1976

# Synthesis and characterization of some reduced zirconium halides

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77-10,308

DAAKE, Richard Lynn, 1946-
SYNTHESIS AND CHARACTERIZATION OF
SOME REDUCED ZIRCONIUM HALIDES.

Iowa State University, Ph.D., 1976
Chemistry, inorganic

**Xerox University Microfilms**, Ann Arbor, Michigan 48106

# Synthesis and characterization of some reduced zirconium halides

by

Richard Lynn Daake

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Inorganic Chemistry

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa
1976

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# INTRODUCTION

Investigations of binary transition metal subhalides in recent years have revealed a large number of new compounds with an intriguing variety of structural and physical properties allied with a propensity toward metal-metal bonding. Since 1960 several reviews of the structural chemistry of metal-metal bonded transition metal halides have appeared in the literature (1-8).

The type of metallic aggregation in these compounds varies from simple pairing in $\alpha$-$NbI_4$ (9) to extended two-dimensional double metal sheets in ZrCl (10,11). Between these extremes are found the $M_3$ units of $Nb_3Cl_8$ (12), $M_6X_8{}^{n+}$ and $M_6X_{12}{}^{n+}$ groups with various degrees of inter-cluster halogen bridge bonding which yield two-dimensional (e.g., $Nb_6Cl_{14}$) (13) or three-dimensional (e.g., $Ta_6Cl_{15}$) (14) network structures, the infinite metal chain structure of $\beta$-$ZrCl_3$ (15,16), and a number of potentially nonstoichiometric layered $MX_2$ polytypes.

The development of experimental methods for preparation of high purity transition metal subhalides has been the object of considerable research. A few reduced transition metal halides such as $Re_3X_9$ (X=Cl, Br,I) vaporize congruently and can therefore be purified simply by sublimation (17,18). However, this tendency markedly decreases as one moves to the left in the transition metal series, yielding to disproportionation to metal and higher volatile halides.

For the group IVB metals, a majority of the chemical literature of the halides has focused on the optimization of yield and purity of the

$MX_3$ phases and their disproportionation behavior. Heretofore, with the exception of ZrCl (10), compounds more reduced than the trihalides were either unknown or very poorly characterized. Most of the synthetic work on these systems has been in glass containers probably for lack of equipment to seal inert materials like Ta under vacuum or in an inert atmosphere.

Since the original preparation of $ZrCl_3$ in 1923 by Ruff and Wallstein (19) via reduction of $ZrCl_4$ with Al, numerous experimental approaches to the preparation of pure zirconium subhalides have appeared in the literature.

Newnham and Watts (20) obtained very finely divided superstoichiometric blue-black trihalides (X=Cl,Br,I) in small yields by atomic hydrogen reduction of $ZrX_4(g)$ in a glow discharge. Although not contaminated with metal or lower halides, the products gave unreportably poor X-ray powder diffraction patterns.

Watt and Baker (21) attempted preparation of $ZrI_3$ by reducing $ZrI_4$ with a variety of metals (Al,Fe,Ge,Hg) which form volatile iodides. Aluminum was concluded to be the best reductant tried, but it was still incompletely consumed after heating with a large excess of $ZrI_4$ at 300° for ten weeks.

Both Struss and Corbett (22) and Copley and Shelton (23) report easy product separation and good yields of green macrocrystalline trichloride by a non-equilibrium reduction of molten $ZrCl_4$ with an excess of Zr foil. After a 3-day reaction period at 410°, Copley and Shelton obtained 3-5g yields of olive-green needles mixed with a small quantity of unreacted $ZrCl_4$ which was sublimed from the trichloride at 115°. The composition of their product varied between $ZrCl_{2.8}$ and $ZrCl_{3.0}$ depending on the extent of heat-treatment. Struss and Corbett (22) obtained somewhat larger yields by employing the more forcing conditions of a 12-day 600°/500° reaction in a weld-sealed tantalum container and, although analytical data were not given, their powder pattern was reportedly in excellent agreement with those of Dahl, et al., (15) and Watts (16) for $ZrCl_3$.

Troyanov, et al., (24) also achieved high yields of $>99\%$ pure $ZrCl_3$ by reduction of $ZrCl_4(l)$ at 550° and 60 atm with Zr powder in a rotated autoclave which contained 1 cm steel balls for exposure of fresh metal surface. This technique was found superior to the stationary bomb method employed by Troyanov, Marek, and Tsirel'nikov (25) to prepare $ZrBr_3$ by heating metal powder with $ZrBr_4(l)$ for 3-4 weeks at 480-500° (30-40 atm). Larsen and Leddy (26) who also used a stationary bomb technique found several cycles of regrinding followed by reheating at 500-700° necessary to obtain $ZrX_3$ (X=Cl,Br,I) of "reasonable" purity. (No detectable reduction of $ZrF_4$ was observed even after three days at 700°.) Dahl, et al., (15) also used this method to prepare $ZrX_3$ powders for structural studies and always found metal in the powder patterns of their products. The reported weight percentages of unreacted zirconium (38.8, 3.0, and 3.4 for X=Cl,Br, and I, respectively) were computed from analyses assuming admixture with $ZrX_{3.00}$ and absence of either intermediate phases or $ZrX_3$ nonstoichiometry.

## Nonstoichiometry of the Zirconium Trihalides

Although the literature of the zirconium trihalides contains frequent reference to their nonstoichiometry, the nonequilibrium nature of many experiments which have been purported to yield nonstoichiometric trihalides and the lack of good X-ray data to demonstrate phase purity leave much to be desired.

Previous thermogravimetric effusion studies of $ZrX_3$ disproportionation at temperatures up to 450° suggest that the trichloride (23) and tribromide (27) are not line compounds but exist over a range of homogeneity from $ZrX_{2.8}$ to $ZrX_{3.0}$ with no detectable change in the powder pattern. (A shear mechanism has been proposed for the associated structural effects (23).) However, because of the nonequilibrium nature of the disproportionation method, and the very poor crystallinity of the "second stage" $ZrCl_{1.6}$ and $ZrBr_{1.1-1.4}$ residues claimed to form by further disproportionation, the "first stage" $ZrX_{2.8}$ residues may well contain undetected "second stage" products. Troyanov and Tsirel'nikov used similar methods to obtain "first stage" compositions of $ZrCl_{2.82}$ (28) and $ZrBr_{2.75}$ (25). However, their "second stage" products were claimed to be pure stoichiometric dihalides but again were poorly crystalline and characterized only by elemental analyses which offers no proof of phase purity.

The disproportionation behavior of $ZrI_3$ is also difficult to assess from the literature. Sale and Shelton (29) have suggested that $ZrI_{2.86}$ and $ZrI_{2.0}$ compositions prepared by triiodide disproportionation are distinct phases and conclude that both are structurally similar to $ZrI_3$ because of the strong similarity of their powder patterns to that of the stoichiometric triiodide. However, admixture of amorphous lower iodides with undisproportionated triiodide may have led to incorrect conclusions from these nonequilibrium experiments. Baev and Shelton (30) have reported heats of formation for a number of $ZrI_n$ "phases" (n=3.2, 3.17, 3.0, 2.8, and 2.5), but no X-ray or analytical data were given.

Perhaps the most conclusive evidence in the literature for nonstoichiometry of a zirconium trihalide is that presented by Troyanov, Marek, and Tsirel'nikov (25) who observed a steady decrease (with increasing composition) for the hexagonal a lattice parameter of $ZrBr_x$ prepared by annealing $ZrBr_{2.75}$ under $ZrBr_4$(g) pressures of 4, 20, and 760 torr but at unspecified temperatures for unspecified durations. They reported that a=6.738(2) Å for $ZrBr_{3.0}$ and 6.752 Å for $ZrBr_{2.8}$ based on diffractometer data but gave no indication of any corresponding change in the c parameter. Analogous "equilibrations" of $ZrCl_{2.8}$ (first stage $ZrCl_3$ disproportionation residues) with $ZrCl_4$ in sealed tubes at 320° (50 torr) and 370° (200 torr) for unreported durations produced final residues of $ZrCl_{2.80}$ and $ZrCl_{2.99}$, respectively, both of which gave the same hexagonal a parameter of 6.373(3) Å (28). (It is doubtful that equilibrium was even closely approached in the 320° experiment, but probably was at 370°.)

With the exception of products prepared by atomic hydrogen reduction (20) of $ZrX_4$(g), the only hitherto reported superstoichiometric zirconium trihalide is the $ZrI_{3.2}$ composition made by Baev and Shelton via reduction of $ZrI_4$(l) with an excess of Zr foil (30). However, in the absence of

X-ray powder data it is not clear that this product was a pure phase.

In related equilibrium work Struss and Corbett (31) have shown that hafnium triiodide has a compositional range of homogeneity at 475° ($3.0 < I/Hf < 3.5$) with a clear variation in both hexagonal lattice constants.

