

detail. The results are given in Fig. 1. The disulfides I and II have a maximum at $371 \text{ m}\mu$ ($\epsilon_{\text{max}} = 58$) and $369 \text{ m}\mu$ ($\epsilon_{\text{max}} = 49$), respectively. We think that this band is due to a transition from the antibonding $3p\pi$ -orbital to the antibonding σ -orbital of the disulfide group^{3,4}. This is in harmony with its almost complete disappearance in the dithiol III; the very small remaining absorption is certainly due to the presence of a trace of II formed by the unavoidable oxidation of III. We cannot at present give a precise interpretation of the absorption at the shorter wave-lengths. Remarkable is the strong absorption maximum at $268 \text{ m}\mu$ for the keto-compound (I). This cannot be due solely to the keto-groups. It may possibly be due to a transannular interaction of the 3-keto-group and the disulfide bridge (*cf.* Leonard *et al.*⁵)

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Received December 16, 1959.

Studies on the Zirconium-Aluminium and Hafnium-Aluminium Systems

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The following phases have been observed in the zirconium-aluminium system: Zr_3Al , Zr_2Al , Zr_2Al_2 , Zr_3Al_2 , Zr_4Al_3 , ZrAl , Zr_2Al_3 , ZrAl_2 and ZrAl_3 ¹. The crystal structures have been reported for Zr_3Al ², Zr_2Al_3 ³, ZrAl_2 ⁴ and ZrAl_3 ⁵.

In the present investigation, metals of high purity were used, *viz.* aluminium (99.99 %) and zirconium (iodide zirconium 99.9 %, oxygen 260 ppm, Foote Mineral Company). The alloys were prepared by melting in an electric arc furnace under an argon atmosphere and heat-treated in

sealed evacuated silica tubes. Tantalum foils protected the alloys from reacting with the silica.

The phase analyses were performed by means of X-ray powder patterns taken in a Guinier camera, potassium chloride being added to the specimens as an internal standard⁶. Single crystal data were obtained in a Weissenberg camera with CuK radiation.

While the crystal structures of Zr_2Al_3 and ZrAl_2 were being studied at this Institute, Wilson *et al.*^{3,4} published the structures of these compounds. Thus, Zr_2Al_3 was reported to have the $\text{D}8_g$ type of structure while ZrAl_2 was found to be of the $\text{C}14$ type. The data given for ZrAl_2 are in perfect agreement with our results but this is, however, not the case with Zr_2Al_3 .

Single crystals of Zr_2Al_3 could be obtained from a melt of the approximate composition $\text{ZrAl}_{0.50}$. The single crystal and powder data showed the structure to be tetragonal with the following unit cell axes:

$$a = 11.049 \text{ \AA}, \quad c = 5.396 \text{ \AA}.$$

The Patterson projections along $[001]$ and $[100]$ were calculated and the following structure was derived:

Unit cell content: 4 Zr_2Al_3 .

Space-group: $I4/mcm$ (No. 140)

	x	y	z
16 Zr in 16 (k)	0.077	0.218	0
4 Zr in 4 (b)	0	$\frac{1}{2}$	$\frac{1}{4}$
8 Al in 8 (h)	0.16	0.66	0
4 Al in 4 (a)	0	0	$\frac{1}{4}$

This structure of the $\text{D}8_m$ type is represented by W_5Si_3 (Aronsson⁷). It may be that the occurrence of the $\text{D}8_g$ and the $\text{D}8_m$ structures depends on the heat-treatment of the sample. It has, however, been suggested that the Me_5X_3 phases with the $\text{D}8_g$ type of structure are stabilized by the presence of impurities such as boron, carbon, nitrogen and oxygen⁸⁻¹⁰. This interesting hypothesis seems to be supported by the observation that a mixture of zirconium, aluminium and aluminium oxide with a composition close to the formula $\text{Zr}_{10}\text{Al}_6\text{O}$ upon melting gave a product with a pure $\text{D}8_g$ structure. The powder pattern was found to give the following parameters for the hexagonal unit cell:

$$a = 8.177 \text{ \AA}, \quad c = 5.674 \text{ \AA}.$$

The axes reported by Wilson *et al.*³ for the $\text{D}8_g$ phase are 8.184 and 5.702 \AA , respectively.

The powder pattern of Zr_4Al_3 was obtained from a sample annealed at 850°C for several days. It was possible to index it with the following hexagonal unit cell dimensions:

$$a = 5.430 \text{ \AA}, \quad c = 5.389 \text{ \AA}.$$

The observed density, 5.32 g cm⁻³, is in good agreement with the value, 5.37 g cm⁻³, calculated for a cell content of one formula unit Zr_4Al_3 . The intensity data suggest that the structure contains chains of zirconium atoms ($Zr-Zr = \frac{1}{2}c$) similar to those present in the Zr_3Al_2 phase.

Further studies on these structures are in progress.

In connection with the investigations on the zirconium-aluminium system, the aluminium-rich region of the hafnium-aluminium system has also been studied. Thus, three compounds, viz. Hf_3Al_2 , $HfAl_2$ and $HfAl_3$, have been prepared so far. The X-ray powder patterns demonstrate clearly that they are all isomorphous with the corresponding phases in the zirconium-aluminium system.

$HfAl_3$ has a hexagonal C14 type of structure with the unit cell axes:

$$a = 5.288 \text{ \AA}, \quad c = 8.739 \text{ \AA}$$

$HfAl_2$ has a tetragonal D0₂₃ type of structure with the unit cell axes:

$$a = 4.010 \text{ \AA}, \quad c = 17.310 \text{ \AA}$$

For valuable discussions and a continuous interest in this research work, the authors are much indebted to Dr. Arne Magnéli.

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Received January 15, 1960.

Ozonolysis of *p*-Benzoquinone. III. Counter-current Ozonisation

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On two previous occasions^{1,2} we have reported on the ozonolysis of *p*-benzoquinone and discussed some of the possible reaction paths. Anomalous ozonolysis and/or rearrangement of normal ozonides occurred to a large extent. This was to be expected since in quinone two carbonyl groups are conjugated with the double bonds attacked by ozone.

The experimental procedure employed — being a batch procedure — had the drawback that the primary reaction products were in contact with ozone for a comparably long time. Consequently some of the isolated products could have been formed by further oxidation. In order to avoid this and especially to investigate closer the formation of a monoazonide and its decomposition products, we adopted a counter-current procedure similar to that of Pummerer and Richtzenhain³ which allowed a brief contact between the quinone solution and ozone, rapidly followed by hydrolysis.

Previous experiments with the batch procedure has shown that even if quinone was present in excess to the amount of ozone required for mono-ozonolysis only minor amounts of reaction products originating from cleavage of one double bond were found. It thus seems that secondary reactions proceed about as fast as the initial ozonolysis.

In Table I is summarised some of the relationships between the amount of applied ozone per mole of quinone, % reacted quinone and consumed ozone as found by the counter-current method. Finally the theoretically possible amount of monoazonide (or products from mono-ozonolysis) in moles per mole of quinone is calculated.

When about one mole of ozone is applied per mole of quinone 65 % of the latter is attacked. A substantial part of the quinone must therefore have consumed two molecules of ozone. From the last column it is clear that mono-ozonolysis occurs in increasing amounts with decreasing ozone-quinone ratio.