Discussion

When examining Table 1, one can see that besides the mentioned improvement of 'temperature factors' and standard deviations, in a few cases rather large changes appeared in the positional parameters when the influence of the secondary extinction errors was depressed. See for example the oxygen parameters z_3, x_4 and y_5. Thus the secondary extinction evidently may cause errors even in the positional parameters of the atoms in a crystal structure although it most strongly affects the vibrational parameters and scale factors. This example also shows that standard deviations cannot be trusted when large systematic errors are not corrected in the data. The rows 2 and 3 in Table 1 are in excellent agreement, which indicates that the secondary extinction corrections are correctly applied. The result thus speaks in favour of the Zachariasen formula.

Further information concerning the refinement and the detailed structure will be given elsewhere (Åsbrink, 1966).

General conclusions

Secondary extinction errors could be appreciable and well worth the correction work. Mainly for two reasons, this has not been done very often. Firstly, because the quality of the intensity data used generally has not been sufficiently good. However, the advent of the modern single-crystal diffractometer has made possible the gathering of intensity data for which the statistical errors are depressed to a large extent so that the systematic errors play a more important role. Secondly, because of the laborious computational work involved. However, owing to the possibility of changing existing absorption programs for electronic computers, the work should not be unreasonable. Lastly, it should be pointed out that if the B values are to be considered as temperature factors and calculated electron densities relied upon as such, it is necessary to take all sources of error into account.

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References

Åsbrink, S. & Brändén, C. I. (1962). IUCr *World List of Crystallographic Computer Programs.* 1st Ed., Program 6023.
Åsbrink, S. (1966). *Acta Chem. Scand.* To be published.
Darwin, C. G. (1922). *Phil. Mag.* **43**, 800.
Margenau, H. & Murphy, G. M. (1956). *The Mathematics of Physics and Chemistry.*
Norrestam, R. (1964). Univ. Stockholm, Inorg. Chem. DIS No. 8.
Werner, P.-E. (1964*a*). Univ. Stockholm, Inorg. Chem. DIS No. 4.
Werner, P.-E. (1964*b*). *Acta Chem. Scand.* **18**, 1851.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139.

Acta Cryst. (1966). **20**, 410

The Yttrium Oxide – Titanium Dioxide System

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By means of X-ray powder photographs, it is shown that between 29 and 42 mol.% of yttrium oxide a solid solution having a pyrochlore structure exists, while between 46 and 61 mol.% a fluorite-type phase occurs. Between 42 and 46 mol.% there is a two-phase region. The phase change mechanism is discussed.

Introduction

'Anomalous' solid solutions with a fluorite-type structure have been found between many oxides of the types M_2O_3 and MO_2 (Zintl & Croatto, 1939; Zintl & Udgard, 1939; Hund, 1951*a*, *b*; Hund, Peetz & Kottenhahn, 1955). These mixed oxides contain a fully occupied and undistorted cation lattice with random vacancies in the anion lattice. Yttrium oxide, Y_2O_3, and titanium dioxide, TiO_2, might be expected to form a similar solid solution, although the quadrivalent titan-

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ium ion is considerably smaller than other quadrivalent cations known to form mixed oxides of this type. The only previously published work on this system is that of Guisca & Popescu (1939), who prepared the single mixed oxide $Y_2Ti_2O_7$ and showed that is has a face-centred pyrochlore-type structure. They suggested that a continuous solid solution range between $Y_2Ti_2O_7$ and Y_2O_3 might exist.

Experimental

Spectroscopic examination of some commercial yttrium oxide and titanium dioxide showed that their total impurity contents ($<0{\cdot}8\%$ and $<0{\cdot}2\%$ respectively) were too small significantly to affect the structure or lattice constants of their solid solutions. Mixtures of the oxides in various proportions from 10 to 90 mol.% yttrium oxide were ground together under ethanol, dried, packed tightly into a platinum boat, and fired in air at 1500 °C. To ensure complete reaction, it was usually necessary to grind and re-fire the products. X-ray powder-photographs of the reaction products were taken with Cu *Kα* radiation, a 9-cm camera of the type designed by Bradley, Lipson & Petch (1941) being used. The patterns were indexed in the cubic system and the lattice parameters calculated from the high angle reflexions, errors due to absorption and divergence of the X-ray beam being eliminated by the method of Nelson & Riley (1945).