Single crystals of $ZrX_3$ have been grown by Larsen, et al., (32,33) from an $Al_2X_6$ - $ZrX_4$ eutectic melt by reduction of solvated Zr(IV) with Al chips or Zr powder at 230-310°; a single crystal structure of $ZrBr_3$ has recently been completed (34). Unfortunately $MX_3$ yields are relatively low, and slow contamination with a brown microcrystalline disproportionation product of approximate composition $(ZrX_2)_2\,AlX_3$ occurs in the chloride and bromide systems. The fact that the same decomposition products are obtained by digesting $ZrX_3$ in the corresponding molten aluminum trihalides suggests that the pure zirconium trihalides are not thermodynamically stable in the presence of excess $Al_2X_6$, thus eliminating this method for quantitative preparation of ultra pure trihalides. Reduction of a $ZrCl_4$-$Al_2Cl_6$ eutectic melt (76 mole percent $Al_2Cl_6$) at 200° with a deficiency of Zr metal has produced black hexagonal prisms of a novel ternary phase $Zr_{12}Al_4Cl_{52}$ (35) which has an average oxidation state of 3.33.

## Lower Halides

Swaroop and Flengas (36) reported preparation of zirconium dichloride by reduction of $ZrCl_3$ with a 50% excess of Zr powder in a Pt-lined fused silica ampoule. However, their "$ZrCl_2$" powder pattern shows considerable overlap with that of $ZrCl_3$ as well as other unidentified lines which do not correspond to any phases found in this laboratory.

Copley and Shelton (23) obtained constant-weight residues analyzing as $ZrCl_{1.6}$ from thermogravimetric effusion studies of the trichloride disproportionation over the temperature range 310-450°. Similar studies on $ZrBr_3$ (27) between 325° and 425° yielded $ZrBr_x$ residues of variable composition ($1.1 < x < 1.4$). Unfortunately, all of these "second stage" residues gave very diffuse X-ray diffraction patterns of unreportable quality.

$ZrI_3$ disproportionation at 360-390° in a glass tube with one end protruding from the furnace to permit condensation of $ZrI_4$ was reported by Sale and Shelton (37) to produce stoichiometric diiodide. However, the absence of reportable analytical data, the striking similarity of the reported X-ray powder data to that of $ZrI_3$, and the low reaction temperatures leave the suspicion that their product may well have been a mixture of triiodide with a more-reduced but amorphous material. Because of the nonequilibrium nature of the disproportionation experiment, and the possibility of reactions with glass, it is doubtful that any such residues represent pure phases.

A number of workers have inferred or assumed the presence of stoichiometric dihalides in thermodynamic studies of the $MX_3$/"$MX_2$" equilibrium in the Zr-Cl (28,38,39), Zr-Br (25,40,41), and Zr-I (29) systems, and similarly in the Ti-Br (42) and Ti-I (43) systems. Atomic hydrogen reduction of finely-divided $ZrF_4$(s) at 350° has been purported to produce a black (metastable) "difluoride", but yields were extremely low ($< 10$ mg) and analytical data of questionable accuracy (44). High temperature ($>700^\circ$) equilibrations of $ZrF_4$ with excess Zr foil in this laboratory have indicated that there are no reduced equilibrium phases in this system (45).

In static thermodynamic studies of the Zr-Cl system, Uchimura and Funaki (39) interpreted the four breaks they observed in the P versus T curve in terms of equilibria between compositionally adjacent pairs of the (assumed) stoichiometric "phases" $ZrCl_4$, $ZrCl_3$, $ZrCl_2$, ZrCl, and Zr. In spite of the poor agreement of their $ZrCl_3/ZrCl_2$ equilibrium measurements with those of other workers, their results on the $ZrCl_2/ZrCl$ (560-680°) and ZrCl/Zr (750-900°) equilibria are the only available data. The free energy of formation they report for ZrCl (56.1 kcal/mol) is probably more reliable than Dean's value of 68.4 kcal/mol determined electrochemically in aqueous HCl. (He originally prepared ZrCl (patent name "Zirklor") via reduction of a $SrCl_2$-NaCl-$ZrCl_4$ melt (63:34:3) onto graphite at 650° (46).)

Struss and Corbett (22) have reported preparation of highly crystalline stoichiometric ZrCl by an isothermal equilibration of $ZrCl_{1.4}$ (obtained from a preliminary reduction of $ZrCl_4$) with an excess of fresh metal foil in a sealed Ta container. Troyanov and Tsirel'nikov (47) employed a two-zone furnace to heat Zr foil at 750-800° in a molybdenum glass boat at one end of a quartz ampoule while maintaining solid tetrachloride at its sublimation temperature of 330° (1 atm) at the other end. Black gleaming scales of ZrCl found growing on the foil gave an X-ray pattern virtually identical to that reported by Struss and Corbett (22) except for nonobservance by Troyanov and Tsirel'nikov (47) of the line at d=9.73 Å. These workers also reported rhombohedral lattice parameters of a=9.12(1) Å, $\alpha$=21.62(8)°, space group R$\bar{3}$m, and a calculated density of 4.69g/cm$^3$ for Z=2.

That the structure finally published by Troyanov (48) was in serious error (R=0.29) has been amply discussed by Adolphson (10) who recently completed refinement of the ZrCl structure on a monclinic cell to a residual of 8%. The hexagonal platelet which he used for data collection was prepared in Ta by a 30-day reaction-equilibration of $ZrCl_4$ with a large excess of electropolished Zr foil in a 700°/900° temperature gradient. His single crystal dataset has since been re-refined on a hexagonal cell in space group R$\bar{3}$m for an alternate structural perspective (11).

Essentially, the structure of ZrCl consists of close packed sheets of Zr or Cl atoms each with an intrasheet atom separation of 3.42 Å (the hexagonal a parameter) bound tightly via strong Zr-Zr and Zr-Cl intersheet interactions into Cl-Zr-Zr-Cl slabs in a pseudo cubic close packing (abca) arrangement. These slabs then stack along the c direction in the sequence abca bcab cabc (hereafter abbreviated A-B-C) to give a 3-slab repeat of 26.6 Å. (Refined lattice parameters based on Guinier powder data will be presented later in this work.) The long interlayer Cl-Cl distance of 3.61 Å is commensurate with a weak (van der Waals) interaction between slabs, which apparently gives rise to the graphitic nature of this material.

## Purpose of the Present Work

Among the goals of the work reported here have been the development of simple techniques for improving product yield and purity of $ZrX_3$ (X=Cl, Br,I), the study of the nonstoichiometry of these phases, and determination of more precise lattice constants for them. However, the primary emphasis here has been the preparation and characterization of compounds more reduced than the trihalides in the Zr-X (X=Cl,Br,I) systems. Although compositions with $X/Zr < 3.0$ have been obtained by several workers using nonequilibrium methods, none of these residues have been properly characterized by X-ray diffraction, and reported elemental analyses are therefore of little value since phase purity was not established.

# EXPERIMENTAL PROCEDURE

## Preparation and Handling of Compounds

### Preparative methods

Zirconium tetrahalides were prepared by reaction of halogen with a 10% excess of reactor-grade (~0.05% Hf) Zr foil at 400° followed by sublimation of the product back over the hot metal and through a coarse frit to remove entrapped halogen. Further purification was accomplished by vacuum sublimation at $<10^{-5}$ torr. Subsequent transfers and manipulations of these and all other zirconium compounds were carried out in a dry box with an atmosphere of pre-purified nitrogen which constantly recirculated through a column of Molecular Sieve.

Tantalum tubing with caps or crimps weld-sealed under 0.5-1 atm He served as a strong inert container for preparation of all reduced compounds. For large batches of ZrX, 10-25 cm long, 13 or 19 mm o.d. tubes with 0.4 mm walls were fitted with 0.7 mm thick formed Ta caps to provide the durability necessary to withstand intermediate reaction pressures of 20-40 atm.

With the advantage of Ta containers, the preparation of decagram quantities of high purity ZrX and $ZrX_3$ (X=Cl,Br) is quite facile. However, obtaining pure intermediate phases requires more sophistocated techniques and often much longer reaction times. Even then, only milligram yields of some phases are obtained via transport in a temperature gradient.

Biphasic isothermal equilibrations of nonadjacent phases (e.g., ZrX and $ZrX_3$) have been done in tubes of various design. The simplest experiment involves placing reacting materials in opposite ends of a short, sealed tube partially crimped in the middle. A more suitable design employs concentric 9.5 and 6.4 mm o.d. tubes crimp-welded together at one end with the outer tube capped at the other. Reaction containers of this type can withstand internal pressures up to 30 atm but were rarely used under such stringent conditions. In cases where the total equilibrium pressure of reactive gas phase species (mostly $ZrX_4$) was expected to be considerably less than that of the He present, and especially when an intercompartment constriction served to separate solid phases, the Ta caps were electron-beam welded under vacuum.

