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Transfer of aligned crystals from Eulerian-cradle orienter to conventional two-circle goniometer head.

By JOSHUA LADELL, *Philips Laboratories, Irvington-on-Hudson, New York, U.S.A.*

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Many presently available Eulerian-cradle crystal orienters are essentially 'two stage' orienters (Furnas & Harker, 1955). Supported in the cradle is an upper stage goniometer head, usually a two-circle orienter (Buerger, 1942), which can be compatibly employed in single-crystal diffraction cameras. Since the Eulerian cradle itself (without the piggy-back goniometer head) provides the necessary modes of rotation for counter detector diffractometry, the small second stage goniometer head is redundant in counter detector usages. Nevertheless, the employment of the upper stage goniometer head is deemed convenient to permit rapid interchange from film to counter detector experiments, particularly in such cases where the counter detector researcher depends upon film methods to make preliminary crystal alignments, space group and crystal symmetry studies, and detect possible crystal twinning.

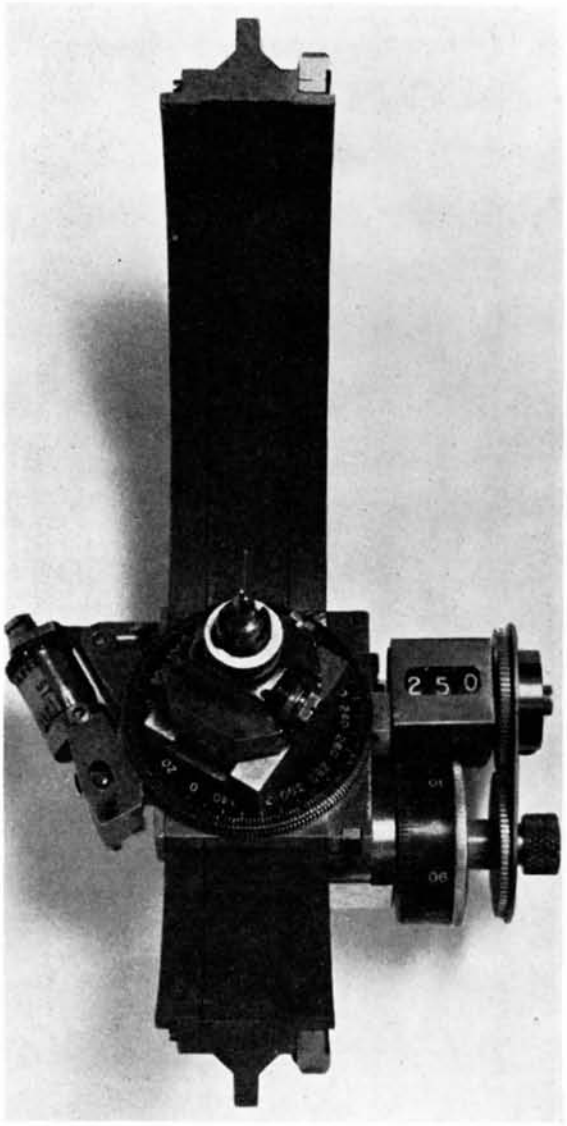

Fig. 1. Eulerian-cradle crystal orienter used in counter diffractometry. Only angular displacements of Eulerian angles, φ (turntable) and ψ (along arc), are used for angular orientation of crystal.

To meet certain requirements in the design of PAILRED II, an automatic linear reciprocal space exploring diffractometer (Ladell & Lowitzsch, 1960; Ladell, 1963), a novel Eulerian-cradle orienter (Fig. 1) is employed. To provide the capability of precise centering and angular orientation of the crystal to exactitudes required with the use of crystal monochromatized radiation and automated integrated intensity data collection, the design omits the redundant upper stage (film methods compatible) goniometer head.

Since PAILRED II is a self-contained instrument, much of the information, previously obtainable primarily by film procedures, is now acquired directly by the counter detector methods using manual and automatic modes of operation. Accordingly, the retention of the goniometer head is no longer desirable.

The minor handicap of inconvenient transfer of aligned crystals from Eulerian-cradle (without goniometer head) to a standard Weissenberg type two-circle goniometer head is easily overcome by the following technique. The

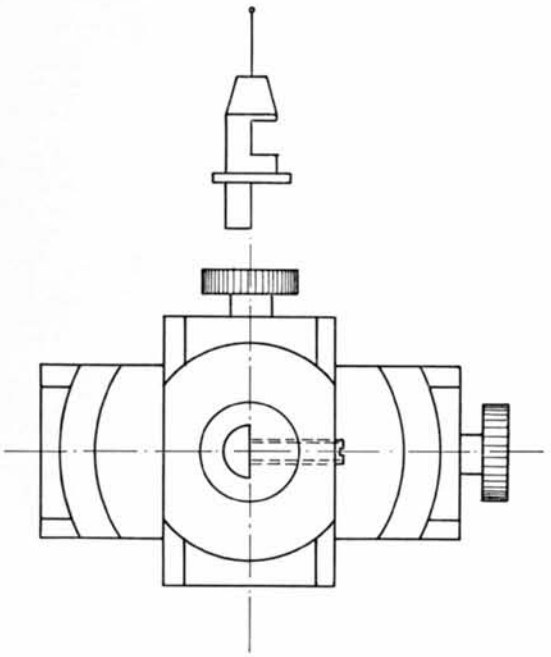

Fig. 2. Keyed-nib crystal holder. Key shape is semicircular as shown. Recess in two-arc goniometer head is also shown. Channel cut in upper portion of nib permits secure cementing of fibre to nib.

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

$$\Lambda_1=\tan^{-1}\{\tan\psi\cos\varphi\}$$
$$\Lambda_2=-\sin^{-1}\{\tan\psi\sin\varphi\}\,. \qquad (1)$$

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

$$-\varphi=\tan^{-1}\{\tan\Lambda_2\csc\Lambda_1\}$$
$$\psi=\cos^{-1}\{\cos\Lambda_1\cos\Lambda_2\}\,. \qquad (2)$$

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'.

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Complex oxide systems of barium and plutonium.

By D. M. CHACKRABURTTY, N. C. JAYADEVAN and C. K. SIVARAMAKRISHNAN, *Radiochemistry and Isotope Division, Atomic Energy Establishment, Trombay, Bombay-71, India*

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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

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

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