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Crystal Structure of Element 43

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Excellent powder diffraction patterns have been obtained from microgram quantities of the long-lived isotope, Tc^{99}, of element 43. Like rhenium, osmium and ruthenium, technetium crystallizes in the hexagonal close-packed arrangement. The cell, which contains two atoms, has the following dimensions:

$$a_1 = 2{\cdot}735 \pm 0{\cdot}001 \text{ A.}, \quad a_3 = 4{\cdot}388 \pm 0{\cdot}001 \text{ A.}, \quad a_3/a_1 = 1{\cdot}604.$$

The calculated density, based on an atomic weight of 99, is 11·497 g.cm.$^{-3}$ Each atom has twelve neighbors, six at 2·735 A. and six at 2·698 A.

Introduction

All of the metallic elements save manganese have at least one crystal phase of the face-centered cubic, body-centered cubic or hexagonal close-packed structure type. Element 43 proves to be no exception. It has been found to crystallize as a hexagonal close-packed structure with dimensions slightly smaller than those of rhenium and slightly larger than those of ruthenium and of osmium.

Element 43, long a missing member of the manganese group, has been collected, purified and studied only in the form of isotopes produced by nuclear reactions, though in 1925 Noddack & Tacke (1925) and Berg & Tacke (1925) attributed to it some X-ray lines obtained from a concentration of natural materials. At that time it was given the name masurium. Since then the element, definitely identified only as an artificial isotope, has become known as technetium. In 1937 a short-lived isotope of element 43 was discovered in deuteron-bombarded molybdenum by Cacciapuoti & Segre (1937) and Perrier & Segre (1937, 1939), who studied many of its properties by means of tracer chemistry. Later, a long-lived isotope of element 43 was established as one of the products of U^{235} fission by Lincoln & Sullivan and by Schuman (Plutonium Project Survey, 1946). Recently a long-lived isotope has been produced from neutron bombardment of molybdenum by Motta, Boyd & Larson (1947).

Origin of samples

A preparation of technetium, separated from fission products by G. W. Parker, J. W. Ruch and J. Reed of the Clinton Laboratories of the Monsanto Chemical Company, was supplied to the Argonne National Laboratory for basic chemistry study of the element on a microchemical scale. The fission technetium contained in the preparation was the long-lived isotope, Tc^{99}, as confirmed by mass spectrometric analysis (Inghram, Hess & Hayden, 1947).

From this supply, a number of chemical preparations intended to produce pure samples of the metal were made in microgram batches by Dr Sherman Fried of the Chemistry Division, Argonne National Laboratory. These preparations, sealed in thin glass tubes suitable for X-ray exposure, were submitted to the author for powder diffraction analysis. The immediate purpose of the X-ray examination was to establish the chemical identity of the samples from structural considerations, since direct chemical analysis of microscopic samples is at best troublesome and often unsatisfactory. The positive identification of the X-ray pattern of a new element, particularly for small samples where the bulk of the material may be impurities, must depend on such considerations as trends in structure type and dimensions shown by neighbouring elements in the periodic table.

X-ray diffraction data and results

The X-ray powder diagrams were taken in a 9 cm. diameter Bradley-type camera, with copper radiation filtered through nickel. Patterns obtained from three of the samples showed the presence of a hexagonal close-packed phase. One pattern was complicated by lines due to other phases to the extent of 40–50 %; one had only faint traces of an additional phase; one, with exceptionally sharp lines, was a single-phase hexagonal pattern. This pattern, shown in Fig. 1 along with patterns of rhenium and ruthenium for comparison, was obtained from an estimated 40 μg. of material, which, under the microscope, appeared as a small nodule with a silvery metallic lustre.

Comparison of the three patterns showed that they must be attributed to the same crystalline structure, undoubtedly a metal. Measurements definitely identified this metal phase as technetium, as will be shown.

The data recorded in Table 1 were obtained from the single-phase pattern. The lines were measured by means of a steel scale and vernier, and the intensities estimated