A third type of biphasic equilibration was designed to estimate the equilibrium $ZrX_4(g)$ pressure in a two-phase region by a restricted volume decomposition of a pure phase. The starting material filled a 1-2 cm long, 6 mm o.d. crimped but unwelded tube which was contained in a larger sealed tube of known volume. The system was slowly heated to a desired equilibration temperature for a few days, and quenched whereupon $ZrX_4(g)$ condensed onto the walls of the outer tube but did not rereact appreciably with the solid phase because of the crimp in the smaller tube. The equilibrium $ZrX_4(g)$ pressure (± 10%) was then calculated based on analysis of $ZrX_4$ for halogen and on the free volume.

The method of Struss and Corbett (22) was employed for preliminary preparation of ZrCl and ZrBr. While the use of Zr foil does permit clean product separation from the metal, the strongly-adhering nature of this product required considerable laborious scraping. Furthermore, first batch yields had compositions of $1.3 < X/M < 1.5$ which necessitated reequilibration with a large excess of clean foil to obtain a layer of the pure monohalide. The development of a fairly thick product layer (2-4 mils) on the foil suggested the possibility of complete consumption of the metal if sufficiently thin Zr turnings were employed.

High purity (>99.5%) ZrCl and ZrBr were prepared stoichiometrically in decagram quantities and virtually 100% yields from 3-4 mil Zr turnings and $ZrX_4$. A one week reaction period at 450° served to reduce most of the $ZrX_4$ to $ZrX_3$ and was followed by a slow elevation of the temperature over the next 5-8 days to 825° where it was maintained for another week before air cooling.

This technique has not only improved reaction efficiency by permitting complete consumption of the Zr, but has made possible the quantitative preparation of up to 50 gram batches of high purity ZrCl and ZrBr which show no metal lines in the X-ray powder patterns.

In practice, compositions of $1.01 < X/M < 1.03$ are prepared to ensure that all metal is consumed. The product is ground, then screened through a 100 mesh sieve as a final precaution to remove any product chunks which may result from the presence of a few unusually thick turnings. (Less than 0.1% by weight of a typical product fails to pass this test.)

The availability of pure ZrCl and ZrBr has in turn simplified production of sizable quantities of >99.5% pure $ZrCl_3$ and $ZrBr_3$ by heating stoichiometric amounts of ZrX and $ZrX_4$ to 500° for a few days followed by cooling to 150° over a 2-3 day period before quenching. This procedure is particularly fruitful because the relatively hard $ZrX_4$ acts as a grinding agent for the very soft, graphitic monohalides to produce a large ZrX surface area and thereby greatly reducing kinetic problems which have plagued reduction of the tetrahalides by Zr powder. Because of the nonexistence of ZrI, the triiodide is prepared from $ZrI_4$ and the diiodide.

Although glass may be a suitable container for preparation of the trihalides by heating well-ground stoichiometric mixtures of ZrX and $ZrX_4$ at 400-500°, it is probably not sufficiently inert to be acceptable for reactions or equilibrations at much above 600°.

## Product Characterization

### Analytical procedures

Elemental analyses for Cl or Br were done by dissolving 0.2-0.4 g subhalide samples in approximately 10 ml of a solution 1.5 M each in HF and $HNO_3$ using a capped polyethylene bottle to prevent loss of HX during the exothermic dissolution. Subiodide samples were placed in ground-glass stoppered flasks containing 25 ml of a solution 0.5 M each in HF and $HNO_3$ and 0.1 g dissolved hydrazine sulfate to reduce the $I_3^-$ formed initially to $I^-$. (In 1 M acid, several hours are required to yield a colorless solution.) Halogen analyses were completed by standard gravimetric techniques.

Analyses for Zr were performed by weighing 0.3-0.6 g samples by difference directly into a preweighed crucible, which was then placed into a mortar containing a few ml of water, covered with a watch glass, and heated in an oven at 120° for a few hours. Reaction of the sample with water vapor leaves a white residue which is then fired to the oxide.

The electron microprobe was used to estimate X/M ratios for transported phases as these were never available in $>100$ mg quantities.

X-ray diffraction techniques

Debye-Scherrer powder patterns for qualitative work were taken on a 11.46 cm camera using Ni-filtered Cu $K_\alpha$ radiation. Powder patterns of excellent quality for high precision line position measurements (±0.02 mm, ±0.005°) were obtained with the evacuable Model XDC-700 Guinier camera (IRDAB, Stockholm) equipped with a quartz monochromator to provide a clean Cu $K_{\alpha_1}$ incident beam. A high precision millimeter scale was photographically printed on the front side of the film using an IRDAB Model XDC-750 scaling device. This procedure eliminates the need for a film shrinkage correction. The back side of the film was covered with a paper tape before developing to maximize line and scale sharpness and to minimize parallax in reading the film.

Special techniques were developed for preparation and transfer of air sensitive samples for Guinier patterns. A small amount (~0.1 mg) of a 200 mesh Si powder (NBS standard reference material 640) was mixed with ~0.5 mg of sample and tamped firmly onto the center portion of a 7 mm diameter circle of Scotch tape mounted over a 5 mm hole in a polyethylene holder. The small circular piece of tape containing the sample was in turn placed on the adhesive side of a larger piece of tape by which it was fastened to one side of a circular brass sample holder before transfer to the camera in a small metal can.

In cases where multiple photographs of different duration were desired for the same sample, the camera box was backfilled with air just long enough ($<5$ sec) to remove the film cassette and then reevacuated during film development and reloading. Even for the extremely air and moisture sensitive trihalides, line broadening was never noticed for successive films nor for $ZrCl_3$ or $ZrBr_3$ samples stored for several days in the dry box or in evacuable containers. However, the triiodide does appear to react slowly with the Scotch tape. Therefore, Guinier patterns of $ZrI_3$ were taken immediately after loading the sample.

One of the major drawbacks of the flat-plate Guinier technique is the tendency of morphologically anisotropic crystalline substances to take on a preferred orientation, resulting in enhancement or attenuation of certain reflections. Although this effect reduces the reliability of Guinier intensity data (particularly for platelet phases), it is sometimes possible to use this effect to learn something about the orientation of the unit cell with respect to crystal morphology or perhaps to gain valuable insight into interreflection relationships which can in turn aid in indexing the powder pattern of a particular phase.

Since preferred orientation does not affect line positions, the Guinier technique can be used to obtain very precise lattice constants for phases of known cell type. Raw film scale readings for both Si standard and sample lines were input to the Guinier Film Measuring Program (GFMP) written by Robert L. Daake. This program computes an extrapolated index ($\theta=0^\circ$) based on each input Si line, a camera constant, and produces standardized values of θ, d, $10^4 d^{-2}$, and $10^4 \sin^2\theta$ for each sample line.

When refined cell constants are to be computed for indexed phases, values of hkl and 2θ for a number of unambiguously assignable reflections are input to the Cell Dimension Refinement (CDR) program written locally by F. Takusagawa. The constants so obtained are then input to the 1969 version of the Parthé program (49) to obtain calculated line positions for comparison with the observed powder pattern. This program has also been used to compute line intensities corrected for Lorentz-polarization according to the reflection geometry and method of monochromatization of the incoming X-ray beam.

## XPS studies

X-ray photoelectron spectra of Zr, ZrCl, ZrBr, and $ZrCl_4$ were taken by Dr. Mirtha Umaña at Argonne National Laboratory on a McPherson ESCA 36 photoelectron spectrometer with a Mg $K_\alpha$ source and modified for handling air and moisture-sensitive compounds by marriage with an argon atmosphere dry box (2-6 ppm $H_2O$ and $O_2$) attached to the spectrometer via an O-ring flange.

Measurements were made under a vacuum of $<10^{-9}$ torr with a several atom layer of gold vaporized onto potentially insulating samples for calibration. Ten-scan spectra of desired regions were taken over 20eV intervals of 111 points each.

Single crystal work

Although oscillation photographs of single-appearing $ZrX_x$ crystal platelets of uncertain composition ($1.6<x<1.8$ for X=Cl; $1.8<x<2.0$ for X=I) give single spots, zero and first level photographs of both phases show extensive streaking along the translation axis indicating their unsuitability for single crystal structure determinations. Approximate lattice parameters were obtained from these films, however.

A very small (0.03 mm diameter) and nearly spherical gem-like crystal of a hitherto unreported phase in the Zr-Cl system was found acceptable for the collection of three-dimensional single crystal data on an automated (50) four-circle diffractometer with Mo $K_\alpha$ radiation ($\lambda=0.70954$ Å).

Crystal alignment was accomplished by inputting to the computer 12-17 operator-measured polar coordinates for spots on Polaroid films taken at several arbitrary crystal orientations. These reflections were searched and tuned by the instrument to obtain precise values of $\chi$, $\phi$, $\omega$, and $2\theta$. The computer then assigned best-fit small integral indices to these reflections and output lattice parameters, cell scalers, an orientation matrix for the selected unit cell, and indices of the input reflections. At this point a rhombohedral to cubic cell transformation option was evoked after which three noncoplanar moderately strong reflections of fairly high $2\theta$ were selected as standards for initial and periodic retuning during data collection ($0^\circ<2\theta<50^\circ$).

