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Determination of the Oxygen *x* Parameter in Rutile by Neutron Powder Methods

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Abstract

Neutron intensity data obtained with the Australian High-Resolution Powder Diffractometer has been analysed by profile-refinement methods to give a value of the oxygen *x* parameter in TiO_2 of 0·3051 ± 0·0002. This is in excellent agreement with the reported X-ray values of 0·3048 ± 0·0001 and 0·30493 ± 0·00007. [$P4_2/mnm$, a = 4·5922 ± 0·0001, c = 2·9590 ± 0·00004 Å; R (nuclear) = 3·90, R (profile) = 10·98, R (weighted, profile) = 12·33.]

1. Introduction

Bertaut (1978), using an electrostatic model, predicted that neutron methods, which locate the position of the nucleus, and X-ray methods, which find the centroid of the extranuclear electron distribution, should give significantly different results for the value of the oxygen *x* parameter which is the only variable positional parameter in TiO_2. From his calculation of the electric dipole moment induced on the oxygen ion, Bertaut suggested that the X-ray value of the parameter would exceed the neutron value by 0·012. With accurate determinations of the *x* parameter from X-ray single-crystal measurements already available it was clear that a neutron powder investigation with data analysis by the Rietveld profile method (Rietveld, 1969; Cheetham & Taylor, 1977) would provide a value for the neutron *x* parameter which could be compared with the X-ray parameter to test this suggestion.

2. Experimental

Analytical reagent grade TiO_2 powder was isostatically pressed at room temperature. The specimens were then sintered in air at 1573 K for 13 h to produce cylinders of diameter 14 mm and density 3·40 Mg m^{-3}. One cylinder weighing 15 g was used in the experiment. Examination by X-ray powder diffraction showed no sign of gross preferred orientation or line broadening resulting from small particle size or residual strain. TiO_2 has the space group $P4_2/mnm$ (No. 136) with Ti at (000) and O at (xx0).

The neutron powder data were collected on the Australian High-Resolution Powder Diffractometer. This instrument, which will be described in detail in a subsequent publication, is the first such instrument installed on a conventional (non-guide tube) research reactor.

The monochromator take-off angle is 120° and the wavelength from the (533) plane of a germanium single crystal is 1·5002 Å. The diffractometer is fitted with a single counter which moves in steps of $\frac{1}{20}°$ (2θ) under monitor control. The average rate of travel is 2° h^{-1}. Data were collected in the range 13 to 160° (2θ).

3. Refinement of data

The experimental results were analysed with the Hewat (1975) version of the Rietveld (1969) computer program, adapted for use on the AAEC IBM 3031 system by Sabine, Kalceff & Sabine (1980). The background was estimated from a plot of neutron count *versus* 2θ. In conformity with the original Rietveld method, the background count was assigned a variance of zero. In the analysis, the quantity minimized is $\sum_i w_i(y_i^{obs} - y_i^{calc})^2$ where y_i^{obs} is the observed neutron count at each value of 2θ.

The weight of each ordinate, w_i, was taken as $1/y_i^{total}$, where y_i^{total} is the value of the observed ordinate before the background is subtracted.

In all refinements the scattering lengths were taken as $b_{Ti} = -3{\cdot}4$, $b_O = 5{\cdot}8$ fm. When the titanium site occupancy was allowed to vary, the initial value changed by less than one standard deviation; it was then fixed.

The data were first refined on a model with isotropic temperature factors for each atom. Refined values of the structural parameters are given in Table 1. Refined values of other parameters were (in the notation of

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Table 1. *Results of refinements*

(*a*) Isotropic refinement

	This investigation	Abrahams & Bernstein
x	0·3051 ± 0·0002	0·3051 ± 0·0002
B_{Ti} (Å²)	0·47 ± 0·03	0·46 ± 0·01
B_O (Å²)	0·39 ± 0·02	0·36 ± 0·02

(*b*) Anisotropic refinement

The anisotropic temperature factor is $\exp\{-[\beta_{11}(h^2 + k^2) + \beta_{33}l^2 + 2\beta_{12}hk]\}$.

	This investigation	Abrahams & Bernstein	Shintani *et al.**
x	0·3051 ± 0·0002	0·3048 ± 0·0001	0·30493 ± 0·00007
Ti, β_{11}	0·0065 ± 0·0006	0·0060 ± 0·0001	0·00654 ± 0·00004
β_{33}	0·0121 ± 0·0024	0·0091 ± 0·0004	0·01053 ± 0·0001
β_{12}	0·0004 ± 0·0007	−0·0002 ± 0·00004	−0·00045 ± 0·00013
O, β_{11}	0·0051 ± 0·0002	0·0047 ± 0·0002	0·00562 ± 0·00009
β_{33}	0·0088 ± 0·0008	0·0081 ± 0·0005	0·01023 ± 0·00044
β_{12}	−0·0021 ± 0·0004	−0·0020 ± 0·0001	−0·0054 ± 0·0003

* Converted from U values.

Rietveld): $a = 4{\cdot}5922 \pm 0{\cdot}0001$, $c = 2{\cdot}9590 \pm 0{\cdot}00004$ Å, $U = 756 \pm 17$, $V = -1660 \pm 43$, $W = 1603 \pm 25$, $P = 0{\cdot}00023 \pm 0{\cdot}00001$, $G = -0{\cdot}022 \pm 0{\cdot}005$ (assumed along [001]), R (nuclear) = 4·50, R (profile) = 11·29, R (weighted, profile) = 12·60.

In the second refinement, the temperature factors for each atom were allowed to vary anisotropically, while the lattice constants, asymmetry parameter and preferred-orientation parameter were given the values obtained in the isotropic refinement. The half-width parameters refined to the values given above. Refined values of the structural parameters are given in Table 1(*b*). The R factors were 3·90, 10·98, 12·33.*

* A table of observed and calculated y values has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36334 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

4. Discussion

There have been two recent X-ray determinations of the structure of rutile. Abrahams & Bernstein (1971) studied two single crystals; after corrections for extinction were applied their data yielded the results shown in Table 1(*a*) and (*b*). Shintani, Sato & Saito (1975) refined data obtained from a single-crystal specimen and corrected for extinction; their final values are shown in Table 1(*b*).

From these tables it can be seen that there is excellent agreement between the X-ray results and those obtained by powder neutron diffraction, there being certainly no discrepancy of the magnitude expected by Bertaut. The standard deviations from the neutron work are higher than those from the X-ray work. This is due, at least in part, to the low value of $\sum y^{obs}$ resulting from the use of only one counter. The value of R expected for these data was 12·7.

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