

X-RAY INVESTIGATIONS ON THE PLATINUM METALS, SILVER, AND GOLD

BY

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(WITH 7 TEXT FIGURES)

Introduction.

The present investigation of the lattice spacings of the platinum metals brings to the foreground the relation between atomic structure and chemistry. The six platinum metals have all nearly the same atomic volumes.

The investigations by V. M. GOLDSCHMIDT¹ and coworkers of the isomorphous relations of the sesquioxides gave for the rare earth metals the result that there is a regular decrease in the lattice spacings (resp. molecular volumes) from lanthanum to cassiopeium (lutecium). This contraction is described by GOLDSCHMIDT as the *lanthanide contraction*, the series of elements from cerium to cassiopeium being included in the term *lanthanides*.

It was also shown that the lanthanide contraction exerts an influence on the lattice spacings of the elements following cassiopeium.

On the suggestion of professor V. M. GOLDSCHMIDT we have recently made new determinations of the lattice spacings of rhodium, palladium, and platinum², and shown how the increase

¹ Geochemische Verteilungsgesetze der Elemente IV and V:

IV: V. M. GOLDSCHMIDT, F. ULRICH und T. BARTH: Zur Krystallstruktur der Oxyde der seltenen Erdmetalle.

V: V. M. GOLDSCHMIDT, T. BARTH und G. LUNDE: Isomorphie und Polymorphie der Sesquioxyde. Die Lanthanidenkontraktion und ihre Konsequenzen.

Vid. Akad. Skr. I. Mat.-Nat. Kl. (Oslo) 1925 No. 5 and No. 7.

² Zeitschr. physikal. Chemie 117, 478 (1925); Norsk Geol. Tidsskrift 8, 220 (1925).

in atomic volume in the vertical series of the periodical system for the element couples *Rh Ir* and *Pd Pt* is almost, but not quite, compensated by the lanthanide contraction.

At about the same time G. v. HEVESY¹ has reached similar results through determination of densities of the octo hydrates of the sulphates of the rare earth metals. He finds in the series lanthanum lanthanides that with rising number of the order there is a decrease in the molecular volume of the compounds examined by him. The same writer also mentions briefly the influence of the lanthanide contraction on the elements following cassiopeium and in an other paper² he has shown how the increase in molecular volume of the dioxides in the homologous series titanium, zirconium, hafnium, thorium has a stagnation between zirconium and hafnium.

Exact X-Ray Measurements.

Our measurements were made according to a method suggested by WYCKOFF³ by which the substance is mixed directly with *Na Cl*, the spacing of which thus serves as a standard. The experimental data, description of apparatus, and calculation of the films are given in *Zeitschr. f. physikal. Chemie* (1926).

Our measurements gave the following values:

Silver	a	4,078 Å	$a = 4,078 \text{ \AA}$	$a = 4,078 \text{ \AA}$
Gold	a	4,070 Å	$a = 4,070 \text{ \AA}$	$a = 4,069 \text{ \AA}$
Palladium	a	3,873 Å		
Platinum .	a	3,903 Å		
Rhodium .	a	3,794 Å	$a = 3,797 \text{ \AA}$	
Iridium ..	a	3,822 Å	$a = 3,824 \text{ \AA}$	
Ruthenium	a	2,695 Å	$c = 4,273 \text{ \AA}$	$c/a = 1,586$.
Osmium ..	a	2,724 Å	$c = 4,314 \text{ \AA}$	$c/a = 1,584$.

¹ *Zeitschr. anorg. Chemie* 147, 217 (1925).

² *Recherches sur les propriétés du Hafnium*. Kgl. Danske Vid. Selsk. Math.-fys. Medd. VI, 7 (1925).

³ *Zeitschr. f. Krist.* 59, 55 (1923).