After checking the first 759 reflections for a primitive cubic cell, a body-centering extinction was indicated; reflections with h+k+l (permutable) $\neq$ 2n were thereafter not checked. Of the 4267 allowed reflections, 1809 were observed with FOBS > 3SIGF and INT > 3SIGI. The systematic absence of hhl reflections for $2h + 1 \neq 4n$ eliminated eight of the ten body-centered space groups (51) while additional absence of 0kl reflections for k,(l) $\neq$ 2n prompted choice of the centric space group Ia3d (No. 230) as opposed to the acentric I$\bar{4}$3d (No. 220). Removal of five symmetry extinct reflections (each "observed" only once and all among the six weakest reflections in the dataset) and elimination of 17 symmetry allowed reflections having $(|F_{obs} - F_{aver}| / F_{aver}) > 0.15$ left 1788 pieces of data which were averaged to give a final reduced dataset of 404 independent reflections.

The final lattice parameter refinement which gave $\underline{a}$=21.141(3) for the cubic cell was carried out by inputting the hkl and 2θ values of 14 moderately strong reflections to the CDR program.

# RESULTS AND DISCUSSION

## The Zirconium Trihalides

The present studies on the zirconium trihalides differ in a number of respects from those of other workers. First, the syntheses reported here involve isothermal equilibrations, not nonequilibrium disproportionations. Second, sealed Ta containers have provided both the inertness and strength which glass containers cannot provide at elevated temperatures and pressures, especially for prolonged periods. Third, higher reaction temperatures and considerably longer reaction periods have not only increased confidence in the attainment of equilibrium, but have also resulted in highly crystalline products for X-ray characterization.

### Experimental evidence for nonstoichiometry

The compositions reported as phase limits in Table 1 were prepared in two-compartment Ta tubes by moderately long-term (6-22 days) equilibrations of trihalide with bracketing phases (e.g., $ZrX_4$ or "$ZrX_2$").

Indirect evidence that the triiodide phase may extend to a lower composition limit near $ZrI_{2.6}$ was obtained from an attempted stoichiometric preparation of $ZrI_2$ from $ZrI_4$ and Zr turnings. Since appreciable metal remained after eleven days at 750°, the product mixture was ground to expose fresh metal surface and reheated at 850° for five days, after which 40% of the metal was still unconsumed. In contrast to the strongly-adhering nature of ZrX (X=Cl,Br) on excess Zr foil or turnings, the $ZrI_x$ product of this reaction was easily separated from the turnings by light grinding

Table 1. Nonstoichiometry of the zirconium trihalides

| Phase Limit[a] | No. Expts. | Product Color | Equilibrated With | Temp. (deg.) | Time (days) | P (atm.) | Analytical % Recovery |
|---|---|---|---|---|---|---|---|
| $ZrCl_{2.94}$[b] | 2 | olive-green | $ZrCl_{1.8}$ | 500 | 22 | 2 | 100.2 |
| $ZrCl_{3.03}$ | 2 | olive-green | $ZrCl_4$ | 440 | 9 | 20 | 100.1 |
| $ZrBr_{2.87}$ | 1 | olive-green | $ZrBr_{1.3}$ | 435 | 14 | $10^{-2}$ | Br only |
| $ZrBr_{3.23}$ | 2 | blue-black | $ZrBr_4$ | 435 | 6 | 12 | Br only |
| $ZrI_{<2.90}$[c] | 1 | blue-black | $ZrI_2$ | - | - | - | I only |
| $ZrI_{3.40(5)}$[d] | 1 | green-black | $ZrI_4$ | 475 | 8 | 3 | mass gain |

[a] All products pure to X-rays.

[b] Two similar 7-day equilibrations at 600° ($P > 25$ atm) with a $ZrCl_3/ZrCl_2$ mixture gave products of compositions 2.87 (99.97% recovery) and 2.91 (100.00% recovery) which show small and trace amounts of $ZrCl_2$, respectively, implying that the trichloride lower limit is virtually temperature independent up to 600°.

[c] See text for discussion.

[d] Product stoichiometry was computed from mass gain assuming reaction with $ZrI_4(g)$.

followed by screening. A final product composition of $ZrI_{2.5}$ was estimated from the mass lost by the turnings.

Except for three weak lines of the diiodide (to be discussed in the next section), a Debye-Scherrer pattern of this $ZrI_{2.5}$ product was indexable on a $\beta$-$ZrI_3$ type hexagonal cell with $a$=7.27 Å and $c$=6.64 Å. This pattern is given in Table 2 along with the practically identical powder pattern reported by Sale and Shelton (37) for the "$ZrI_2$" residue of a $ZrI_3$ disproportionation. These workers noted a striking similarity between the powder pattern of their "diiodide" and that of the $ZrI_3$ starting material quite probably because their "diiodide" composition was actually a mixture of $ZrI_{3-}$ (i.e., the triiodide lower limit) with more-reduced but amorphous products.

Although not an equilibrium product, $ZrI_{2.90}$ is also included in Table 1 because of the implication of substoichiometry. Approximately 1.5 g of this material was obtained as 5-15 mm long blue-black needles along with 0.2-0.3 g $ZrI_4$ and a few mg of $I_2$ (readily soluble in $CCl_4$) after an attempt to reduce a $ZrI_{2.5}$ composition at 900° for seven days in the presence of a large excess of Zr foil. The system pressure was estimated from the bulge in the Ta caps to be 15-20 atm (considerably higher than expected), with Zr apparently the only condensed phase at 900°. The $ZrI_{2.9}$ needles appear to have formed at a "cold" spot in the tube during slow cooling of the system in a Marshall furnace. The composition of $ZrI_{2.90}$ was determined by a standard gravimetric iodide analysis of 0.2 g of medium to large hand-picked needles.

Precise lattice parameter measurements of trihalides at various

Table 2. Comparison of a Debye-Scherrer pattern of a $ZrI_{2.5}$ composition with the literature pattern of zirconium "diiodide"

| $ZrI_{2.5}$ (this work)[a] | | | "$ZrI_2$" (Sale and Shelton)[b] | |
|---|---|---|---|---|
| $d_{obs}$ | $I_{obs}$ | h k l | $d_{obs}$ | $I_{obs}$ |
| 7.35* | vw | - | - | - |
| - | - | ? | 7.091 | vw |
| 6.21 | w | 1 0 0 | 6.212 | w |
| 3.69* | vw | - | - | - |
| 3.61 | w | 1 1 0 | 3.646 | w |
| 3.305 | w | 0 0 2 | 3.319 | w |
| 3.18 | s | 1 1 1 | 3.172 | vs |
| - | - | 1 0 2 | 2.945 | vw |
| - | - | ? | 2.824 | vw |
| - | - | ? | 2.695 | vw |
| 2.45 | m | 1 1 2 | 2.453 | m |
| 2.38 | w | 2 1 0 | 2.385 | vw |
| 2.31 | vw | 2 0 2 | 2.287 | vw |
| 2.097 | s | 3 0 0 | 2.097 | vs |
| 1.935 | w | 2 1 2 | 1.934 | vw |
| 1.890 | w | 1 1 3 | 1.891 | m |
| 1.855* | vw | - | - | - |
| 1.780 | w | 3 0 2 | 1.776 | w |
| 1.753 | m | 2 2 1 | 1.753 | m |
| 1.660 | vw | 0 0 4 | 1.660 | vw |
| 1.595 | mw | 2 2 2 | 1.595 | m |
| 1.410 | w | 2 2 3 | 1.407 | w |
| 1.347 | ms | 4 1 1 | 1.347 | s |
| 1.305 | w | 3 0 4 | 1.304 | m |
| 1.272 | w | 4 1 2 | 1.270 | m |
| 1.250 | vw | 1 1 5 | 1.250 | w |
| 1.214 | w | 3 3 0 | 1.213 | m |

[a] Except for three (*) $ZrI_{1.8}$ lines, the pattern of $ZrI_{2.5}$ fits a $\beta$-$ZrI_3$ type hexagonal cell with a=7.27Å and c=6.64Å. (A Guinier pattern of $ZrI_{1.8}$ appears in Table A-1.)

[b] Reference 37.

compositions lend further support to nonstoichiometry for $ZrBr_3$ and $ZrI_3$. These results are presented in Table 3 along with comparative data for $HfI_3$. The hexagonal lattice parameters for $ZrBr_3$ at four different compositions are also plotted in Figure 1 as a function of composition.

Although the behavior of the $ZrI_3$ parameters parallels that of $HfI_3$ (a increases and c decreases as I/M increases), both parameters of $ZrBr_3$ decrease with increasing composition and with no apparent break at $ZrBr_{3.00}$ or superstructure lines in the powder patterns of nonstoichiometric compositions. For $ZrCl_3$, the composition range is fairly small ($2.94 < X/M < 3.03$) and no line position shifts have ever been observed in Guinier patterns of this phase.

