peaks in the Fourier section. This pseudo-plane is not used in the structure as a whole. There is an intramolecular hydrogen bond of length 2·46 Å (the shortest yet observed), effectively closing a six-membered ring system. This probably accounts for the high diamagnetic anisotropy of the molecule (Lonsdale, 1939).

2. Neighbouring molecules are linked by longer intermolecular hydrogen bonds (2·75 Å) to form rows along the [100] direction, and these rows are inter-linked by still weaker hydrogen bonds (2·98 Å) to form layers parallel to the (001) planes. The existence of the rows accounts for the strong diffuse streaks on c-axis Laue photographs taken with a strong characteristic component present in the radiation used (Fig. 1). The molecules linked by 2·75 Å hydrogen bonds are related to them by symmetry about a screw [010] axis in the layer plane. The molecules in any one layer are therefore cross linked by a system of bifurcated hydrogen bonds of unequal length.

3. The layers, which are bound together only by van der Waals forces, are inter-related by centres of symmetry. The weakness of the forces between layers accounts for the large thermal vibration amplitudes normal to the layers, which give the intense diffuse spots associated with the 002 and 004 reflexions, not only on Laue but also on rotation and Weissenberg photographs. It also accounts for the perfect cleavage parallel to (001).

Other crystallographic properties can be explained as follows:

The easy distortion of the crystals about the [100] axis is due to the possibility of slip of the layers over one another, combined with a bending of the layers themselves. The partial cleavage parallel to (010) must be associated with the relative weakness of the 2·98 Å hydrogen bonds.

Growth takes place more easily in than perpendicular to the molecular layers, and therefore the crystal tends to grow from acetone as plates on (001). If crystallized from water or alcohol, however, the hydrogen bonding is less dominant and the habit is no longer platy although, of course, the (001) cleavage remains.

The author wishes to express his gratitude to Professor Kathleen Lonsdale, F.R.S., for her kind supervision and advice and to Fouad the 1st University, Cairo, for a period of study leave during which this work was carried out.

References

Buerger, M. J. & Klein, G. E. (1945). *J. Appl. Phys.* **16**, 408.
Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
Lonsdale, K. (1939). *Proc. Roy. Soc.* A, **171**, 541.
Lonsdale, K. & Smith, H. (1941). *Proc. Roy. Soc.* A, **179**, 8.
Robertson, J. M. A. & Morrison, J. S. (1949). *J. Chem. Soc.* p. 987.
Shahat, M. (1951). Second International Congress of Crystallography, Paper O 12.
Verweel, H. J. & MacGillavry, C. H. (1939). *Z. Krystallogr.* **102**, 60.
Yardley, K. (1927). *J. Chem. Soc.* p. 2207.

Acta Cryst. (1952). **5**, 768

Lattice Constants and Magnetic Susceptibilities of Solid Solutions of Uranium and Thorium Dioxide*

By Emil Slowinski† and Norman Elliott

Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, New York, U.S.A.

(*Received* 7 *July* 1952)

Thorium and uranium dioxides are miscible in all proportions. Solid solutions may be prepared by fusion in borax at 1000–1200° C., and the lattice constants of the cubic crystals are those predicted by Vegard's rule. Magnetic susceptibilities of these solutions obey the Weiss–Curie law. The magnetic moment of the U^{4+} ion decreases with dilution, and approaches the 'spin-only' value, a result in agreement with the observations of other investigators.

The use of fluxes such as borax and magnesium chloride to grow single crystals of refractory oxides is well known (Hillebrand, 1893; Hoffmann & Höschele, 1915; Troost & Ouvrard, 1886; Sterba, 1904). We used borax to obtain homogenous solid solutions of thorium and uranium dioxides in the temperature range 1000–1200° C. Appropriate quantites of very pure UO_2 and ThO_2 were weighed out and intimately mixed. The

---

* Research carried out under the auspices of the Atomic Energy Commission.

† Present address: Chemistry Department, Swarthmore College, Swarthmore, Pa., U. S. A.

mixture was placed in a platinum crucible with an excess of borax, covered, and suspended in a vertical glass tube. The air in the system was replaced by hydrogen, and the crucible was then brought to the desired temperature by an induction coil. After heating 2–4 hr. the crucible was cooled and its contents were leached with dilute hydrochloric acid.

X-ray powder photographs were taken of the solid solutions and the pure oxides with Cu $K\alpha$ radiation filtered through nickel. The lattice constants of the cubic unit cell were determined, using the reflections of NaCl photographed on the same film as a standard of comparison. All photographs gave very sharp reflections, the α doublet being well resolved in the higher orders. The results are given in Table 1 and in Fig. 1. The average deviation was ±0·0015 Å.

