used later for a comparison with the X-ray results. Moreover, predetermined positional and thermal parameters for H (*e.g.* from neutron data) are needed for the X-ray deformation refinements. The results from the deformation refinements will be given in a later paper.

Experimental

A spherically ground crystal with radius 2.19 (4) mm was used for data collection on a computer-controlled Hilger & Watts four-circle diffractometer at the Swedish R2 reactor at Studsvik. The surface layer of the crystal, damaged by the mechanical treatment, had been removed by gently rolling the sphere on a wet filter paper until the crystal was optically transparent. The neutron beam had a mean wavelength of 1.210 Å ($\Delta\lambda/\lambda \sim 0.08$). A total of 1284 reflexions with $\sin \theta/\lambda < 0.69 \text{ \AA}^{-1}$ (excluding test reflexions and space-group extinctions) were measured at 294 K. These, if averaged, would result in 175 independent reflexions. About seven reflexions were thus measured within each form. The intensities of the three test reflexions,

measured at regular intervals during the experiment, showed no systematic variations with elapsed time. Intensities were corrected for background using the profile-analysis method of Lehmann & Larsen (1974). Variances of the intensities were estimated from Poisson counting statistics and from the scatter observed in the test reflexions (McCandlish, Stout & Andrews, 1975). The intensities were corrected for Lorentz and absorption effects. The transmission factors were in the range 0.48 to 0.51.

A test for possible multiple diffraction was made with *MULREF* (Coppens, 1968; Helmholdt & Vos, 1977). It was found that, for *all* strong and medium intensity reflexions, there was a risk of multiple diffraction from the five strongest reflexions (forms) in the material. Due to the present high crystal symmetry and the substantial 'thickness' of the Ewald sphere, it is probably difficult to find setting angles which eliminate the risk of multiple scattering for all reflexions. However, amongst the weak reflexions it may be noted that no significant intensity [$>3\sigma(I)$] was observed for any of the 52 reflexions predicted to be absent due to space-group extinction.

Elastic constants needed for the correction of the structure factors for thermal diffuse scattering are available for $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ (Haussühl, 1978). Different approaches are used for the TDS correction of neutron diffraction data depending on the ratio between the velocity of sound in the crystal and the velocity of the scattered neutrons (Willis, 1970). In the present case the neutrons used are faster than sound in some directions and slower than sound in other directions. For the scattering of slower-than-sound neutrons the correction is expected to be smaller than for faster-than-sound neutrons, and under certain conditions there will be no correction. A TDS correction including all scattered neutrons gave a maximum correction factor α of 0.17, [$I_{\text{corr}} = I_{\text{obs}}/(1 + \alpha)$]. A correction where only faster-than-sound neutrons contribute gave values less than 15% different from those in the first case. These two cases then represent the upper and lower limits of the TDS correction, respectively. Data corresponding to the correction including all scattered neutrons were used in the following. The corrections were calculated using a local modification of a program by Stevens (1974).

The agreement among symmetry-related reflexions was analysed in a normal probability plot, Fig. 1(*a*) (Abrahams & Keve, 1971). The slope of the plot indicates that the e.s.d.'s are underestimated by a factor 1.4; all $\sigma(F_o^2)$ values were later multiplied by this factor. The linearity of the central part of the plot indicates that there are no serious anisotropic, systematic errors in the data. The agreement among the symmetry-related reflexions, $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$, was 0.028. The non-averaged data set was used in all subsequent refinements.