The $\beta$-$ZrX_3$ (X=Cl,Br,I) structure was first deduced from powder data to consist of parallel linear chains of face-sharing $ZrX_6$ octahedra formed by filling appropriate octahedral holes in a close packed halide lattice (15,16). The tendency of macroscopic $ZrX_3$ needles (prepared in this laboratory) to fray into a multitude of very thin fibers when cut or crushed is a clear indication of the weak interchain bonding.

Magnetic studies on $\beta$-$TiCl_3$ (52) and $\beta$-$MI_3$ (M=Zr,Hf) (53), on the other hand, are consistent with strong intrachain metal-metal interactions, but whether the metal ions are paired or equally spaced along the chains was answered only recently. In a single crystal structure of $ZrBr_3$, Kleppinger, Calabrese, and Larsen inferred equal spacing from the near sphericity of the thermal elipsoids (34). It is puzzling, however, that the hexagonal lattice parameters, a=6.7275(20) Å and c=6.2992(14) Å, reported by these workers are nearly identical to those given here for

Table 3. Hexagonal lattice constants for nonstoichiometric zirconium trihalides[a] and hafnium triiodide[b]

| Phase Composition | N[c] | a (Å) | c (Å) | Preparative Method |
|---|---|---|---|---|
| $ZrCl_{3.00}$ | 21 | 6.3842(4) | 6.1341(5) | ZrCl + $ZrCl_4$ (450°,10d) |
| $ZrBr_{2.87}$ | 21 | 6.7565(5) | 6.3245(5) | $ZrBr_3$--$ZrBr_{1.3}$ (435°,14d)[d] |
| $ZrBr_{3.00}$ | 21 | 6.7472(6) | 6.3135(5) | ZrBr + $ZrBr_4$ (450°,14d) |
| $ZrBr_{3.10}$ | 21 | 6.7399(5) | 6.3050(5) | $ZrBr_{3.00}$+ $ZrBr_{3.23}$(400°,7d) |
| $ZrBr_{3.23}$ | 21 | 6.7309(5) | 6.2995(6) | $ZrBr_3$--$ZrBr_4$ (435°,14d)[d] |
| $ZrI_{3.0}$ | 26 | 7.285(1) | 6.659(1) | $ZrI_{1.8}$+ $ZrI_4$ (600°,10d) |
| $ZrI_{3.4}$ | 22 | 7.235(1) | 6.698(2) | $ZrI_{2.9}$ -- $ZrI_4$ (475°,8d)[d] |
| $HfI_{3.0}$[b] | - | 7.27(1) | 6.58(1) | $HfI_{3.2}$ -- Hf (575°)[d] |
| $HfI_{3.5}$[b] | - | 7.23(1) | 6.67(1) | $HfI_{3.2}$ -- $HfI_4$ (475°)[d] |

[a] This work.

[b] Reference 31.

[c] The number of unambiguously assigned lines input to the CDR program.

[d] Biphasic equilibration.

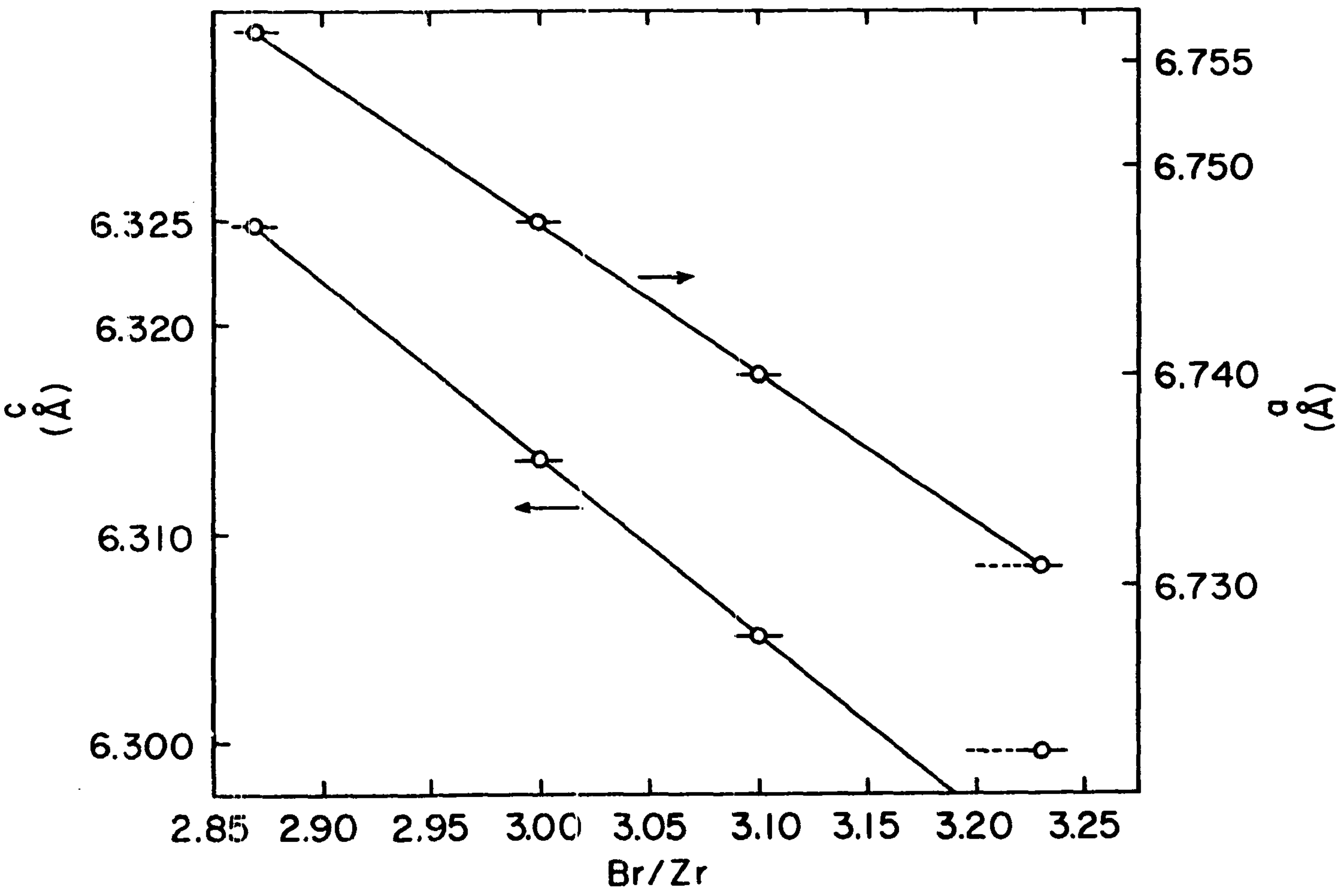

Figure 1. Variation of hexagonal lattice parameters of $\beta$-$ZrBr_3$ with composition

$ZrBr_{3.23}$. Since the difference between a and c (Figure 1) remains fairly constant as the tribromide composition varies, it is not clear whether the independently determined lattice constants are accidentally similar because of different methods and/or standards for lattice constant determination, or whether the crystal used for data collection was unknowingly superstoichiometric.

A couple of observations support the latter postulate. First, the method of preparation described by Larsen, Moyer, Gil-Arnao, and Camp (32,33) involves reduction of a $ZrBr_4$-$Al_2Br_6$ eutectic melt with metallic Zr or Al at 270-290°. Brown-black hexagonal needles of $ZrBr_3$ reportedly grow separate from the metal near the gas-liquid interface by decomposition of some Zr(III)-containing solvated species. First batch yields are typically only 5%, and in light of the several mole ratio excess of solvated Zr(IV), it would be rather surprising for trihalide crystals grown under such oxidizing conditions not to approach the upper limit composition.

Secondly, single crystal needles of $ZrX_3$ grown by the above method are reportedly yellow-green for X=Cl, brown-black for X=Br, and black for X=I. In contrast, needles of slightly substoichiometric trihalides grown from the gas phase in this laboratory are golden-green for X=Cl,Br and blue-black for X=I while powders of stoichiometric $ZrX_3$ prepared here are olive-green for X=Cl,Br and greenish-black for X=I. Furthermore, $ZrBr_{3.23}$ prepared here by equilibrating olive-green $ZrBr_3$ powder with $ZrBr_4$ at 435° for 14 days is blue-black in color and leaves a deep blue halo on a mortar after grinding, while $ZrBr_{3.0}$ leaves a residual golden-green color.

Hence both color and conditions suggest that the recently reported structure of $\beta$-$ZrBr_3$ was perhaps unknowingly done on a significantly superstoichiometric tribromide crystal. It is of particular interest that no superstructure was reported even though the examined crystal was grown at temperatures below $300^{o}$ where long-range ordering of defects would be favored.

