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X-ray Studies on the Thermal Expansion of Ruthenium Dioxide

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A precise X-ray determination of the lattice constants of ruthenium dioxide, RuO_2, has been made in the temperature range 30° to 702°C using a Unicam 19 cm high-temperature powder camera. It has been observed that the *c* parameter decreases with increasing temperature as in the case of FeF_2 and CrO_2 which also have a rutile-type structure.

Introduction

Earlier studies (Goldschmidt, 1926; Cotton & Mague, 1966) showed that ruthenium dioxide (RuO_2) has a tetragonal rutile-type structure. As some of the rutile-type compounds like iron fluoride (FeF_2) and chromium dioxide (CrO_2) showed interesting thermal behaviour (Rao, Naidu & Iyengar, 1966, 1967), and as no data on the thermal expansion of RuO_2 are available in the literature, it was thought desirable to determine precisely the lattice parameters of RuO_2 at various temperatures, and to study its thermal expansion.

Experimental

The crystal sample was crushed to a powder of appropriate particle size and a specimen was prepared by coating the powder on to a quartz fibre with Araldite. Using a Unicam 19 cm high-temperature powder camera and Cu *K* radiation from a Raymax-60 X-ray unit, powder photographs were taken at different temperatures in the temperature range 30°C to 702°C. The procedure followed to evaluate the lattice parameters and the coefficients of thermal expansion has been described in an earlier paper (Rao, Naidu & Setty, 1962).

Results

The lattice parameters at room temperature, obtained in the present study, are given in Table 1 along with the earlier data available in the literature. The lattice parameters obtained at different temperatures are given in Table 2 and are shown graphically in Fig. 1. The *a* parameter increases continuously, while the *c* parameter decreases. Table 2 and Fig. 1.

The coefficients of thermal expansion at different temperatures are given in Table 3. The powder photographs, taken at four different temperatures, are shown in Fig. 2. The sign of α_{11} is evident from the shift of

Table 2. *Lattice parameters of* RuO_2 *at different temperatures*

Temperature °C	*a* (Å)	*c* (Å)
30	4·4909	3·1064
165	4·4958	3·1062
267	4·5003	3·1051
361	4·5053	3·1037
461	4·5109	3·1033
563	4·5173	3·1012
608	4·5198	3·1008
702	4·5258	3 0995

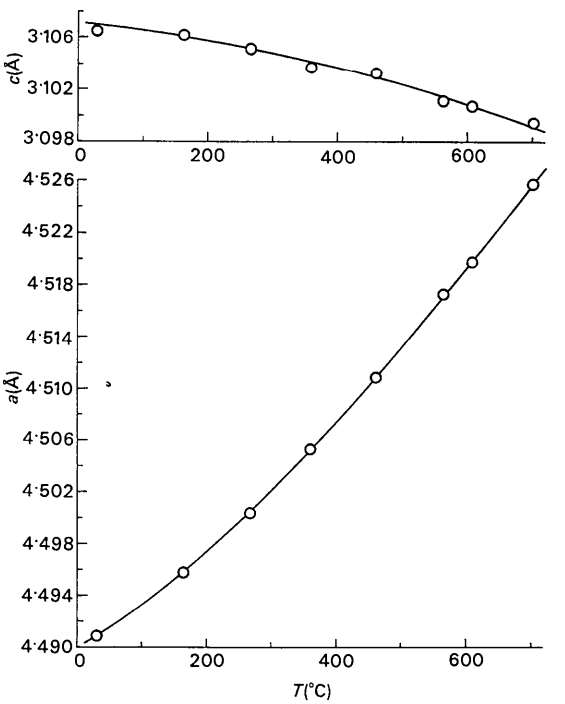

Fig. 1. Lattice parameters of RuO_2 at different temperatures.

Table 1. *Lattice parameters of* RuO_2 *at room temperature*

Source	*a* (Å)	*c* (Å)
Goldschmidt (1926)	4·51	3·11
Cotton & Mague (1966)	4·491 ± 0·007	3·107 ± 0·005
Authors	4·4909 ± 0·0003	3·1064 ± 0·0004