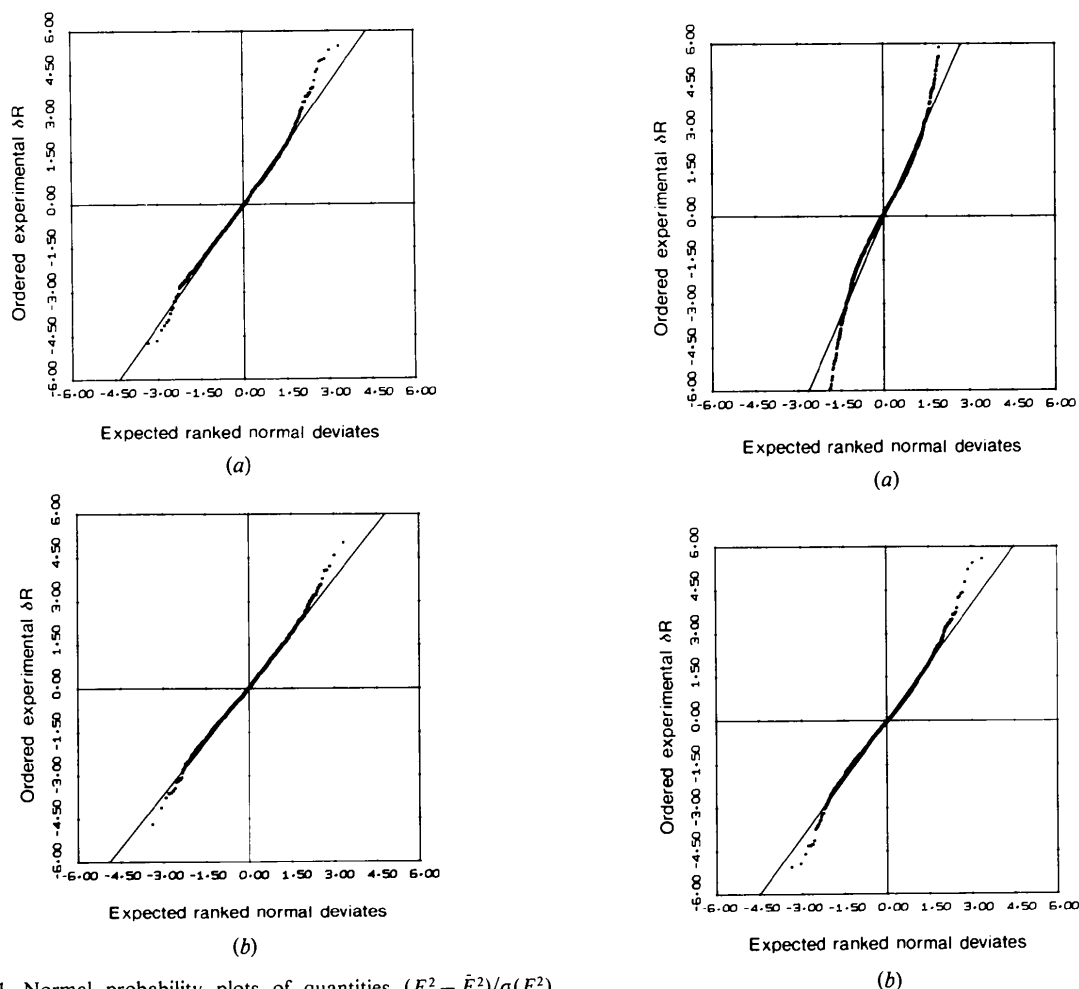


Fig. 1. Normal probability plots of quantities $(F_o^2 - \bar{F}_o^2)/\sigma(F_o^2)$ versus expected values for a normal distribution (0,1). All reflexions for which at least two symmetry-related reflexions were measured are included. (a) Before extinction correction. The slope of the least-squares line through the points is 1.38; the y intercept is 0.02. (b) After anisotropic-extinction correction. The slope of the least-squares line is 1.23; the y intercept is 0.02.

Refinements

The structure was refined starting with parameter values from Chomnilpan *et al.* (1977). The function minimized was $\sum w(F_o^2 - k^2 F_c^2)^2$, where $w^{-1} = \sigma^2(F_o^2)$. Coherent scattering amplitudes were taken from Bacon (1974). The data were seriously affected by extinction and several secondary-extinction models were tried, according to the formalism developed by Becker & Coppens (1974a,b,1975). Details of the best refinements including isotropic- and anisotropic-extinction correction, respectively, are given in Table 1. δR plots of the data are given in Fig. 2. It should be noted that the anisotropic-extinction model gives a markedly better δR plot than the isotropic model. The plot for the anisotropic model is not the ideal straight line, however, suggesting that large $F_o^2 - F_c^2$ discrepancies remain in the data set. Inspection of the structure factors also

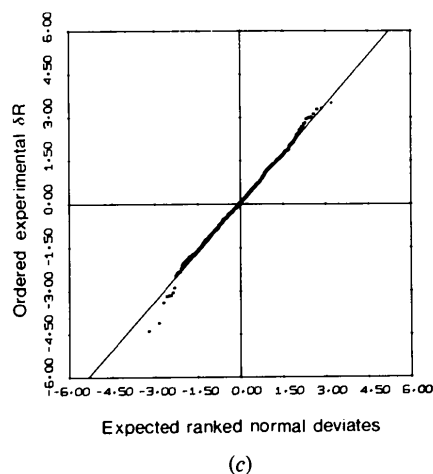


Fig. 2. Normal probability plots of δR plot of the data following the isotropic-extinction refinement (series A); slope 2.36, y intercept 0.01. The points for 77 reflexions fall outside the plot range. (b) δR plot following the anisotropic-extinction refinement (series B); slope 1.52, y intercept 0.00. The points for 14 reflexions fall outside the plot range. (c) δR plot following isotropic-extinction refinement series (C); slope 1.25, y intercept 0.07. The points for all reflexions are within the plot range.

