crystal is supported on a fibre mounted in a keyed nib (Fig. 2). The key of the nib fits into a recess in the Eulerian-cradle orienter secured by a set screw so that the attitude of the fibre supported crystal with respect to the Eulerian cradle is always preserved. Thus, by recording the Eulerian angles (ψ for angular displacement along the arc, and φ for angular displacement about the turntable) when the crystal is in a given alignment the nib can be removed and reinserted as often as desired without serious loss of alignment. A similar recess is easily adapted to a conventional two-circle goniometer head as shown in Fig. 2. Designating angular displacement along the larger arc of the two-circle goniometer head as Λ_1, and angular displacement along the smaller arc Λ_2, the orientation of the recess in the two-circle goniometer head when $\Lambda_1=\Lambda_2=0$ is constrained to be parallel to the recess in the Eulerian cradle when that is set to $\psi=\varphi=0$.

If a crystal is oriented so that a given axis is collinear with the axis of rotation of the Eulerian cradle at the setting (ψ, φ) and is then transferred to the goniometer head, the crystal will have the same orientation of the given axis with respect to the spindle axis of the two-circle goniometer head if the arcs of the two-circle goniometer head are set at

$$\begin{aligned}\Lambda_1 &= \tan^{-1}\ \{\tan\psi\cos\varphi\}\\ \Lambda_2 &= -\sin^{-1}\{\tan\psi\sin\varphi\}\,.\end{aligned}\tag{1}$$

Conversely, transferring from the two-circle goniometer head to the Eulerian cradle is accomplished by setting the Eulerian cradle such that

$$\begin{aligned}-\varphi &= \tan^{-1}\{\tan\Lambda_2\csc\Lambda_1\}\\ \psi &= \cos^{-1}\{\cos\Lambda_1\cos\Lambda_2\}\,.\end{aligned}\tag{2}$$

The sense of these angular displacements is as follows. With reference to the goniometer head shown (in projection) in Fig. 2, a positive displacement Λ_1 is effected by rotating the Λ_1 screw clockwise. Similarly a positive displacement Λ_2 is effected by moving the Λ_2 screw clockwise.

The precision to which the alignment of the crystal is preserved depends of course upon the tolerances maintained in the orientation of the recesses and fitting of the nib for both the Eulerian cradle and goniometer head. In practice, the transfer of an aligned cradle from the Eulerian cradle to a 'Supper' goniometer head mounted on a precession camera preserves the alignment to within one quarter degree for recesses made to accommodate a 'slide fit'.

References

BUERGER, M. J. (1942). *X-Ray Crystallography*, p. 184. New York: Wiley.

FURNAS, T. C. & HARKER, D. (1955). *Rev. Sci. Instrum.* **26**. 449.

LADELL, J. (1963). To be published.

LADELL, J. & LOWITZSCH, K. (1960). *Acta Cryst.* **13**, 205.

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Complex oxide systems of barium and plutonium.

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Some work on barium–plutonium–oxygen systems, particularly on their preparation, has been reported by Moore & Kraus (1949), Cunningham (1954) and Russel, Harrison & Brett (1960). In this communication further work is presented in light of the crystallographic studies obtained with a 19 cm powder camera and Cu $K\alpha$ radiation.

Following the method suggested by Moore & Kraus and by Cunningham, barium plutonate(VI) was precipitated from an acid solution of plutonium(VI) and barium ions with ammonium hydroxide or sodium hydroxide solution. These preparations seemed to have an indefinite composition, the ratio of the Pu atoms to Ba atoms in our experiments being found to change from 0·6 to 6·7. X-ray examination revealed mainly amorphous patterns in all samples and barium carbonate as impurity, possibly as a result of absorption of carbon dioxide during or after precipitation. In these preparations some polymeric types of compound were probably being formed, as suggested by Gevantman & Kraus (1949).

These samples were heated to 900 °C to observe any phase change that might take place. On heating, the precipitates obtained in presence of ammonium hydroxide developed PuO_2 lines, whereas those obtained in presence of sodium hydroxide revealed a cubic ABO_3 perovskite structure with cell dimensions $a=4{\cdot}322\pm0{\cdot}003$ Å. The plutonium in the ABO_3 compound was found by spectrophotometry and titration, to be present mainly as plutonium(VI).

For further work, freshly prepared pure barium oxide mixed with plutonium dioxide in approximately 1:1 ratio was heated in an argon atmosphere in a tantalum crucible inside a resistance vacuum furnace similar to that described by Drummond, MacDonald, Ockenden & Welch (1957). The preparations obtained at 1100 °C gave along with PuO_2 a cubic perovskite structure with bigger cell dimensions $a=4{\cdot}373\pm0{\cdot}003$ Å, somewhat similar to the value obtained recently by Russel (1960). At 1600 °C the cubic perovskite underwent a phase change to an orthorhombic form with

$$\begin{gathered}a=5{\cdot}795\pm0{\cdot}004,\ b=5{\cdot}861\pm0{\cdot}004,\\ c=5{\cdot}983\pm0{\cdot}004\ \text{Å};\ Z=2\,.\end{gathered}$$

The valency of plutonium in both orthorhombic and cubic forms was found from chemical evidence to be IV.