Results

Two phases, one having a pyrochlore structure and the other a fluorite structure, occur within the mixed oxide range. The distinct regions observed over the complete range of oxide mixtures are given in Table 1.

Table 1. *Distinct phase regions*

Mol. % Y_2O^3	Product	Lattice parameters of solid solutions (Å)
0–29	Pyrochlore + excess TiO_2	10·088
29–42	Pyrochlore	10·088 to 10·127
42–46	Pyrochlore + fluorite	10·127 and 5·135
46–61	Fluorite	5·135 to 5·200
61–100	Fluorite + excess Y_2O_3	5·200

The systematic absences in the X-ray reflexions demanded by the pyrochlore structure (*Fd*3*m*) were clearly apparent in the fully indexed X-ray powder patterns of the pyrochlore phase. Those lines present in a pyrochlore pattern but necessarily absent in one of a fluorite structure were readily observed by visual comparison of typical patterns of the two distinct phase regions. The coexistence of the pyrochlore and fluorite phases between 42 and 46 mol.% yttrium oxide was demonstrated in a similar manner.

Within the discrete phase regions 29–42 and 46–61 mol.% yttrium oxide, the lattice constant varied linearly with composition. The lattice constant of the pyrochlore phase at the composition $Y_2Ti_2O_7$ was $10{\cdot}100 \pm 0{\cdot}001$ Å, which agrees with the figure of $10{\cdot}08 \pm 0{\cdot}03$ Å obtained by Giusca & Popescu (1939).

Discussion

The pyrochlore structure of many minerals and artificially prepared substances has been examined by von Gaertner (1930), Rosen & Westgren (1938), Machatschki (1941), and Byström (1945). By analogy with Machatschki's work, the structure of the pyrochlore phase at the composition $Y_2Ti_2O_7$ may be considered as a three-dimensional continuous framework of linked (TiO_6) octahedra with the seventh oxygen ion and the yttrium ions occupying open spaces in the framework and taking no part in its formation. Each yttrium ion is surrounded by 8 oxygen ions at the corners of a distorted cube. On the basis of this theory, a limiting composition when there is no seventh oxygen ion outside the $(Ti_2O_6)_\infty$ framework should be $Y_{4/3}Ti_2O_6$, which is equivalent to 25 mol.% yttrium oxide. The phase region actually ends at 29 mol.%.

The 'anomalous' fluorite phase is of particular interest in that the radius of the quadrivalent titanium ion is only 0·68 Å. In the systems ThO_2–Y_2O_3, CeO_2–Y_2O_3 (Brauer & Gradinger, 1954), PrO_2–Y_2O_3 (McCullough & Britton, 1952) and ZrO_2–Y_2O_3 (Hund, 1951*a*) the radii of the quadrivalent cations are 1·02, 0·94, 0·92, and 0·79 Å respectively (Ahrens, 1952). Theoretically, the fluorite structure is stable only when the cation/anion radius ratio is greater than 0·73. In the TiO_2–Y_2O_3 fluorite phase, if the cation radius is taken to be the average of the radii of the yttrium and titanium ions, the ratio is always less than 0·73, but it becomes even smaller as the percentage of yttrium oxide decreases, with a consequent decrease in the stability of the structure. It may be that this aids the change-over from the fluorite to the pyrochlore phase.

This change-over may be considered as a simple rearrangement of 8 fluorite unit cells to give one pyrochlore unit cell. In such a rearrangement the cation lattice need not alter beyond a very small contraction, indeed, if much distortion were required, it is doubtful whether the phase change would occur, owing to the great stability of the cation lattice in 'anomalous' fluorite solid solutions of this type. Brauer & Gradinger (1954) have shown that complete miscibility between oxides of the fluorite type and oxides of the body-centred cubic M_2O_3 *C*-type seems to be possible only when the difference between the lattice constant of the fluorite and half the lattice constant of the sesquioxide is less than 0·12 Å. In the yttrium oxide–titanium dioxide system, this difference is greater than 0·12 Å, and, in fact the fluorite phase reaches a limiting composition at 61 mol.% yttrium oxide.