shows that the strongest reflexions are over-corrected. An isotropic-extinction refinement using only reflexions with intensity loss < 15%, as calculated in series (B), was therefore calculated. The δR plot of data from this refinement is close to the ideal shape, Fig. 2(c). Details of this refinement are given in Table 1.

E.s.d.'s of the refined parameters, R values, normal probability plots (for all reflexions and for most extinction-affected ones only) and agreement between symmetry-related reflexions were used as criteria for the suitability of the extinction model in question. The refinements indicate that the extinction is anisotropic, type I (mosaic-spread dominated) with Lorentzian mosaic-spread distribution with anisotropy of mosaic spread according to Thornley & Nelmes (1974). About 45% of the data suffered an intensity loss exceeding 15%, with a maximum of 80%.

It should be noted that the large anisotropy of the extinction correction is not visible in the normal

probability plot (Fig. 1a), where symmetry-related reflexions are compared. The extinction-correction factors for reflexions within a form differ by less than 10% and the plot of the extinction-corrected data shows only minor improvements, Fig. 1(b).

Parameters from the best refinement using a full data set (series B, Table 1) are given in Table 2.* Distances and angles quoted below are derived from the values in Table 2 unless stated otherwise. The programs used for all calculations on IBM 370/155, IBM 1800 and NORD-100 computers have been described by Lundgren (1979b).

Discussion

The crystal structure has been described elsewhere (*e.g.* Chomnilpan *et al.*, 1977) and will be mentioned only briefly here. The structure is built up from $\text{Li}(\text{H}_2\text{O})_6^+$ octahedra with an average $\text{Li}\cdots\text{O}$ distance of 2.13 Å, and ClO_4^- ions. Three O atoms of the perchlorate ion are related by symmetry. Each of them accepts two weak H bonds, 2.990 (1) Å, from water molecules. The bonds are bent: the angle $\text{O}(w)\text{---H}\cdots\text{O}(2)$ is 161.9 (1)°, and the distance $\text{O}(2)\cdots\text{H}$ is 2.073 (1) Å. The Cl atom and the remaining O(1) are located on a threefold axis. O(1) is surrounded by three water molecules; $\text{O}(1)\cdots\text{O}(w)$ is 3.045 (1) Å. However, the long $\text{O}(1)\cdots\text{H}$ distance, 2.624 (1) Å, and the small $\text{O}(w)\text{---H}\cdots\text{O}(1)$ angle, 107.4 (1)°, mean that these contacts cannot be considered as H bonds (*e.g.* Baur, 1972).

The objective of the present study is to obtain precise and accurate structure parameters to be used with X-ray data for $X\text{---}N$ syntheses and deformation refinements. The atomic parameters (in particular, thermal parameters) are often found to be different in an X-ray and a neutron data refinement. The extinction correction is substantial in the present case, and it was therefore thought to be of interest to analyse how

Table 1. *Some data on the refinements*

(A) Isotropic extinction type I; Lorentzian distribution. (B) Anisotropic extinction type I; Lorentzian distribution; anisotropy of mosaic spread according to Thornley & Nelmes (1974). (C) As (A), but data with more than 15% intensity loss due to extinction as obtained in (B) were deleted. $\Delta = F_o^2 - F_c^2$; $\sigma = \sigma(F_o^2)$.

	(A)	(B)	(C)
k (scale factor $\times F_o$)	0.9736 (56)	1.0000 (34)*	1.0082 (90)
g (isotropic-extinction coefficient)	$1.61 (5) \times 10^4$	—	$0.57 (9) \times 10^4$
M (numbers of reflections)	1284	1284	706
N (numbers of refined parameters)	31	36	31
$S = \left[\sum w\Delta^2 / (M-N) \right]^{1/2}$	3.01	1.78	1.28
$R = \sum \Delta / \sum F_o^2$	0.067	0.047	0.051
$R_w = \left[\sum w\Delta^2 / \sum wF_o^4 \right]^{1/2}$	0.081	0.048	0.058
Number of reflexions with $ \Delta/\sigma > 4$	162	39	2
Maximum $ \Delta/\sigma $	19.7	12.2	5.3
Maximum extinction correction factor ($\times F_o^2$)	4.7	5.5	1.17