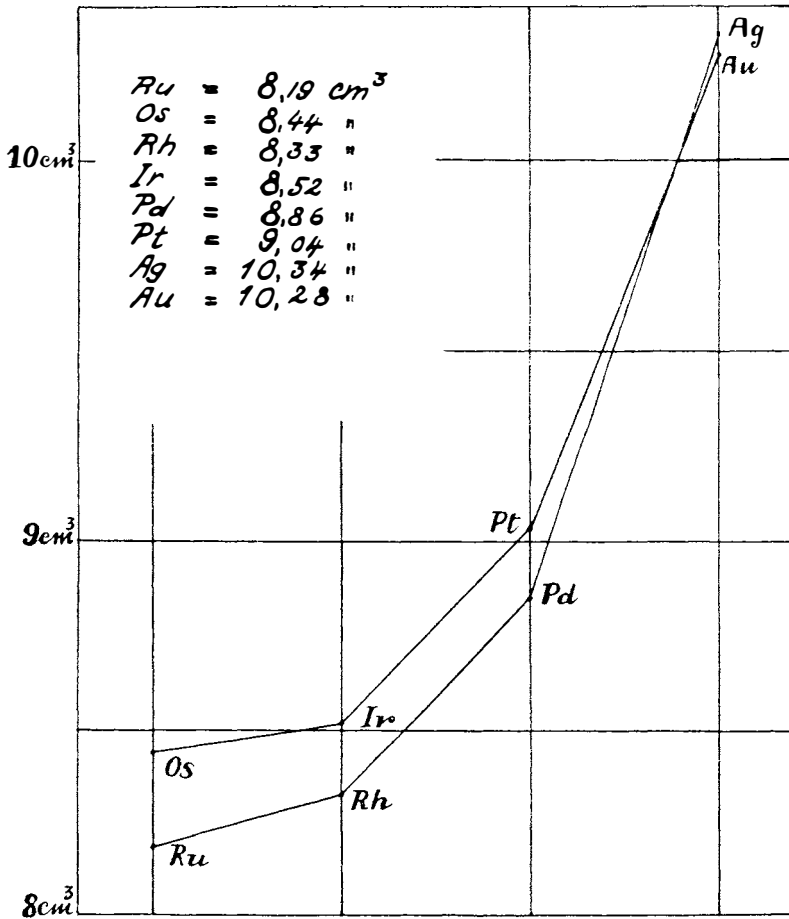


Fig. 1. Atomic volumes.

These measurements show that the progressive increase in the spacings that takes place on advancing from one element to its higher homologue in the group of the platinum metals is almost, but not quite, compensated by the lanthanide contraction, while for Ag Au there is an over-compensation. (Fig. 1).

Influence of temperature and pressure on spacings.

In the course of our investigations it became necessary to compute the spacings for various temperatures and pressures as the actual measurements were not all made under comparable conditions.

We based the computations on the values for the spacings obtained by our measurements, using the available data for heat expansion and compressibility, and presuming constancy of the type of the lattice.

For ruthenium osmium and rhodium iridium, the few determinations of the thermal coefficient of expansion are inadequate for our purposes. For platinum there are available more exact measurements which show that the spacings of palladium and platinum approach each other at rising temperatures and become almost equal at the melting point of palladium. (Fig. 2). Also for silver and gold it is shown that the lighter element has the greater expansion. (Fig. 3).

A consideration of the available measurements of the compressibility shows that ruthenium, rhodium, palladium, and silver are always more compressible than their higher homologues.

Using the measurements of P. W. BRIDGMAN¹ of $x = \frac{\partial V}{\partial P}$ where V designates the volume of 1 ccm at ordinary temperature and pressure, we arrive at the results plotted in the diagrams of Figs 4 and 5.

The change in compressibility with temperature and pressure is so insignificant¹ that it is not expressed in our curves. (See also BORN, *Atomtheorie des festen Zustandes*, 2 Aufl. (1923). *Fortschr. der Mathem. Wissensch.* 4, p. 745, who for his own considerations even reckons with a constant compressibility).

It is of special interest that the overcompensations observed for silver-gold at ordinary pressure decreases steadily at higher pressures. At about 14 000 atmospheres silver and gold have equal spacings and at still higher pressures the curves have a similar shape as for palladium platinum.

¹ Proc. Nat. Acad. Sc. Washington, 8, 361 (1922).

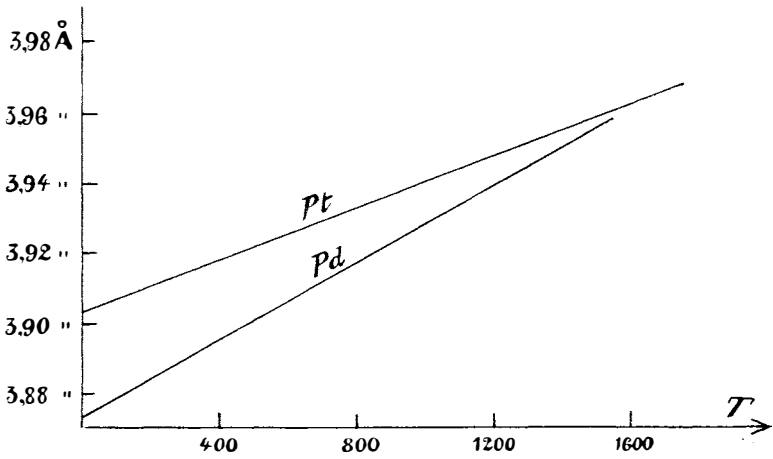


Fig. 2. Influence of temperature on the spacings of palladium and platinum.