### Mechanisms for nonstoichiometry

A shear mechanism for development of substoichiometry during $ZrX_3$ disproportionation has been proposed by Copley and Shelton (23), whereas a combination cation vacancy - substitution mechanism has been suggested by Struss and Corbett (31) for superstoichiometry in hafnium triiodide. The absence of an observable break at Br/Zr=3.0 in Figure 1 is rather puzzling in light of the difference in the mechanisms proposed for substoichiometry and superstoichiometry. Perhaps both mechanisms are operative in the neighborhood of $ZrBr_{3.00}$. However, a break in one or both lattice parameter curves does apparently occur somewhere between $ZrBr_{3.10}$ and $ZrBr_{3.23}$. The unsymmetrical dashed error bars in Figure 1 for the $ZrBr_{3.23}$ composition simply indicate the possibility of undetected $ZrBr_4$ which *may* have condensed onto the $ZrBr_{3+}$ upon cooling the high activity (P=12 atm) $ZrBr_4/ZrBr_{3+}$ system from $435^{o}$. It is certainly reasonable under these circumstances, although not provable from available data, that both curves *might* break simultaneously but in opposite directions somewhere between $ZrBr_{1.10}$ and $ZrBr_{3.23}$.

If, on the other hand, $ZrBr_{3.23}$ is a precisely pure phase, perhaps a break in only the *c* parameter can be understood in terms of a mechanism similar in principle but opposite in effect to the shear process proposed by Copley and Shelton (23) for achieving substoichiometry in the $\beta$-$ZrX_3$ structure.

Charge balance requires satisfaction of the cation vacancy - substitution formalism proposed by Struss and Corbett ($4M_M^{3+}=3M_M^{4+}+V_M$) for $HfI_3$ superstoichiometry (31). The presence of extended Zr-Zr interactions along the metal chain in these structures eliminates the distinction between intrachain $M^{3+}$ and $M^{4+}$ ions. Occasionally isolated $M^{4+}$ ions may occur in the otherwise empty interchain interstices, shortening the average chain length and decreasing the average interchain distance (the *a* lattice parameter).

The mechanism for substoichiometry proposed by Copley and Shelton (23) involves organization of additional metal atoms into 001 shear planes. Superstoichiometry on the other hand might give rise to 001 *vacancy* shear planes resulting in an increased repulsion along the *c* direction between adjacent halide layers which are bisected by these metal-vacancy planes. Although speculative, these ideas are consistent with a gradual decrease in the *a* parameter while allowing for a rather sudden attenuation of the decrease in the *c* parameter as the tribromide upper limit is approached.

## The Zirconium "Dihalides"

In spite of relatively frequent reference to "dihalides" in the thermodynamics literature of the Zr-X systems, compositional and structural characterization of these materials has remained far from adequate.

### The diiodide

The incomplete consumption of zirconium turnings in an attempted stoichiometric preparation of $ZrI_2$ by reaction with $ZrI_4$ at 750° for eleven days and 850° for five days is especially puzzling in light of the ease of making ZrCl and ZrBr by this method. From the shiny surface of the unconsumed (40%) metal, it at first appeared that $ZrI_{3-}$ was the most reduced phase in the Zr-I system. However, the fact that further reduction was finally achieved by using fresh metal indicated that the surface of the turnings had become blocked with a thin product or impurity layer through which diffusion, and hence further reduction, became extremely slow. Reequilibration of the $ZrI_{2.5}$ with a 50-fold excess of fresh Zr foil at 750° for two weeks gave a loosely-adhering black platelet phase of composition $ZrI_{1.81}$ (99.93% recovery) on the foil. This material has a unique powder pattern (Appendix Table A-1) quite distinct from $ZrI_{2.5}$ and Shelton's "diiodide" (Table 2). Several other pure $ZrI_x$ products made by reduction of $ZrI_3$ or $ZrI_4$ with a large excess of Zr foil or turnings invariably have compositions of $1.8 < x < 1.95$ with excellent (>99.8%) analytical recoveries and the same powder pattern. This phase will henceforth be referred to generically as the diiodide.

The morphology of the diiodide has been observed to vary from large

1-2 mm triangular or hexagonal platelets to needles up to 1 cm long. Close examination of these needles under the microscope revealed them to be stacks of paper-thin platelets randomly joined at various points. Their general overall appearance raised suspicion that they may have formed directly from $ZrI_3$ single crystals produced during an intermediate stage of the reduction.

In order to test the implied topotactic relationship between the $ZrI_3$ and $ZrI_2$ phases, a few well-formed needles of $ZrI_{2.90}$ (referred to in the previous section of this chapter) were heated very slowly to 750° over three days in the presence of excess Zr and maintained there for 15 days. Interestingly, the general crystal size and shape as well as the mirror-smooth platelet faces were retained, although the larger $ZrI_3$ single crystals had degenerated to needle-platelet bundles. Oscillation ($\pm 10^\circ$) photographs of these crystals gave single spots when orientated with the platelet face perpendicular to the beam, but gave stacked multiple spots when the incident beam was roughly parallel to the platelet. However, in all cases the needle axis (also the spindle axis) gave a crystallographic repeat of 3.75 Å compared with a needle axis repeat of 6.70 Å for the triiodide single crystals from which they were derived.

One of the very small $ZrI_{1.8}$ crystals which gave no multiple spots was selected for zero and first-level Weissenberg photographs. In spite of very bad streaking of the spots along the translation axis (indicative of two dimensional disorder perpendicular to the spindle axis), the films were of sufficient quality to obtain approximate orthorhombic lattice parameters of $\underline{a}$=3.75 Å, $\underline{b}$=6.85 Å, and $\underline{c}$=15.0 Å.

## The dibromide and sesquibromide

A number of static thermodynamic studies (25,40,41) have either produced or assumed $ZrBr_2$ compositions by thermal decomposition of $ZrBr_3$; vacuum disproportionation in an effusion cell (27) has yielded $ZrBr_x$ residues with x=1.1-1.4. Perhaps because of their poor crystallinity no X-ray powder data on any of these residues have been published. Hence the literature contains no conclusive evidence for, or X-ray characterization of, either a dibromide or any zirconium subbromide other than $ZrBr_3$.

In the present study, biphasic equilibrations of ZrBr with $ZrBr_3$ were employed as a major means of examining the intermediate region. However, because of the approximately stoichiometric "dibromide" residues claimed by some workers to form during tribromide disproportionation, preparation of a $ZrBr_{2.0}$ composition was attempted in this laboratory by heating a well-ground mixture of ZrBr and $ZrBr_4$ over seven days to 650° and equilibrating there for two more days. The olive-green product of this reaction was shown quite clearly from a powder pattern to consist of a mixture of $ZrBr_3$ and ZrBr with some new phase(s). The tribromide in this nonequilibrium multiphasic mixture was simply an outer layer on the product granules and was easily removed by washing with anhydrous acetone or 10% methanol in trichloroethylene. The excellent quality Guinier powder pattern obtained for the vacuum-dried black $ZrBr_x$ residue (x=1.32 based on Br) is given in Appendix Table A-2. The presence of perhaps 20-40% ZrBr in this material makes an estimated composition of $ZrBr_{1.5(1)}$ reasonable for this phase. Lines of the sesquibromide have appeared in powder patterns of numerous reaction products but always in the presence of both ZrBr and $ZrBr_3$. They are especially prominent in reactions of relatively short duration and net compositions greater than $ZrBr_{1.5}$.

Longer duration preparations of compositions more reduced than $ZrBr_{1.7}$ produce a silvery-gray $ZrBr_y$ phase which has a much simpler powder pattern than that of the sesquibromide. Unfortunately, like the sesquibromide, this phase has never been obtained in pure form, but always as a coating on the ZrBr starting material and often in the presence of tribromide when net system compositions were more oxidized than $ZrBr_{1.3}$.