From the above it appears that cubic perovskite formations could exist with both plutonium(IV) and plutonium (VI). The diffraction data for both are very similar. Since in perovskites of ABO_3 type the sum of the charges on A and B ions should be six (Wells, 1950), the cubic compound obtained by the dry method may be written $BaPu^{IV}O_3$. The other, obtained by precipitation, could be interpreted as either (i) a PuO_3 compound with barium in a semimetallic bonding state occupying the interstitial position or (ii) a compound of the type Ba_xPuO_3 (with x very small) analogous to sodium and potassium tungstates (Hägg, 1935; Magnéli & Nilson, 1950). Both cubic compounds have space group $Pm3m\,(O_h^1)$ with one molecule per unit cell. In $BaPu^{IV}O_3$ the calculated and observed plutonium oxygen distances were 2·25 Å and 2·18 Å respectively and compared favourably with calculated and observed values of 2·28 Å and 2·20 Å based on the data for $BaU^{IV}O_3$ reported by Russel (oxygen ionic radii taken here as 1·35 Å (Lipson, 1953) and actinide radii taken from Zachariasen, 1954). Similarly in the perovskite of plutonium(VI), the observed distance Pu–O was 2·16 Å, which is identical with the calculated value.

The X-ray data of the orthorhombic phase obtained at 1600 °C are given in Table 1. The phase change from cubic to orthorhombic form could be followed from Roth's diagram showing how the formation of perovskites depends on the ionic radii of A and B elements (Roth, 1957). Considering the ionic radii of barium and plutonium, the point for $BaPu^{IV}O_3$ in the diagram was found to be in the cubic region, but very near the borderline, indicating the possibility of both cubic and pseudocubic systems. The heating of the system probably caused sufficient change to induce a reduction in the coordination number of barium leading to the formation of a pseudo-cubic cell, the true cell being orthorhombic.

Table 1. *X-ray data on* $BaPuO_3$ *(orthorhombic form) obtained at* 1600 °C

The data are indexed with

$a=5{\cdot}795,\ b=5{\cdot}861,\ c=5{\cdot}983$ Å

d (Å)	$q^2{}_o$ (10^{-4})	$q^2{}_c$ (10^{-4})	*hkl*	I_o
3·392	517	516	111	*vw*
2·991	664	664	002	*s*
2·918	698	698	020	*m*
2·899	707	708	200	*m*
2·423	1012	1014	112	*vw*
2·085	1367	1371	202	*w*
		1359	022	
1·958	1550	1545	212	*w*
1·855	1726	1728	031	*w*
1·751	1938	1932	311	*w*
1·695	2068	2066	222	*w*
1·461	2786	2776	040	*vw*
1·448	2832	2833	104	*vw*
		2832	400	
1·307	3479	3489	240	*w*
1·178	4285	4270	043	*w*

For unreacted BaO and PuO_2 weak lines were also noticed in the pattern, but are not recorded here.

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References

CUNNINGHAM, B. B. (1954). *The Actinide Elements*. N. N. E. S. IV., 14A, p. 403. New York: McGraw Hill.

DRUMMOND, J. L., MACDONALD, B. J., OCKENDEN, H. M. & WELCH, G. A. (1957). *J. Chem. Soc.* p. 4785.

GEVANTMAN, L. H. & KRAUS, K. A. (1949). *The Transuranium Elements*. N. N. E. S. Div. IV, 14B, Paper 4·21, p. 602. New York: McGraw Hill.

HÄGG, G. (1935). *Z. Phys. Chem.* B, **29**, 192.

LIPSON, H. & COCHRAN, W. (1953). *The Crystalline State*. Vol. III, p. 315. London: Bell.

MAGNÉLI, A. & NILSSON, R. (1950). *Acta Chem. Scand.* **4**, 398.

MOORE, G. E. & KRAUS, K. A. (1949). *The Transuranium Elements*. N. N. E. S. Div. IV, 14B, paper 4·22, p. 609. New York: McGraw Hill.

ROTH, R. S. (1957). *J. Res. Nat. Bur. Stand.* **58**, 75.

RUSSEL, L. E., HARRISON, J. D. L. & BRETT, N. H. (1960). *J. Nuclear Mater.* **2**, 310.

WELLS, A. F. (1950). *Structural Inorganic Chemistry*, p. 378. Oxford: Clarendon Press.

ZACHARIASEN, W. H. (1954). *The Actinide Elements*. N. N. E. S. Div. IV, 14A, p. 776. New York: McGraw Hill.

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X-ray scattering factor of a hydrogen atom in a hydrogen molecule.*

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The effective scattering factor f^e of a hydrogen atom in a hydrogen molecule was calculated by McWeeny (1952) with a charge density function based on a Heitler–London wave function

$$\Psi=(1/\sqrt{(2(1+S^2_{AB}))})\,\{\varphi_A(1)\varphi_B(2)+\varphi_A(2)\varphi_B(1)\}$$

where

$$\varphi_A(1)=\varphi_{1s}(r_{1A})=N_{1s}\exp\,(-\mu r_{1A})\,,$$
$$\varphi_B(2)=\varphi_{1s}(r_{2B})=N_{1s}\exp\,(-\mu r_{2B})$$

and S_{AB} is the overlap integral.

The parameter μ was chosen to be 1 a.u. in McWeeny's calculation, and the magnitude of the effective factor was found to be generally less than that for an isolated hydrogen atom. This fact was interpreted as due to migration of electrons away from the nucleus into the bond.

The authors have evaluated the scattering factor f^e

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