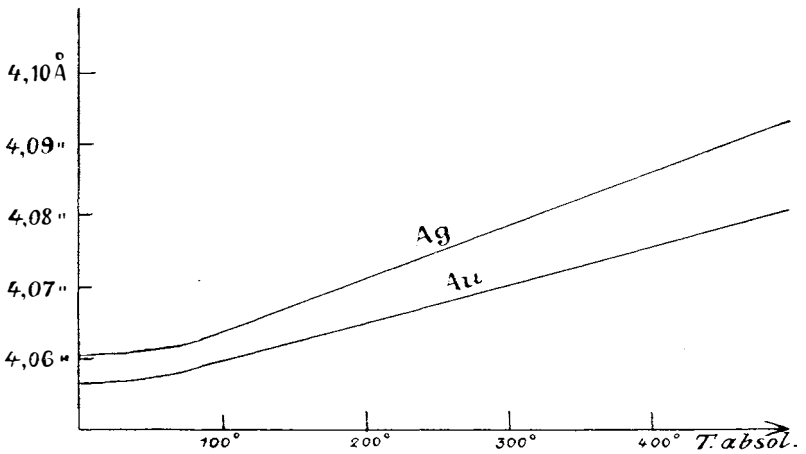


Fig. 3. Influence of temperature on the spacings of silver and gold.

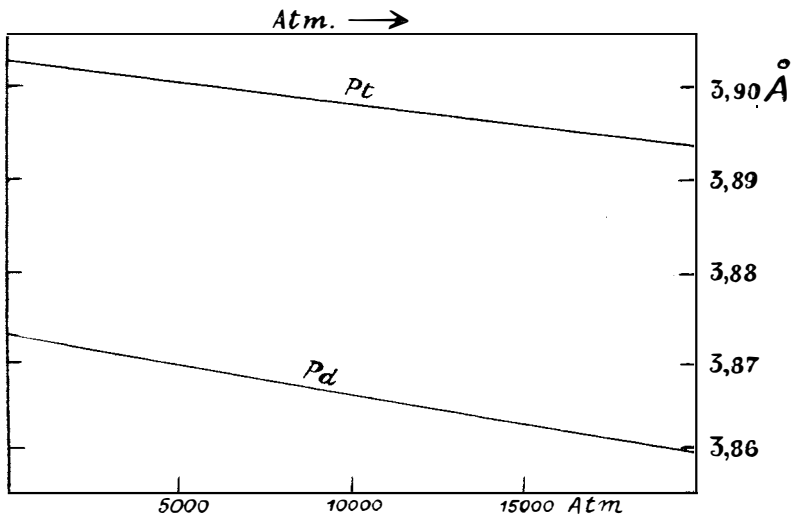


Fig. 4. Influence of pressure on the spacings of palladium and platinum.

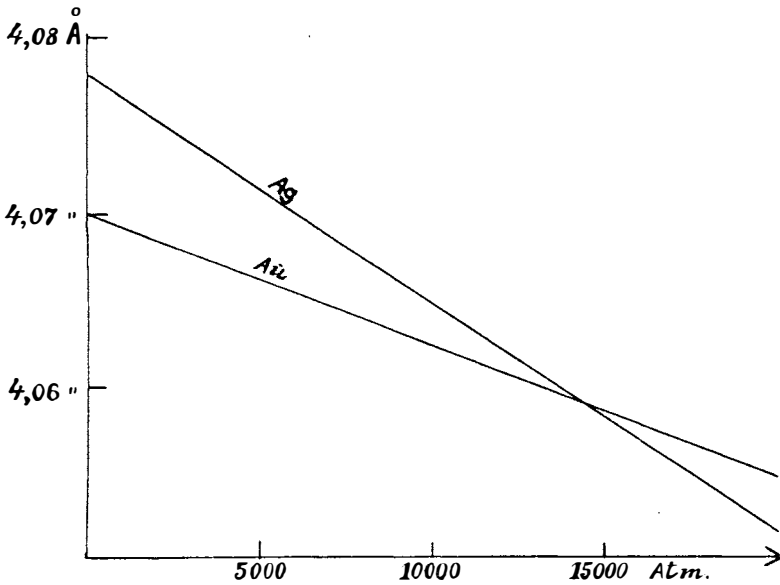


Fig. 5. Influence of pressure on the spacings of silver and gold.