Apparently, attainment of thermodynamic equilibrium between ZrBr or $ZrBr_3$ and $ZrBr_y$, at temperatures where system pressures are manageable in Ta containers, may require many months. Experience has shown that both ZrBr and $ZrBr_3$ are much easier to prepare in pure form than are the intermediate phases. For example, a ZrBr-$ZrBr_4$ mixture (net reaction composition Br/Zr=1.7) was slowly heated over a 7-day period in a short tube of minimal free volume to 600° followed by a 26-day reaction period. The presence of an unintended temperature gradient resulted in product zoning--a hard olive-green plug of $ZrBr_3$ mixed with ZrBr and the new $ZrBr_y$ phase at one end, and a loose granular silvery-gray product containing $ZrBr_y$ and ZrBr but no tribromide and analyzing as $ZrBr_{1.42}$ (100.0% recovery) at the other end. A product of composition $ZrBr_{1.2}$ prepared under the same conditions is identical except for the relatively stronger ZrBr lines. Compositions $ZrBr_{1.15}$ and $ZrBr_{1.10}$ prepared by reacting ZrBr and $ZrBr_3$ for ten days at 750° also show corresponding new lines, but still more weakly. Judging from the intensity of $ZrBr_y$ lines relative

Table 4. Guinier powder pattern of $ZrBr_{1.42}(ZrBr + ZrBr_{1.8(2)})$

| $d_{obs}$ | $I_{obs}$ $ZrBr_{1.42}$ | $ZrBr_{1.8}$[a] h k l | ZrBr h k l | $d_{obs}$ | $I_{obs}$ $ZrBr_{1.42}$ | $ZrBr_{1.8}$[a] h k l | ZrBr h k l |
|---|---|---|---|---|---|---|---|
| 9.38 | 1 | | 0 0 3 | 1.5267 | 3 | | 1 1 9 |
| 6.88 | 4 | 0 0 2 | | 1.5208 | 1 | | 1 0 16 |
| 4.685 | 1 | | 0 0 6 | 1.5157 | 1 | | 2 0 1 |
| 3.434 | 1 | 0 0 4 | | 1.5093 | 1 | | 2 0 2 |
| 3.137 | Si | | | 1.4959 | 1 | 1 0 8 | |
| 3.055 | 5 | 1 0 0 | | 1.4898 | 1 | 2 0 2 | |
| 3.019 | 2 | | 1 0 1 | 1.4650 | 3 | | 2 0 5 |
| 2.968 | 3 | | 1 0 2 | 1.4481 | 4 | 2 0 3 | |
| 2.790 | 2 | 1 0 2 | 1 0 4 | 1.4197 | 1 | | 2 0 7 |
| 2.671 | 7 | | 1 0 5 | 1.4021 | 2 | | 1 1 12 |
| 2.541 | 8 | 1 0 3 | | 1.3964 | 2 | 1 1 6 | |
| 2.421 | 2 | | 1 0 7 | 1.3573 | Si | | |
| 2.338 | 1 | | 0 0 12 | 1.3344 | 3 | 2 0 5 | 2 0 10 |
| 2.288 | 1 | 0 0 6 | | 1.2787 | 1 | | 1 1 15 |
| 2.280 | 1 | 1 0 4 | | 1.2699 | 1 | 2 0 6 | |
| 2.061 | 2 | | 1 0 10 | 1.2457 | Si | | |
| 2.041 | 3 | 1 0 5 | | 1.2295 | 2 | 1 1 8 | |
| 1.9203 | Si | | | 1.1541 | 2 | 2 1 0 | |
| 1.8307 | 1 | 1 0 6 | | 1.1436 | 1 | 0 0 12 | 2 1 2 |
| 1.7633 | 10 | 1 1 0 | | 1.1405 | 1 | 2 0 8 | |
| 1.7525 | 10 | | 1 1 0 | 1.1380 | 1 | 2 1 2 | |
| 1.7224 | 1 | | 1 1 3 | 1.1241 | 2 | | 2 1 5 |
| 1.7159 | 1 | 0 0 8 | | 1.1192 | 5 | 2 1 3 | |
| 1.7074 | 2 | 1 1 2 | | 1.1158 | 1 | | 2 0 17 |
| 1.6373 | Si | | | 1.1089 | Si | | |
| 1.5676 | 1 | 1 1 4 | | 1.1035 | 1 | | 2 1 7 |

[a] The powder pattern of $ZrBr_{1.8(2)}$ is given in Appendix Table A-3 relative to a primitive hexagonal cell with *a*=3.5257(2) and *c*=13.726(2), and the Guinier pattern of ZrBr in Table A-6.

to those of ZrBr for various biphasic compositions, an extrapolated composition of $ZrBr_{1.8(2)}$ is reasonable for the pure new phase, hereafter referred to generically as the dibromide.

All 23 new lines in the powder pattern of $ZrBr_{1.42}$ (Table 4) have been indexed on a hexagonal unit cell with $\underline{a}$=3.5257(2) and $\underline{c}$=13.726(2) which is reasonable for, but does not prove, a 2-slab $MX_2$ type structure like those of 2S-$Nb_{1+x}Se_2$ (54,55).

The powder pattern of $ZrBr_{1.8}$ is given in Appendix Table A-3 in terms of the primitive hexagonal cell on which it has been indexed. Accidental overlap with three observed ZrBr lines is appropriately indicated and $ZrBr_{1.8}$ intensities for lines at those positions have been estimated by subtraction of overlapping intensities assuming a 50-50 mixture.

It can be inferred from the foregoing that the sesquibromide is probably a metastable phase prepared by rapid reaction of ZrBr with $ZrBr_4$(g) under moderately oxidizing conditions and temperatures below 700°, while the substoichiometric "dibromide" may be the only thermodynamically stable phase between ZrBr and $ZrBr_3$. Unfortunately, serious kinetic problems have prevented preparation of this phase in high purity, hence determination of either phase limit has been thwarted.

## The "dichloride"

X-ray diffraction data for a powdered product alleged to be zirconium dichloride was first published in 1965 by Swaroop and Flengas (36), but is in gross disagreement with results obtained in this laboratory. These workers reduced 95-99% pure $ZrCl_3$ with an excess of reactor-grade Zr powder in a platinum-lined silica container. Analytical recoveries varied from 96% to 105%, and while the powder pattern of their product does not show lines of Pt or $PtCl_2$, the possibility of a ternary phase was ignored. This is particularly unfortunate in the light of a recent observation by Lascelles and Shelton (56) that $ZrI_4$ vapor reacts rapidly with both copper and silver even at 200° to give velvet-like $MZr_3I_{12}$ products.

The only other powder diffraction data for "$ZrCl_2$" in the literature is that presented by Struss and Corbett (22) who first noticed transport of a Zr-rich phase while studying the reduction of $MCl_4$ with M(M=97% Hf, 3% Zr). Their preliminary powder pattern for the "dichloride" is substantially in agreement with that to be presented here.

Analogous to the Zr-Br system, an attempt to make stoichiometric $ZrCl_2$ (at 500°) from ZrCl and $ZrCl_4$ resulted in a three phase mixture of $ZrCl_3$, unreacted ZrCl, and a new phase with a very strong line at d=6.46 Å. An unintended temperature gradient had again resulted in product zoning into an olive-green plug at one end (containing 40-60% $ZrCl_3$), and a brownish-black free-flowing granular product at the other end analyzing as $ZrCl_{1.83}$ (based on two analyses for Zr) and which contained 5-10% unreacted ZrCl and 3-5% $ZrCl_3$. A two-compartment equilibration of this $ZrCl_{1.83}$ with ZrCl at 500° for 22 days gave a product ($ZrCl_{1.66}$, 99.97% recovery) with an identical powder pattern except for the complete absence of trichloride lines.

Another attempt was made to prepare an equilibrium $ZrCl_{2.0}$ composition from ZrCl and $ZrCl_4$ by the more forcing conditions of a 4-week reaction at 600° followed by grinding and reheating at 650° ($P \approx 40$ atm) for two more weeks. Again, true thermodynamic equilibrium was not attained but was more closely approached since only a faint trace of ZrCl was evident in the powder pattern. However, sufficient $ZrCl_3$ (20-30%) was present to leave the impression that zirconium "dichloride" may well be substoichiometric even at its upper limit.

Approximately 20 g of a $ZrCl_{1.74}$ composition for use in biphasic equilibrations was prepared from ZrCl and $ZrCl_4$ via a 38-day reaction at 575°. A powder pattern of the homogeneous-looking granular blue-black product showed only a small amount of ZrCl ($<10\%$) and a faint trace (1-3%) of $ZrCl_3$ which may have formed by reaction with $ZrCl_4$(g) on cooling. Two-compartment equilibrations of the $ZrCl_{1.7}$ product with ZrCl at 605° for eleven days and at 700° for three days gave products of composition $ZrCl_{1.54}$ (99.98% recovery) and $ZrCl_{1.51}$ (100.12% recovery), respectively, indicating that the "dichloride" which coated unconsumed ZrCl crystallites in the $ZrCl_{1.7}$ mixture could indeed be further reduced by providing fresh (uncoated) ZrCl as a kinetically more accessible $ZrCl_4$(g) sink.

The implication of a concentration gradient across the outer dichloride layer of $ZrCl_{1.7}$ product granules leads to inference of a homogeneity region for this phase. To test this postulate, biphasic equilibrations of a $ZrCl_{1.45}$ composition with dichloride/trichloride mixtures were performed for twelve days at 600° and fifteen days at 500°. Equilibrium was not even closely approached in the latter case, but at 600° a composition of $ZrCl_{1.75}$ (99.87% recovery) was obtained which showed a trace of $ZrCl_3$ and perhaps 5-8% ZrCl. With no knowledge of the composition profile across the product granules, assessment of the upper limit of the "dichloride" phase is difficult, although an estimated limit of $ZrCl_{1.75(5)}$ is reasonable in light of available data.