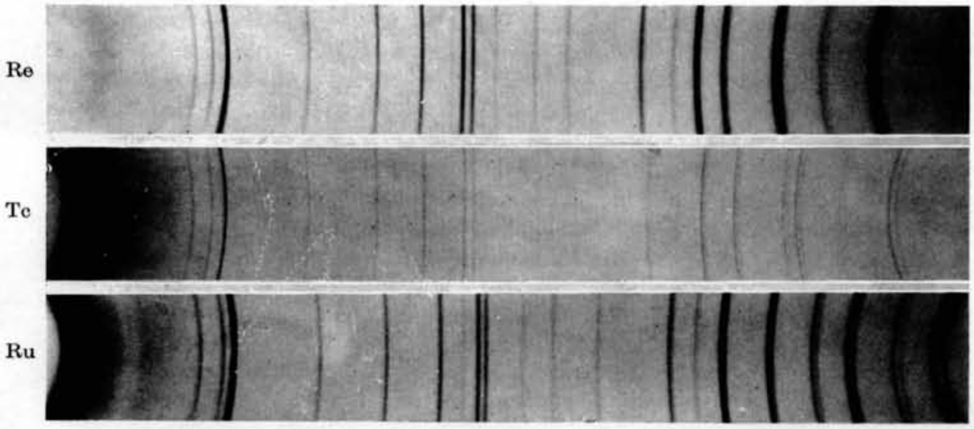

Fig. 1. Comparison of X-ray diffraction powder patterns of Re, Tc, and Ru.

visually. They correspond closely with those observed for rhenium.

Table 1. *Powder diffraction pattern of element 43, technetium*

Plane index	Observed intensity	$\sin^2 \theta$
10*0	*m*−	0·1065
00*2	*m*−	0·1241
10*1	*vs*	0·1376
10*2	*w*	0·2306
11*0	*m*−	0·3182
10*3	*m*+	0·3829
20*0	*vvw*	0·4237
11*2	*s*−	0·4406
20*1	*m*	0·4533
00*4	*vvw*	0·4930
20*2	*vw*+	0·5465
10*4	*vw*	0·5980
†20*3	*m*−	0·6984
21*0	*vw*	0·7377
21*1	*s*	0·7687
11*4	*m*	0·8070
21*2	*m*−	0·8604
10*5	*m*+	0·8727
20*4	*w*	0·9124
30*0	*m*+	0·9481

† Measurements from 20*3 to the end were made on resolved $K\alpha$ lines.

The cell dimensions deduced from the high-angle reflections of this diffraction pattern are as follows:

$$a_1 = 2{\cdot}735 \pm 0{\cdot}001 \text{ A.},$$
$$a_3 = 4{\cdot}388 \pm 0{\cdot}001 \text{ A.},$$
$$a_3/a_1 = 1{\cdot}604.$$

On the basis of two atoms per unit cell and an atomic weight of 99, the calculated density is 11·497 g.cm.$^{-3}$

The measurements on the pattern showing traces of a second phase yielded an identical value for the a_1 dimension, but gave 4·391 A. for the a_3 translation. Assuming the accuracy of measurement to be the same in both cases, this might be due to a slight impurity in the mixed sample.

Every technetium atom has twelve nearest neighbors. Six are at a distance of 2·735 A., the a_1 unit cell translation, and six somewhat nearer, at 2·698 A. The metallic radius of closest approach is therefore 1·349 A.; the average value of the metallic radius for twelve co-ordination is 1·358 A. This radius may now be compared with the metallic radii for twelve co-ordination found or calculated for neighboring elements in the periodic table. It can be seen from the following that the metallic radius found for technetium fits excellently in the progression of values found for metals in this region of the periodic table:

Atomic no.	42	43	44	45
Element	Mo	Tc	Ru	Rh
Radius	1·386	1·358	1·336	1·342

Atomic no.	74	75	76	77
Element	W	Re	Os	Ir
Radius	1·394	1·373	1·350	1·355

The values of the metallic radii for twelve co-ordination used for comparison are taken from a table given by Pauling (1947).

Of the elements shown in the preceding list, three are isomorphous with technetium. The following table shows the comparison between the dimensions of the technetium structure and those of the isomorphous rhenium, ruthenium and osmium structures. The values given were obtained from *Strukturbericht*, **1**.

Element	a_1	a_3	a_3/a_1	d_1	d_2
43 Tc	2·735	4·388	1·604	2·735	2·698
44 Ru	2·69	4·28	1·59	2·69	2·65
75 Re	2·752	4·448	1·616	2·752	2·733
76 Os	2·714	4·315	1·59	2·714	2·671

Here again, the results are what would be expected for an element preceding ruthenium in the row, and rhenium in the column of the periodic table.

It is reasonable to expect that the structures of the compounds of technetium will tend to be like those of analogous rhenium compounds. At any rate it is quite certain that the pertechnetates of cations such as sodium, ammonium and rubidium will have the scheelite structure, which is common, not only to the analogous perrhennates, but also to the molybdates and tungstates of lead, strontium, calcium and barium.

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