A calculation of the physical conditions under which the spacings of silver and gold become equal gives the diagram represented in Fig. 6. At relatively high pressures and low temperatures $Ag < Au$, while at lower pressures and higher temperatures $Ag > Au$.

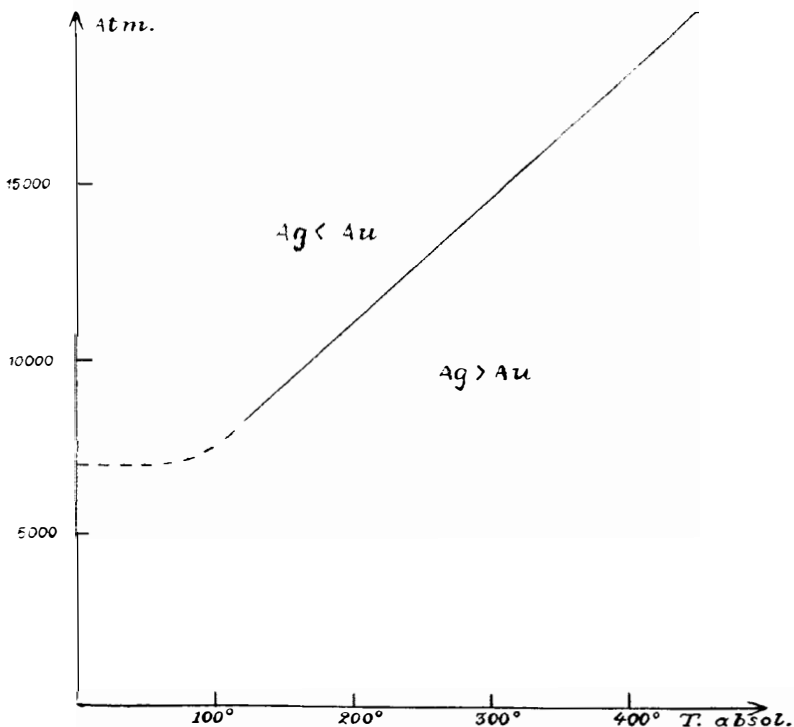


Fig. 6.

Near the absolute zero the curve by and by assumes a horizontal course, the heat expansion becoming zero and the compressibility being independent of the temperature, which is directly inferred from NERNT'S heat theorem.

In order to see to what extent the lanthanide contraction exerts its influence on the elements following cassiopeium the percentic increase in the lattice constant (in BORN'S sense) for

the element couples *Ru-Os* to *Ag-Au* have been listed in table 1 for various physical conditions.

Table 1. Percentic Increase of Spacings.

Homologous Pairs	Percentic Increase		
	20° C 1 Atm.	1000° C 1 Atm.	20° C 20 000 Atm.
<i>Ru Os</i>	1,28	1,0	—
<i>Rh Ir</i>	0,74	0,6	—
<i>Pd—Pt</i>	0,77	0,4	0,9
<i>Ag Au</i>	— 0,20	[— 0,6] ¹	0,1

From table 1 the following inferences are made:

1. The percentic increase in the lattice constant when advancing from *Ru, Rh, Pd, Ag*, to the higher homologues becomes smaller at rising pressures and greater at rising temperatures.

2. Independent of the physical conditions the increase of the lattice constant always becomes smaller with rising atomic number. This makes the apparently abnormal over-compensation for gold easily understood.

The rules formulated in 1 and 2 affect the lanthanide contraction in as much as the decrease in atomic volumes obtained at high pressures can not only be explained by an approach of the valency electrons to the core; it is also conditioned by the contraction of the inner spheres of electrons, which may be shown by means of the lattice potentials (BORN, loc. cit). P. W. BRIDGMAN² has also been able to explain "the persistence of compressibility in a number of solids at high pressures only by a compressibility of the atoms themselves".