* This scale factor is arbitrarily given the value 1.0. The scale factors for (A) and (C) are given relative to this value.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36248 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic coordinates ($\times 10^5$) and anisotropic thermal parameters ($\text{\AA}^2 \times 10^4$)*

The form of the temperature factor is $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \dots + 2U_{12}a^*b^*hk + \dots)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Li	0	0	27671 (60)	329 (6)	$=U_{11}$	245 (9)	$=U_{11}/2$	0	0
Cl	$\frac{1}{3}$	$\frac{1}{3}$	0	180 (1)	$=U_{11}$	307 (3)	$=U_{11}/2$	0	0
O(1)	$\frac{1}{3}$	$\frac{1}{3}$	-26190 (19)	431 (3)	$=U_{11}$	311 (5)	$=U_{11}/2$	0	0
O(2)	56534 (4)	43466 (4)	8902 (16)	308 (2)	$=U_{11}$	553 (4)	200 (2)	43 (1)	$=-U_{13}$
O(w)	-12232 (4)	12232 (4)	52787 (14)	271 (2)	$=U_{11}$	312 (2)	167 (2)	5 (1)	$=-U_{13}$
H	-6662 (14)	26326 (12)	53382 (23)	707 (5)	342 (4)	662 (4)	290 (3)	34 (5)	5 (3)

Table 3. Covalent bond lengths (Å) and angles (°)

Notation of refinements (A), (B) and (C) is as in Table 1. (S) is for quantities calculated from data given by Sequeira *et al.* (1975). Distances corrected for riding thermal motion are given within square brackets.

	(A)	(B)	(C)	(S)
Cl—O(1)	1.429 (2) [1.448]	1.428 (1) [1.446]	1.430 (1) [1.449]	1.440 (8) [1.459]
Cl—O(2) × 3	1.439 (1) [1.453]	1.439 (1) [1.454]	1.441 (1) [1.456]	1.443 (3) [1.459]
O(w)—H	0.949 (1) [0.990]	0.950 (1) [0.992]	0.955 (1) [0.997]	0.968 (7) [1.007]
H—O(w)—H	106.06 (19)	106.11 (12)	106.85 (19)	108.4 (8)
O(1)—Cl—O(2)	109.59 (6)	109.71 (4)	109.58 (5)	110.2 (3)
O(2)—Cl—O(2)	109.36 (7)	109.23 (4)	109.36 (6)	108.7 (4)

different extinction models influence the refined atomic coordinates and thermal parameters. Covalent bonds and angles calculated using coordinates from some of the refinements are given in Table 3.

No significant differences ($\leq 1.9\sigma$, 0.004 \AA) in the positional parameters are found in the refinements based on the complete data set and including isotropic or anisotropic extinction correction. This is also true for a comparison which also includes a set of parameters from a data set not corrected for TDS. The thermal parameters are much more sensitive to the extinction model and significant differences are found for all refinements. Barely significant differences ($\leq 4.1\sigma$, 0.001 \AA^2) between the anisotropic-extinction refinements represent changes in the U_{ii} values of up to 10%. The coupling between the extinction factor, the scale factor and the thermal parameters is illustrated in the isotropic refinements, series (A) and (C), where the large decrease in the extinction factor in the latter case is compensated by an increase in the scale factor (Table 1) and an increase in the U_{ii} values. In refinement (C), significant changes are also found for H coordinates (4.9σ , 0.009 \AA). For other atoms the changes are insignificant ($\leq 2.6\sigma$, 0.002 \AA). If no extinction correction is made, appreciable differences are found for both positional ($\leq 10\sigma$, 0.054 \AA) and thermal parameters ($\leq 17\sigma$, 0.025 \AA^2). The data set not corrected for TDS gave U_{ii} values $0.022 (3) \text{ \AA}^2$ lower than the values obtained for the TDS-corrected data set.

As a check of the validity of the refinements, a rigid-bond test (Hirshfeld, 1976) was applied to the covalent bonds (Table 4). In a covalent bond not involving H, the relative motion of the atoms along the bond direction should be well below 0.001 \AA^2 . For

covalent bonds involving H, this value is 0.005 \AA^2 due to the zero-point mean-square amplitude of H. Satisfactory values are found in Table 4 only for the refinements (B) and (C). This test may confirm the physical acceptability of the vibrational parameters, but it gives no guarantee that these parameters are correct. The vibrational parameters may be affected by some systematic effect which gives no anomaly in the relative amplitudes of neighbouring atoms (*e.g.* the data not corrected for TDS gave the same values as those quoted in Table 4).