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References

AHRENS, L. H. (1952). *Geochim. Cosmochim.* **2**, 155.
BRADLEY, A. J., LIPSON, H. & PETCH, N. J. (1941). *J. Sci. Instrum.* **18**, 216.
BRAUER, G. & GRADINGER, H. (1954). *Z. anorg. Chem.* **276**, 209.
BYSTRÖM, A. (1945). *Ark. Kemi* **18A**, No. 21.
GAERTNER, H. R. VON (1930). *Neues Jb. Min. Geol. Pal. Beil.* A, **61**, 1.
GIUSCA, D. & POPESCU, I. (1939). *Bull. Soc. Roum. Phys.* **40**, 18.
HUND, F. (1951*a*). *Z. Elektrochem.* **55**, 363.
HUND, F. (1951*b*). *Z. anorg. Chem.* **265**, 62.
HUND, F., PEETZ, U. & KOTTENHAHN, G. (1955). *Z. anorg. Chem.* **278**, 184.
MACHATSCHKI, F. (1941). *Zbl. Min. Geol. Pal. Abt. A*, 55.
MCCULLOUGH, J. D. & BRITTON, J. D. (1952). *J. Amer. Chem. Soc.* **74**, 5225.
NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc.* **57**, 160.
ROSEN, O. & WESTGREN, A. (1938). *Geol. Förh. Stockholm Förh.* **60**, 226.
ZINTL, E. & CROATTO, U. (1939). *Z. anorg. Chem.* **242**, 79.
ZINTL, E. & UDGARD, A. (1939). *Z. anorg. Chem.* **240**, 150.

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The Equilibrium Hydrogen—Hydrogen Distances in the Water Molecules in Potassium and Rubidium Oxalate Monohydrates

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From the proton magnetic-resonance spectra of single crystals of $K_2C_2O_4 . H_2O$ and $Rb_2C_2O_4 . H_2O$ held at room temperature, the equilibrium length, R_e, and orientation of the proton–proton line segments in the water molecules have been determined. The two salts are isomorphous, and the water molecules are situated on the twofold axes making an angle φ_0 with the c axis. The following results are obtained:

$K_2C_2O_4 . H_2O$ $R_e = 1{\cdot}5341 \pm 0{\cdot}0030$ Å $\varphi_0 = 22 \pm 1°$
$Rb_2C_2O_4 . H_2O$ $R_e = 1{\cdot}5474 \pm 0{\cdot}0030$ Å $\varphi_0 = 26 \pm 1°$

These results are discussed on the basis of the known crystal structures.

Pake (1948) first detected and analysed the presence of fine structure in the proton magnetic-resonance spectra of hydrate single crystals and powders. He showed that it is possible from the distance between the fine-structure components to calculate the distance between the hydrogen atoms in the water molecules bound in the lattice of the hydrate. Since this classical study the question has existed whether or not it is possible to detect a significant variation in this distance from one hydrate to another, which would indicate variations in the shape of the water molecule. McGrath & Silvidi (1961) concluded, after re-evaluating data on ten different hydrates, that the observed variations were not significant. But later investigations have shown that the distances deduced in earlier studies may include systematic errors due to intermolecular interactions (Holcomb & Pedersen, 1963; Pedersen & Holcomb, 1963), and further that the motion of the water molecules has a large effect on the deduced value of the intramolecular proton–proton distance (Pedersen, B, 1964), invalidating the conclusion of McGrath & Silvidi (1961).

When the effects of the motion were corrected for, Pedersen (1964) found that the equilibrium proton–proton distances deduced from studies of four different hydrates and ice, where the necessary data were available, were all equal within the experimental uncertainty ±0·01 Å, and equal to the value observed for an isolated water molecule, 1·51 Å.

In this paper we shall report on a room temperature proton magnetic-resonance study of potassium oxalate monohydrate (KOMH) and rubidium oxalate monohydrate (RbOMH) where a significant difference between the nuclear magnetic-resonance data for the two components has been detected, and where this difference will be interpreted as arising from a significant difference in the equilibrium intramolecular proton–proton distances between the two compounds.

The compounds chosen for this study are isomorphous and ideally suited for a proton magnetic-resonance study for several reasons. The water molecules are located on the twofold axes in the monoclinic structure, and they are all structurally equivalent with all intramolecular proton–proton vectors parallel. The water molecules are well separated from each other, reducing the intermolecular effects to a tolerable minimum. The compounds do not contain any other nuclei with large magnetic moments, in particular no protons other than those situated in the water molecules. It is further fairly easy to grow single crystals