The fact already emphasized in 2 that the increase in the lattice constant is not steady by advance to higher homologues, but gradually becoming smaller, shows that here is still a second effect, a contraction, appearing, caused by the following relations:

The filling in of the *O*-spheres to 18 electrons in the heavy platinum metals is accompanied by a stronger contraction in the

¹ Extrapolated above the melting point.

² Journ. Franklin Institute. 200, 147 (1925).

atomic structure than the corresponding filling in of the N -sphere in the light platinum metals. The over-compensation of gold is thus produced by the combined effects of these two contractions.

As the lanthanide contraction caused by the filling in of the N -spheres, takes place in the series of elements Ce – Cp , all elements following Cp must be influenced by the effect of this contraction. This contraction effect is *constant* only as long as the electron orbits of the N -spheres of Cp remain unchanged.

Volume effects in the vertical series.

When going from an element to a higher homologue in the periodic system an increase in the atomic volume is generally found. This change is produced by two opposite causes. On the one hand the number of charges in the core is raised when proceeding to a higher homologue (as discussed by G. v. HEVESY¹) and thus the core will exert a stronger attraction on the electrons.

On the other hand the valency electrons reach a higher quantum orbit and become under less influence from the core. This latter effect as a rule exceeds the contraction effect produced by the larger charge of the core, and we have for instance in the series of the alkali metals a steady rise in atomic volume from lithium to cæsium.

On proceeding to the higher homologues of the fourth and fifth horizontal column of the periodic system this increase of volume with rising atomic number becomes ever less noticeable. The same holds true, to a certain extent, for ions with the same charges.

The similarity in physical and chemical properties reaches an optimum in the homologue couple zirconium-hafnium. The atomic volumes of the pure elements differ however by not less than about $12,3\%$ ², the molecular volumes of the corresponding dioxides differ by only $1,5\%$ ³.

¹ Zeitschr. anorg. Chemie 147, 217 (1925).

² NOETHLING, TOLKSDORF, Zeitschr. f. Krist. 62, 255 (1925).

³ G. v. HEVESY, Recherches sur les propriétés du hafnium, (loc. cit) p. 52.

HASSEL and MARK found by X-ray investigations on the isomorphous compounds $(NH_4)_3 Zr F_7$ and $(NH_4)_3 Hf F_7$ a difference less than 1% between the molecular volumes (Zeitschr. f. Physik 27, 89 (1924).

Assuming the same structure of the investigated dioxides, and an approximately equal radius of action of the corresponding ions it is evident that the relatively great difference in the atomic volumes of the metals must be ascribed to the configuration of the valency electrons in space. A closer consideration would probably show that the true atomic volume¹ and the volume in the crystalline state differ less from each other for hafnium than for zirconium.

This is concluded from the experimental facts that for the element couples from *Ru Os* to *Ag Au* the lower homologue is always the more easily compressible, which is probably to be ascribed to the presence of a smaller number of strongly condensed electron groups.

The optimum of similarity of zirconium hafnium is produced by the simultaneous presence of two different effects. The first is the rise of the positive ion valency with rising number of order (from the first to the fourth vertical column of the periodic system) with persistence of the configuration of the ions. This explains the growing similarity between the element couples from *Rb Cs* to *Yt La* (cfr. G. v. HEVESY²). The second effect is the lanthanide contraction which produces a still closer similarity between hafnium, the element immediately following cassiopeium, and its lower homologue zirconium. For the elements coming after hafnium the gradual decline in similarity is explained by the appearance of new groups of electrons in the region of the ion periphery. The spacings of the pure metals, on the other hand, as far as measurements go, always become more similar and are for silver and gold almost identical. (Fig. 1). This is explained by the interaction between the lanthanide contraction and the diminishing influence of the single electrons in comparison with the charge of the core.

For the same reasons as those discussed in connection with zirconium-hafnium, the growing similarity of the spacings of the metals does not cause any corresponding similarity in the chemical properties (ion properties).

¹ I. e. the volume acquired by the single atom when outside the influence of an exterior field of force, a condition approximately reached in the gaseous state.

² Loc. cit.

Atomic Volumes.

From the spacings of the platinum metals, silver, and gold obtained by us we have computed the atomic volumes of the same elements (table 2).

Table 2.