Sequeira *et al.* (1975) have, for both their X-ray and neutron data structure refinements of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$, explained the thermal parameters by a model in which a number of independent motions are superimposed. In view of the present findings, it would appear that such analyses should be regarded with extreme caution, especially when data are seriously affected by extinction and a correction cannot readily be made.

Further analysis of the parameters will be made in connexion with the X-ray deformation refinement in progress at this Institute. It may be noted here that distances and angles involving non-H atoms from the X-ray study by Chomnilpan *et al.* (1977) are in complete agreement with results from refinements (A), (B) and (C). The thermal parameters for Cl and O, however, are up to 0.007 \AA^2 larger in the X-ray study, in spite of the fact that no TDS correction was made for the X-ray data.

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Table 4. Rigid-bond tests

$Z_{x,y}^2$ is the mean-square component of thermal motion of X in the direction of Y. Notation for the refinements is as in Table 3.

Refinement	$Z_{\text{Cl},\text{O}(1)}^2 - Z_{\text{O}(1),\text{Cl}}^2$ (\AA^2)	$Z_{\text{Cl},\text{O}(2)}^2 - Z_{\text{O}(2),\text{Cl}}^2$ (\AA^2)	$Z_{\text{O}(w),\text{H}}^2 - Z_{\text{H},\text{O}(w)}^2$ (\AA^2)
(A)	0.0048 (9)	-0.0004 (8)	-0.0063 (7)
(B)	-0.0004 (6)	-0.0004 (5)	-0.0054 (5)
(C)	-0.0007 (7)	-0.0007 (7)	-0.0047 (6)
(S)	-0.0073 (40)	-0.0062 (39)	-0.0145 (45)

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Structure of Solid α' -Oxygen

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Abstract

A monoclinic unit cell for solid α' -O₂ was determined. Its dimensions are: $a = 9.225 \pm 0.006$, $b = 6.668 \pm 0.004$, $c = 3.414 \pm 0.004$ Å and $\beta = 85.05 \pm 0.1^\circ$. A triangular net of O₂ molecules in an ab projection may be expected with the centers of the molecules near the ab positions 00, $\frac{1}{3}0$, $\frac{2}{3}0$, $\frac{1}{6}\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}$ and $\frac{5}{6}\frac{1}{2}$.

Introduction

In previous publications of electron diffraction work on solid oxygen (Hörl, 1962, 1969) one of us reported on a modification of solid oxygen called α' which was formed in the temperature range of the α phase when oxygen gas was deposited as a thin film on a cold substrate at a low gas-flow rate. This modification was also observed in due course by a number of other groups, but up to now its crystal structure could not be determined.

In spite of many attempts it was not possible to produce single crystals of this modification for a structure determination. One of the reasons was the transition of the α' to the β and/or γ phase during attempts to recrystallize the condensed layers (Hörl, 1969). On the other hand there were found new α' -O₂ diffraction rings on our plates obtained in these

numerous experiments and, in addition, it was possible to measure some of the d values of the rings already known, with higher accuracy than before. In this way our powder pattern data on α' -O₂ increased substantially and the application of our computer programs (Kohlbeck & Hörl, 1976, 1978) for indexing ring patterns of triclinic, monoclinic and orthorhombic crystals promised to yield the dimensions of the unit cell. Furthermore, a special graphical technique was expected to provide also the cell parameters and to confirm the computer data. In addition, the estimated ring intensities made it possible for us to perform a Patterson analysis to obtain information on the positions of the O₂ molecules within the unit cell.

Features of the α' -O₂ powder patterns

The experiments were performed with the aid of a liquid-helium cooling stage (Hörl, 1974) in a transmission electron microscope (Siemens Elmiskop I). Formvar substrate mounted on a copper specimen holder was used. Large-area as well as selected-area diffraction patterns were obtained together with images of the specimens (see Hörl, 1969). All experiments were carried out at a specimen-holder temperature of 4.2 K; the temperature of the α' deposit may have been a few degrees higher.

Most of our α' -O₂ electron diffraction patterns (see Table 1) consisted of rings with two kinds of profiles: sharp ones which showed in many cases a slightly

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