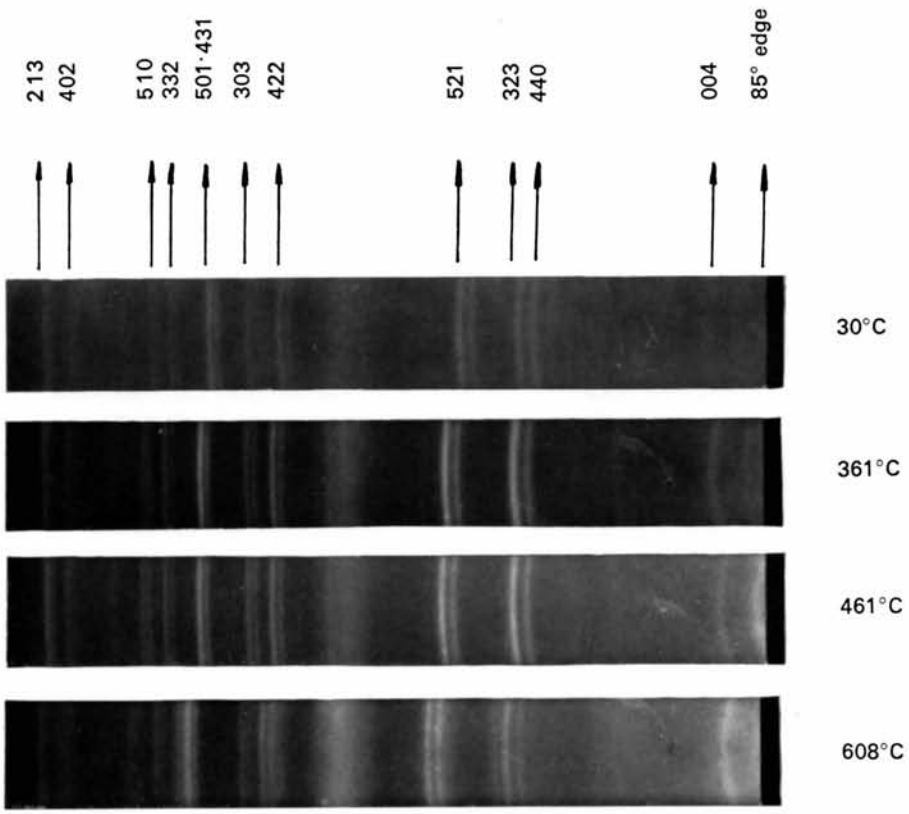

Fig. 2. Powder photographs of RuO_2 at different temperatures.

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the 004 reflexion towards the higher Bragg angle side at higher temperatures. The temperature dependence of the coefficients is represented by the following equations:

$$\alpha_{11} = -(1{\cdot}248 \times 10^{-6}) - (5{\cdot}392 \times 10^{-9}t) - (2{\cdot}273 \times 10^{-12}t^2) \quad (1)$$

$$\alpha_{\perp} = (6{\cdot}447 \times 10^{-6}) + (1{\cdot}920 \times 10^{-8}t) - (1{\cdot}075 \times 10^{-11}t^2) \quad (2)$$

The calculated values of α in Table 3 are obtained by using equations (1) and (2).

Table 3. *Coefficients of thermal expansion of* RuO_2 *at different temperatures*

Temperature	$\alpha_{\parallel} \times 10^6$		$\alpha_{\perp} \times 10^6$	
(°C)	obs.	calc.	obs.	calc.
50	−1·53	−1·52	7·96	7·38
90	−1·77	−1·75	8·30	8·09
130	−2·01	−1·99	8·52	8·76
170	−2·25	−2·23	9·13	9·40
210	−2·41	−2·48	9·69	10·01
250	−2·74	−2·74	10·30	10·58
290	−2·90	−3·00	10·74	11·11
330	−3·30	−3·27	11·25	11·61
370	−3·54	−3·55	11·91	12·08
410	−3·86	−3·84	12·64	12·51
450	−4·19	−4·13	13·47	12·91
490	−4·51	−4·44	14·08	13·28
530	−4·75	−4·74	14·14	13·60
570	−5·07	−5·06	14·20	13·90
610	−5·31	−5·38	13·69	14·16
650	−5·71	−5·71	13·75	14·39

Discussion

Among the rutile-type compounds so far studied, RuO_2, FeF_2 and CrO_2 exhibit a negative c expansion coefficient. However, there are many differences in their individual behaviour, as shown in Table 4.

The numerical value of α_{11} increases with temperature in the case of RuO_2 and FeF_2 whereas it decreases in the case of CrO_2. The increase of α_{11} is much larger for FeF_2 than is the case for RuO_2. In all the three cases, the coefficient of volume expansion, Δ, is positive and increases with increasing temperature.

The negative coefficient of expansion ($\alpha_{\perp}$) in the case of substances like calcite and graphite has been explained (Rao, Naidu & Murthy, 1968; Nelson & Riley, 1945) as due to the Poisson contraction in that direction arising from the large coefficient of expansion in a perpendicular direction. Such an explanation is not applicable in the case of the present compounds which do not have a large coefficient of expansion along the other direction. $\alpha_{\perp}$ for RuO_2 is only $7{\cdot}01 \times 10^{-6}$. The abnormal behaviour of these compounds may be due to changes in Jahn–Teller distortion with temperature as has been pointed out by Siratori & Iida (1962) for CrO_2.

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References

Cotton, F. A. & Mague, J. T. (1966). *J. Inorg. Chem.* **5**, 317.

Goldschmidt, V. M. (1926). *Nordske Vid. Akad. Oslo.* **1**.

Nelson, J. B. & Riley, D. P. (1945). *Proc. Phys. Soc.* **57**, 477.

Rao Krishna, K. V., Naidu Nagender, S. V. & Iyengar, L. (1966). *Curr. Sci.* **35**, 280.

Rao Krishna, K. V., Naidu Nagender, S. V. & Iyengar, L. (1967). Presented at the Indian Science Congress.

Rao Krishna, K. V., Naidu Nagender, S. V. & Murthy, K. S. N. (1968). *J. Phys. Chem. Solids* **29**, 245.

Rao Krishna, K. V., Naidu Nagender, S. V. & Setty, P. L. N. (1962). *Acta Cryst.* **15**, 528.

Siratori, K. & Iida, S. (1962). *J. Phys. Soc. Japan.* **17**, Suppl. B-I 208.

Table 4. *Comparison of* α_{11}, $\alpha_{\perp}$ *and* Δ *of* RuO_2, FeF_2 *and* CrO_2

Temperature	RuO_2			FeF_2			CrO_2		
(°C)	$\alpha_{\parallel} \times 10^6$	$\alpha_{\perp} \times 10^6$	$\Delta \times 10^6$	$\alpha_{\parallel} \times 10^6$	$\alpha_{\perp} \times 10^6$	$\Delta \times 10^6$	$\alpha_{\parallel} \times 10^6$	$\alpha_{\perp} \times 10^6$	$\Delta \times 10^6$
30	−1·41	7·01	12·6	−0·40	16·80	33·2	−14·84	18·61	22·4
370	−3·55	12·08	20·6	−10·18	27·16	44·1	−0·10	13.52	26·9