N	Element	Structure	"Lattice constante"	Shortest atomic distance	Atomic volume
24	<i>Cr</i>	cubic, body centered ¹	2,895	2,507	7,40
25	<i>α Mn</i>	cubic, 56 atoms in unit cell. ²	8,894	2,585	7,62
	<i>β Mn</i>	cubic, 20 atoms - - ²	6,289		7,54
	<i>γ Mn</i>	tetragonal, face centered ²	3,692		7,62
26	<i>α Fe</i>	cubic, body centered ³	2,8603	2,477	7,13
	<i>γ Fe</i>	cubic, face centered ⁴	3,60	2,55	7,11
27	<i>Co</i>	cubic, - - - ⁵	3,554	2,513	6,84
28	<i>Ni</i>	cubic, - - - ⁶	3,499	2,486	6,53
29	<i>Cu</i>	cubic, - - - ⁶	3,597	2,544	7,09
42	<i>Mo</i>	cubic, body centered ⁶	3,149	2,727	9,46
43	—				
44	<i>Ru</i>	hexagonal, close packed	2,996	2,592	8,19
45	<i>Rh</i>	cubic, face centered	3,795	2,683	8,33
46	<i>Pd</i>	cubic, - - -	3,873	2,739	8,86
47	<i>Ag</i>	cubic, - - -	4,078	2,884	10,34
74	<i>W</i>	cubic, body centered ⁶	3,155	2,732	9,57
75	—				
76	<i>Os</i>	hexagonal, close packed	3,027	2,621	8,44
77	<i>Ir</i>	cubic, face centered	3,823	2,703	8,52
78	<i>Pt</i>	cubic, - - -	3,903	2,760	9,04
79	<i>Au</i>	cubic, - - -	4,070	2,878	10,28

¹ HULL, Phys. Rev. 17, 571 (1921).

² WESTGREN, PHRAGMÉN, Zeitschr. f. Physik 33, 777 (1925).

³ BLAKE, Phys. Rev. 26, 60 (1925).

⁴ WESTGREN, LINDH., Zeitschr. f. physikal. Chemie 98, 181 (1921).

⁵ HULL, Phys. Rev. 14, 540; 17, 571 (1921).

⁶ DAVEY, Phys. Rev. 25, 755 (1925).

In order to arrive at a comprehensive picture of the course of the atomic volume curve in this region, which is particularly important for geochemical considerations, the atomic volumes for *Cr*, *Fe*, *Co*, *Ni*, *Cu*, *Mo*, and *W* were also calculated from the available data of the spacings. These data are compiled in table 2. Fig. 7 shows the atomic volume curve.

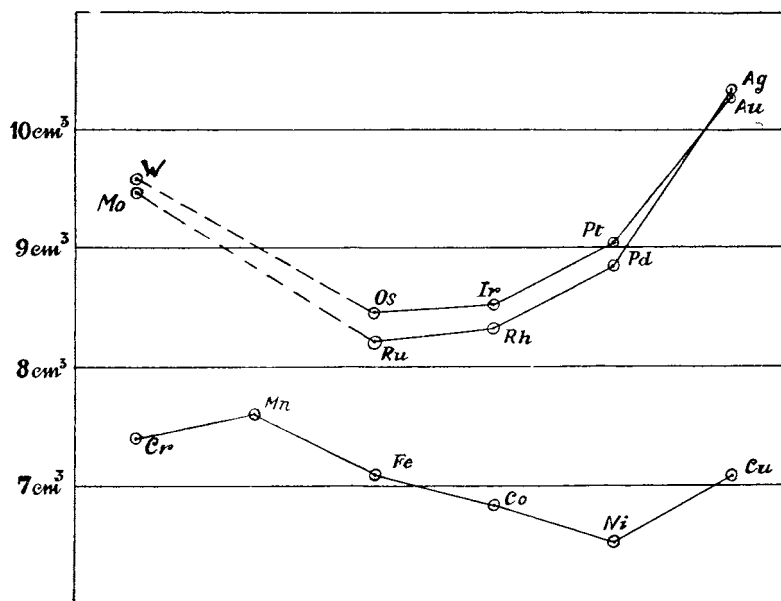


Fig. 7. Atomic volumes.

We wish to express our sincere thanks to professor dr. V. M. GOLDSCHMIDT, director of the institute, for his great helpfulness.

We are also very much obliged to dr. E. HERLINGER (Munich) for his contributions to the theoretical part of the paper.

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Oslo, Jan. 20th, 1926.