[CONTRIBUTION FROM THE NATIONAL LEAD CO., TITANIUM DIVISION]

The Structures of Anatase and Rutile

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Using powder data obtained with a Norelco X-ray diffractometer, the crystal structures of anatase and rutile have been determined with greater precision than has been previously reported. The cell parameters are for rutile $a = 4.5929 \pm 0.0005$ and $c = 2.9591 \pm 0.0003$ Å.; for anatase $a = 3.785 \pm 0.001$ and $c = 9.514 \pm 0.006$ Å. The oxygen parameter for rutile is 0.3056 ± 0.0006 and for anatase is 0.2066 ± 0.0009. There are four Ti–O distances of 1.946 ± 0.003 Å. and two Ti–O distances of 1.984 ± 0.004 Å. in rutile. In anatase there are four Ti–O distances of 1.937 ± 0.003 and two Ti–O distances of 1.964 ± 0.009 Å. These results are qualitatively correlated with the color differences of the two materials.

Introduction

The first investigation of the structures of anatase and rutile was reported in 1916 by Vegard.[2] These early studies were made using Bragg's ionization method. In 1926 the structures were determined by the Debye–Scherrer method.[3] Greenwood[4] and Tokody[5] confirmed Vegard's results for rutile, and Huggins[6] verified the results for both anatase and rutile. The early investigations definitely established the structures of these forms of titanium dioxide but they are not sufficiently precise to permit a detailed study of minor differences between the two structures. Consequently, these structures have been redetermined with the considerably greater accuracy made possible by modern equipment. The results reported here are in good agreement with those recently published by the National Bureau of Standards.[7]

Experimental

Materals.—Rutile was prepared from colorless titanium tetrachloride by hydrolysis and subsequent calcination at 800°. The anatase was commercial pigmentary material. Both powders were ground and seived through a 325 mesh screen prior to use.

A Norelco high angle X-ray diffractometer was used to obtain the intensity data. Nickel-filtered Cu radiation was used. With one degree slits, each line was scanned at a rate of $^1/_4$° 2θ per minute. The total counts occurring during the traverse of the line, after correction for background, were taken as proportional to the integrated intensity. A scan of 2° was usually made, although neighboring lines in some cases necessitated a smaller scan. At high angles a scan of 3° was made in order to include the $\alpha_1\alpha_2$ doublet. The background intensity was obtained by either of two generally equivalent methods. One method was to scan adjacent to the peak through the same distance used to measure the peak. Alternatively the average counting rate was measured at fixed points on each side of the peak. From this rate the number of counts that occurred in the time required to scan the peak was computed.

Debye–Scherrer photographs, taken in a 114.6 mm. diameter camera with Cu radiation, were used for the determination of lattice constants. No attempt was made to provide constant temperature during the exposures. Lattice constant computations were made by the method of Hess.[8] For rutile $a = 4.5929 \pm 0.0005$ and $c = 2.9591 \pm 0.0003$ Å.; for anatase $a = 3.785 \pm 0.001$ and $c = 9.514 \pm 0.006$ Å. The error, as evaluated by the method of Jette and Foote,[9] is such that there is a 95% certainty that the true value lies within the prescribed limits.

Determination of the Parameters.—The integrated intensities were converted to relative structure factors by correction for Lorentz, polarization and multiplicity factors. The few lines that had more than one component were omitted to simplify the computations. In each form of TiO_2, one oxygen parameter is required to define the structure. The temperature factor and a scale factor to convert the structure factors from the relative to the absolute scale must also be determined. By a process of trial and error the function $R = \Sigma||F_{obs}| - |F_{calc}||/\Sigma|F_{obs}|$ was minimized with respect to the structural parameter, the scale factor, S, and the temperature factor. This process gave the results listed in Table I.

TABLE I

RESULTS OF TRIAL AND ERROR TREATMENT OF DATA

	Rutile	Anatase
Oxygen parameter	0.306	0.207
Temp. factor	.7	.5
R (all values included for which $F_{obs} \neq 0$)	.034	.039

The above method is deficient because there exists no objective method for estimating the error in the results. A least-squares[10] refinement was therefore made using the trial and error results as a starting point. Form factors for Ti^{+4} and O^{-2} were taken from the Internationale Tabellen.[11] The observations were given a weight proportional to $1/F^2_{obs}$. The scale factor and a single isotropic temperature factor were determined from the least-squares solution to the plot of log (F_{obs}/F_{calc}) *versus* $\sin^2\theta/\lambda^2$. A few observations (three in each case, see Table V) departed appreciably from linearity in the semilog plot and were omitted from the computations. The separate least-squares computations of the scale and temperature factors and the positional parameter were repeated until the changes in the variables were small compared to the indicated error. These least-squares results are given in Table II. The error given is the standard deviation determined in the usual fashion.[12] The results are not significantly different in magnitude from those obtained by the trial and

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(2) L. Vegard, *Phil. Mag.*, **32**, 505 (1916).

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(11) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Vol. II, Borntraeger, Berlin, 1935, p. 571.

(12) E. T. Whittaker and G. Robinson, "The Calculus of Observations," Chapter 9, 4th Edition, Blackie and Son, Ltd., London, 1944.

error minimization of R, but are, of course, superior because of a knowledge of the error.