Table 1. *Lattice constants of* UO_2–ThO_2 *solid solutions*

Mol % UO_2	a(Å)
100	5·457
77·16	5·487
45·14	5·528
31·50	5·545
9·22	5·573
0	5·586

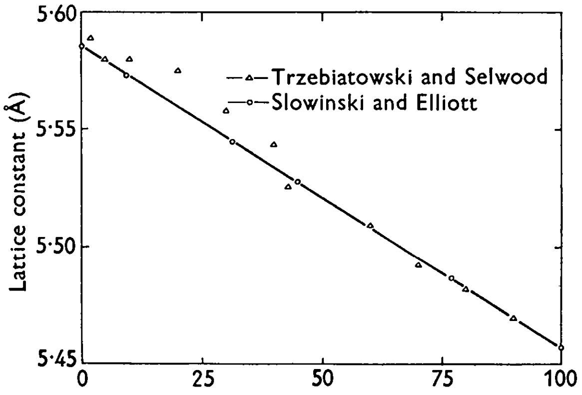

Fig. 1. Unit-cell dimension of system UO_2–ThO_2.

The lattice constants for the pure oxides are in good agreement with the more precise measurements of Zachariasen (1947). Those of the mixtures are seen to follow Vegard's rule (Vegard, 1921). The data of Trzebiatowski & Selwood (1950) are also included for comparison in Fig. 1.

The magnetic susceptibilities of the solid solutions and the pure oxides were measured by the Gouy method. The results were reproducible to better than ±1%, using three samples of each mixture. A single correction was made for the force exerted by the magnet on the susceptibility tube and the ThO_2. The diamagnetism of UO_2 was taken to be -43×10^{-6} from the work of Angus (1932). Measurements were made in the temperature range 66–296° K.

The magnetic susceptibilities, corrected for diamagnetism, could be fitted by a Weiss–Curie formula,

$$\chi_{\text{mol.}} = C/(T+\theta)\ .$$

This is shown in Fig. 2.

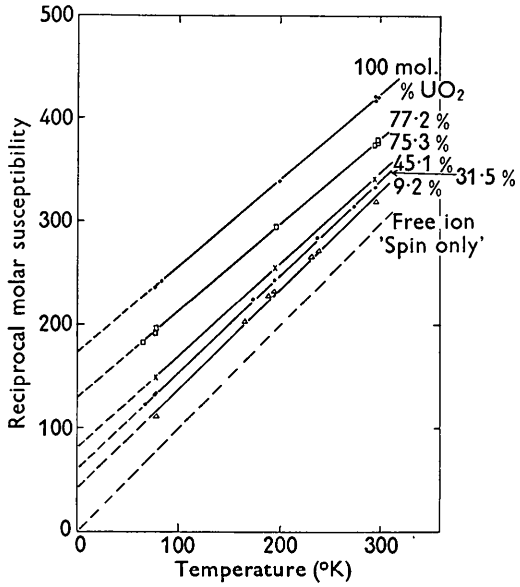

Fig. 2. Magnetic susceptibilities of solid solutions of UO_2 and ThO_2 as a function of temperature.

Values of the Curie constant C, and of θ were calculated. These are given in Table 2, together with the magnetic moments.

Table 2. *Magnetic constants*

Mol % U	C	θ(°K.)	μ
100·0	1·21	208	3·11β
77·2	1·21	160	3·11β
75·3	1·20	154	3.11β
45·1	1·13	93	3·02β
31·5	1·08	67	2·94β
9·2	1·02	42	2·86β

The effects of dilution on the Weiss constant and the magnetic moment are shown in Figs. 3 and 4. These results are qualitatively in agreement with the work of Trzebiatowski & Selwood (1950) and of Dawson (1951), and support their observation that the magnetic moment of the U^{4+} ion approaches the 'spin-only' value at large dilution.

