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X-ray determination of the atomic positions in α -uranium at 22 °C and 600 °C. By W. T. Eeles, Central Electricity Generating Board, Berkeley Nuclear Laboratories, England and A. L. Sutton, Northampton College of Advanced Technology, London, England

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The y co-ordinate of the α -uranium atom is the only one not fixed by space-group requirements. There have been several independent determinations of it at room temperature by X-ray and neutron diffraction, yielding closely similar values between 0.102 and 0.1025 (Sturcken & Post, 1961; Cash, Hughes & Murdock, 1961; Mueller, Kitterman & Knott, 1962).

There appear to have been only two determinations at temperatures just below the α - β transition temperature, and Mueller *et al.* (1962) have drawn attention to the discrepancy between their value of y at 625 °C, 0.1057 ± 0.0006 and that of Chebotarev (1961), 0.1120. However Chebotarev's value at 625 °C is calculated from a room-temperature value of $y = 0.105$, the known variation of the α -uranium lattice parameters with temperature, and some assumptions about changes of interatomic distances presumably based on early observations of high-order X-ray reflexions (Konobeevskii, Bubrovin, Levitskii, Panteleev & Pravdyuk, 1958). An unpublished determination by the present authors in 1959 based on X-ray powder photographs of α -uranium filings gave $y = 0.1095$ at 630 °C. We have repeated this determination with greater precautions to eliminate experimental errors.

The specimen used was of high purity α -uranium powder of granular diameter not greater than 20μ , sealed in an evacuated thin-walled quartz capillary tube 0.5 mm in diameter. Exposures were made on fine-grain film at room temperature (22 °C) and at 597 ± 4 °C with Ni-filtered Cu radiation. The resulting powder patterns were free from preferred orientation and from impurity lines with the exception of weak UO_2 lines. The intensities of the lines were measured with a microdensitometer and used in three-dimensional Fourier and $F_o - F_c$ analyses. In each case 26 easily measurable lines were used; lines which were too weak to be microdensitometered accurately or were overlapped by UO_2 lines were omitted. Lines representing groups of overlapping reflexions were divided in their calculated proportions and used in the later stages of the analyses. Absorption corrections were made empirically as it was found that those calculated by the method of Bond (1959) for heavily absorbing specimens led to negative values of the temperature factor. The empirical corrections were derived by comparison of the intensities of the room-temperature exposure with those obtained from a fine-grained block of α -uranium with a plane surface, a proportional-counter diffractometer being used.

Except for the very-lowest-order reflexions the corrections were a smooth and approximately linear function of $\sin^2 \theta$. The enhanced absorption can be attributed to surface roughness, which even with fine powders has a significant effect if the linear absorption is high.

The resultant values of y were 0.1021 at 22 °C and 0.1071 at 597 °C. Corresponding values of the temperature factors (necessarily isotropic as based to some extent on overlapping reflexions) were 0.42 \AA^2 and 1.1 \AA^2 . The

final R values were 0.062 and 0.07 and from the final $F_o - F_c$ syntheses the standard deviations of y were estimated by the method of Cruickshank (1949) to be 0.0003 and 0.00045.

The room-temperature y value agrees satisfactorily with the previously reported values. The high temperature value is much closer to Mueller's neutron-diffraction value (0.1057 ± 0.0006) than either Chebotarev's or our own earlier value. The difference between our present value and that of Mueller *et al.* is rather more than their estimated limit of error and about three times our estimated standard deviation, though it is an exceedingly small distance physically (0.007 Å). As Mueller *et al.* used only a few $0k0$ reflexions their result may possibly be affected by extinction or, as wide-angle collimators are used in neutron diffraction, by inclusion of some of the thermal diffuse scattering in the integrated intensities. The former source of error is presumably absent as their room-temperature value was obtained with the same single crystal. The latter effect would indeed be enhanced by the increase in temperature to 600 °C. It would, however, be largely compensated by being taken up in the empirically determined temperature factor. Though the temperature factors of Mueller *et al.* agree closely with our own the comparison is hardly relevant, as ours are isotropic and are not determined with sufficient precision.

There are many possible sources of error in our own experiments. With the use of a larger number of reflexions these may be presumed to be random and to be related to the estimate of standard deviation. Since the peak electron density as indicated by X-rays may not be in precisely the same place as the nucleus even in as large an atom as uranium, the agreement between the two methods seems to be as much as can be expected.

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References

- BOND, W. L. (1959). *International Tables for X-ray Crystallography*, Vol. II, p. 292.
 CASH, A. H., HUGHES, E. W. & MURDOCK, C. C. (1961). *Acta Cryst.* **14**, 313.
 CHEBOTAREV, N. T. (1961). *Atomnaya Energiya*, **10** (1), 43.
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **21**, 65.
 KONOBEEVSKII, S. T., BUBROVIN, K. P., LEVITSKII, B. M., PANTELEEV, L. D. & PRAVDYUK, N. F. (1958). *Proc. U.N. Intern. Conf. Peaceful Uses of At. Energy*, 2nd., Geneva, **5**, 574.
 MUELLER, M. H., KITTERMAN, R. L. & KNOTT, H. W. (1962). *Acta Cryst.* **15**, 421.
 STURCKEN, E. F. & POST, B. (1961). *Acta Cryst.* **13**, 852.