TABLE II

RESULTS OF FIRST LEAST SQUARES TREATMENT OF DATA

	Rutile	Anatase
Oxygen parameter	0.3055 ± 0.0007	0.2064 ± 0.0006
Temp., factor	0.82	0.73
R (all values included for which $F_{obs} \neq 0$)	.040	.043

The validity of omitting some of the observations was now considered. The ratio $\Delta F/F_{obs}$ for each of the reflections was evaluated. Grubbs'[13] statistical test for detecting outlying observations was applied to these ratios. Let $\bar{x}$ = the mean value of this ratio, $T_n = (x_n - \bar{x})/s$ and $s^2 = (\Sigma x^2 - (\Sigma x)^2/n)/(n - 1)$ where n is the number of observations and x_n is the particular observation it is desired to test. Grubbs gives critical values of T_n above which it is justifiable on statistical grounds to omit an observation. This test supported the belief that the observations in question could indeed be omitted. However, it was necessary to apply the test twice in succession; that is, after one or two points were found to be outlying observations, these points were omitted and the test reapplied to the remainder.

As a final calculation a more rigorous model was considered. Separate isotropic temperature factors for titanium and oxygen and the scale factor were included as variables in the least-squares calculations. Further, the more accurate recently computed form factors for O[14] and Ti[15] were used. The data were weighted as before. Again the same observations were omitted. The results, given in Table III, are not significantly different from the first least-squares results. The observed and calculated structure factors for this final model are given in Table V. The various interatomic distances with their standard deviations are given in Table IV.

TABLE III

RESULTS OF SECOND LEAST SQUARES TREATMENT OF DATA

	Rutile	Anatase
Oxygen parameter	0.3056 ± 0.0006	0.2064 ± 0.0009
Oxygen temp. factor	0.785 ± 0.080	0.664 ± 0.159
Titanium temp. factor	0.519 ± 0.068	±0.510 ± 0.096
Standard dev. scale factor	±1.8%	±2.2%
R (all values included for which $F_{obs} \neq 0$)	0.041	0.048

TABLE IV

INTERATOMIC DISTANCES IN RUTILE AND ANATASE, Å.

	Rutile	Anatase
4 Ti–O	1.946 ± 0.003	1.937 ± 0.003
2 Ti–O	1.984 ± .004	1.964 ± .009
O–O	2.779 ± .001	2.802 ± .005
O–O	2.526 ± .009	2.446 ± .010
O–O		3.040 ± .001

TABLE V

OBSERVED AND CALCULATED STRUCTURE FACTORS

hkl	Rutile $F_{calcd.}$	$F_{obsd.}$	*hkl*	Anatase $F_{calcd.}$	$F_{obsd.}$
110	+35.3	34.7	101	+56.9	54.8
101	+21.3	21.7	103	−17.5	19.9
200	+11.6	12.8	004	−76.9	77.7
211	+28.2	27.4	112	−19.3	22.0
220	+32.3	31.8	200	+88.0	85.6
002	+35.5	34.4	105	−56.9	55.2
310	+17.8	17.4	211	−39.9	38.2
301	+30.7	30.8	213[a]	−17.0	20.4
112	+21.6	22.0	204	−56.6	55.0
202	+10.7	11.9	116	+42.8	40.9
321	+11.5	11.8	220	−63.3	65.2
400	+19.00	18.5	107[a]	+12.4	17.0
222	+21.7	22.7	215	+41.8	40.9
330	+22.9	22.0	301	+30.7	29.5
411	+15.5	15.3	008	+24.4	26.0
312	+13.6	14.2	217[a]	+11.9	14.6
420	+14.8	14.3	305	−34.3	32.2
402	+14.9	15.6	321	−25.8	27.6
510	+16.0	16.1	109	+29.1	28.4
332	+18.0	19.1	208	+22.1	19.9
303	+17.6	18.1	323	+13.9	12.9
521	+16.8	16.4	316	+30.6	32.6
440	+14.3	12.7	400	+43.2	45.6
530	+ 7.9	7.8	307	+11.3	11.2
111	−18.2	17.9	325	+29.4	30.1
210	−11.8	11.4	411	−22.6	22.2
221	− 5.3	5.1	228	−20.2	21.1
311	− 5.3	5.4	327	−10.6	10.5
320[a]	− 3.5	4.9	415	+26.1	26.0
212	− 6.0	6.4	309	+22.8	23.7
410	− 8.1	8.0	424	+29.7	29.1
331[a]	− 1.9	3.1			
421	− 4.4	4.4			
113	− 5.9	5.5			
430	+ 3.2	0			
511	+ 1.0	0			
520	− 0.9	0			
313[a]	+ 2.5	4.9			
441	− 4.9	5.5			

[a] Omitted from least-squares computations.

Discussion of Results

In both rutile and anatase there are two elongated titanium–oxygen bonds in each octahedron. Further, the lengthening of these two bonds is greater in the case of rutile. This would indicate relative weakening of these bonds and, consequently, a lowering of the energy requirements for the excitation of these bonds. This can be qualitatively correlated with the observed optical properties of the two materials as evidenced by the reflection spectra of pigmentary samples, shown in Fig. 1. As yet it has not been possible to quantitatively correlate these two effects. Additional research is in progress on this subject, particularly on the optical properties of titanium dioxide crystals.

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