However, quantitative agreement is poor. We find the lattice constants of solid solutions of the system UO_2–ThO_2 follow Vegard's rule, in contrastt o Trzebiatowski & Selwood, who observed deviations for mixtures containing more than 50% ThO_2. We also find a linear relation between the Weiss constant θ and the molecular % UO_2 in the range 31–100 mol. % UO_2. This function extrapolates through the origin at infinite dilution, indicating that θ may be entirely due to the exchange energy in this concentration range

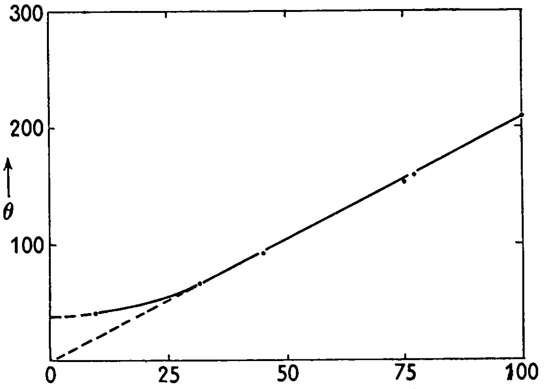

Fig. 3. Paramagnetic Curie temperature as a function of composition.

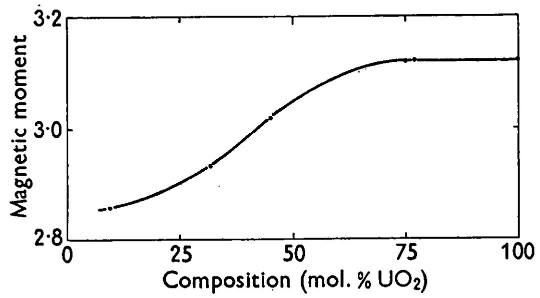

Fig. 4. Magnetic moment as a function of composition.

(Corliss, Delabarre & Elliott, 1950). This interpretation is not the only one, however, and further work with other systems is needed to give better understanding of the importance of the several modes of exchange (Zener, 1951; Anderson, 1950). Below 31 mol. % UO_2 deviation from linearity was observed. The effect seems to be real, for it was found in three solid solutions containing 5, 9 and 15 mol. % UO_2. Data for the 5 and 15 mol. % solutions have not been included because the X-ray photographs indicated somewhat less satisfactory solid-solution formation than in the other cases.

The suggestion we have here of a residual θ at high dilution indicates a crystalline field of considerable magnitude. This in turn casts some doubt on the calculation of magnetic moments from the Curie constants, for it is well known that the Weiss–Curie law is only approximate in this case (Van Vleck, 1932, Chap. 11).

We wish to thank Dr Raymond Stoenner for making the chemical analyses of the materials, and Drs Jacob Bigeleisen, Lester Corliss, Julius Hastings and Max Wolfsberg for their interest in the problem.

References

Anderson, P. W. (1950). *Phys. Rev.* **79**, 350.
Angus, W. R. (1932). *Proc. Roy. Soc.* A, **136**, 569.
Corliss, L., Delabarre, Y. & Elliott, N. (1950). *J. Chem. Phys.* **18**, 1256.
Dawson, J. K. (1951). *J. Chem. Soc.* p. 2889.
Hillebrand, W. F. (1893). *Z. anorg. Chem.* **3**, 243.
Hoffmann, K. A. & Höschele, K. (1915). *Ber. dtsch. chem. Ges.* **48**, 20.
Sterba, J. (1904). *Ann. Chim. (Phys.)* (8), **2**, 207.
Troost, L. & Ouvrard, M. (1886). *C. R. Acad. Sci.* Paris, **102**, 1422.
Trzebiatowski, W. & Selwood, P. W. (1950). *J. Amer. Chem. Soc.* **72**, 4504.
Van Vleck, J. H. (1932). *The Theory of Electric and Magnetic Susceptibilities.* Oxford: University Press.
Vegard, L. (1921). *Z. Phys.* **5**, 17.
Zachariasen, W. H. (1947). MDDC 1572, U. S. Atomic Energy Commission.
Zener, C. (1951). *Phys. Rev.* **81**, 440.

Acta Cryst. (1952). **5**, 770

A Refinement of the Crystal Structure of Potassium Benzylpenicillin

By Geoffrey J. Pitt

Laboratory of Chemical Crystallography, Oxford, England

(*Received* 22 *April* 1952)

Better crystals of potassium benzylpenicillin have been obtained which give many more reflexions than were used in the previous analysis. The terms derived from these have been included in one further stage of refinement of the atomic coordinates by Fourier synthesis.

Introduction

The X-ray analyses of sodium and potassium benzylpenicillin were first undertaken to assist in determining the chemical structure of penicillin at a time when this was largely unknown (Crowfoot, Bunn & Rogers-Low, 1949, p. 310). The details of the crystal structures of these two salts, as eventually derived from the second three-dimensional Fourier synthesis in each case, proved amply sufficient to show the bonding