Transport and properties of pure $ZrCl_{1.7}$

This phase was finally obtained in pure form only by transport in a temperature gradient. Reaction conditions and yields are given in Table 5. Electron microprobe analyses on several ferns and platelets from the 42-day reaction gave Cl/Zr=1.75(5) with no obvious relationship between crystal form and composition. (A pellet of composition $ZrCl_{1.46}$ was used as the reference standard.)

One of the apparently more important factors controlling both yield and product morphology is the temperature at the hot end, where $ZrCl_4$(g) is apparently reduced to $ZrCl_3$(g) and/or $ZrCl_2$(g) by the $ZrCl/ZrCl_{1.6}$ solid phase mixture. Average autogenous $ZrCl_4$(g) pressures are estimated to vary from 1 atm for a hot-end temperature of $700^\circ$ to greater than 20 atm at $850^\circ$. Interestingly, no transport occurs (even in a $900^\circ/600^\circ$ gradient) from a ZrCl/Zr mixture ($P_{900^\circ}$=1 atm of $ZrCl_4$).

The transport rate has been observed to vary from 1-15 mg per week and seems to be greatest for a hot-end temperature of $750^\circ$. In all cases reaction tubes were inclined $10-30^\circ$ from the horizontal to encourage convection in the gas phase. Deposition zones never exceeded 5 cm ($\Delta t < 50^\circ$) implying a rather limited activity range for $ZrCl_4$(g) and possibly also a fairly small homogeneity range for the depositing phase.

As indicated in Table 5, the platelet form seems to dominate for

Table 5. Some attempts to transport the $ZrCl_{1.7}$ phase

| Starting Material (Cl/Zr) | Temperature Gradient | Reaction Time, P[a] (days,atm) | Tube Length (cm) | Product Zone (cm from hot end) | Product Yield (mg) | Crystal Morphology[b] |
|---|---|---|---|---|---|---|
| 1.16 | 700°/550° | 7, <1 | 28 | 27-28 | 1 | p |
| 1.5 | 700°/600° | 7, 1 | 28 | 26-28 | 1 | p |
| 1.35 | 750°/600° | 35, 5 | 28 | 10-15 | 40 | f,p,g |
| 1.35 | 750°/600° | 16, ? | 20 | 14-17 | 10 | f,p |
| 1.6 | 750°/650° | 42, ? | 18 | 16-18 | 100 | f,p |
| 1.3 | 780°/650° | 7, ? | 20 | 17-20 | 5 | f,p |
| 1.4 | 800°/625° | 6, 10 | 27 | 10-14 | 5 | f,p |
| 1.4 | 850°/700° | 5, > 20 | 26 | 10-15 | 5 | p |

[a] Calculated from the mass of recovered $ZrCl_4(s)$ and the "average" temperature.

[b] Abbreviations: p=platelet, f=fern, g=gem-like; listed in decreasing order of abundance.

products transported from $700^\circ \geq t(\text{hot-end}) \geq 800^\circ$, while under intermediate conditions a fern-like growth pattern is more common. For reactions with hot-end temperatures around 700°, very small ($<0.5$ mm diameter) platelets deposit at the cold end but in less than 1 mg yields. However, in the 850° reaction, much larger (some 1-2 mm in diameter) paper-thin hexagonal platelets grow on or near the solid at the hot end. In fact some of these crystals are so thin that they transmit red light under the microscope; grinding this phase leaves a pink tinge on the mortar.

For intermediate conditions, there is frequently a steady morphological change across the deposition zone with very thin platelets near the hot end fading into platelets with fern-like patterns, then into ferns which thicken until branches have a triangular cross section. Similar spire-like growth has also been observed from the sides of thick triangular platelets.

Oscillation photographs of spires and ferns have shown them to be polycrystalline, whereas the thin parallepiped platelets (with 60° and 120° interedge angles) are single with a spindle axis repeat of 3.38 Å. However, zero and first level photographs show very bad streaking parallel to the translation axis. The implication of two-dimensional disorder parallel to the platelet face is further supported by banding between certain pairs of reflections in powder patterns of microcrystalline products.

An excellent quality powder pattern (Appendix Table A-4) of this phase at its lower limit ($ZrCl_{1.6}$) has been obtained from the jet-black macrocrystalline platelet product of a 35-day biphasic equilibration of microcrystalline $ZrCl_3$ with excess $ZrCl_{1.2}$ at 600°. The development of macrocrystalline platelets by reduction of microcrystalline $ZrCl_3$ hints at a growth mechanism which may involve recrystallization from the gas phase.

Indexing this $ZrCl_{1.6}$ powder pattern on a hexagonal cell with $\underline{a}$=3.3830(2) and $\underline{c}$=19.390(1) was accomplished by using preliminary data from oscillation and Weissenberg photographs of transported $ZrCl_{1.7}$ platelets. Although the structure of this phase is unknown, the unit cell dimensions are quite reasonable for a 3-slab $MX_2$ structure possibly similar to 3s-$Nb_{1+x}S_2$ ($0.12 < x < 0.25$) which is trigonal (space group R3m) with $\underline{a}$=3.33 Å and $\underline{c}$=17.9 Å (57). The only three observed reflections (100, 008, and 109) which break the rhombohedral extinction conditions in the powder pattern of $ZrCl_{1.6}$ (Appendix Table A-4) are absent in transported $ZrCl_{1.7}$ products.

If interlayer coordination about Zr is assumed to be trigonal antiprismatic, as is the case for all binary zirconium halides of known structure, then the only 3-slab sequences possible are abc bca cab and abc acb cab. The fact that no powder pattern simple enough to represent a 1s-$MX_2$ structure (abc abc ...) has ever been observed indicates preference for trigonal prismatic coordination about halogen. Hence, of the two proposed sequences, the first seems most feasible for the postulated $Zr_{1+x}Cl_2$($0.15 < x < 0.25$) structure.

## The Monohalides

### The preparation and structure of ZrBr

The existence of the hitherto unreported zirconium monobromide was easily confirmed by heating $ZrBr_4$ with a large excess of Zr foil at 800° for a few days. Analysis of the black platelet phase scraped from the foil gave a Br/Zr ratio of $1.02 \pm 0.02$. Because of the similar physical properties and some resemblance of the ZrBr Guinier pattern to that of ZrCl, an attempt was made to index a Guinier pattern of ZrBr so prepared. The 001 and 110 reflections were easily assigned and preliminary hexagonal lattice parameters determined. However, the calculated powder pattern of ZrBr based on ZrCl positional parameters gave generally poor agreement with the observed pattern.

A consideration of polytypism in a variety of layered $MX_2$ compounds led to solution of this problem. A trial structure was developed for the alternate (A-C-B) slab stacking sequence by using identical fractional coordinates for halogen but with $z' = 1/3 - z$ for Zr. A comparison of calculated and observed powder patterns for both ZrCl and ZrBr in each of the two possible 3-slab sequences (Table 6) leads to the obvious conclusion that ZrBr does have the alternate stacking and that ZrCl and ZrBr are isotypic but not isostructural.

The structures of ZrCl and ZrBr are similar in their trigonal antiprismatic interlayer coordination about zirconium but opposite in coordination about halogen. This is easily seen in a side-by-side comparison of the layer sequences for these isotypic compounds:

Table 6. Comparison of $I_{obs}$ with $I_{calc}$ for A-B-C and A-C-B ZrX[a]

| $I_{calc}$ A-B-C | $I_{obs}$[b] ZrCl | $I_{calc}$ A-C-B | h k l | $I_{calc}$ A-B-C | $I_{obs}$[c] ZrBr | $I_{calc}$ A-C-B |
|---|---|---|---|---|---|---|
| 12 | 20 | 0 | 1 0 1 | 0 | 15 | 9 |
| 1 | 0 | 51 | 1 0 2 | 1 | 17 | 21 |
| 100 | 100 | 3 | 1 0 4 | 100 | 9 | 2 |
| 8 | 10 | 100 | 1 0 5 | 0 | 100 | 100 |
| 11 | 10 | 48 | 1 0 7 | 5 | 19 | 29 |
| 50 | 30 | 0 | 1 0 8 | 47 | 0 | 2 |
| 5 | 10 | 31 | 1 0 10 | 11 | 30 | 34 |
| 8 | 5 | 7 | 1 0 11 | 7 | 3 | 6 |
| 4 | 0 | 2 | 1 0 13 | 0 | 3 | 6 |
| 5 | 0 | 6 | 1 0 14 | 9 | 0 | 0 |
| 9 | 5 | 6 | 1 0 16 | 6 | 5 | 3 |
| 4 | 0 | 12 | 1 0 17 | 0 | 8 | 12 |
| 4 | 5 | 4 | 1 0 19 | 6 | 0 | 0 |
| 5 | 10 | 1 | 1 0 20 | 2 | 1 | 1 |
| 3 | 0 | 7 | 1 0 22 | 5 | 4 | 8 |
| 2 | 5 | 0 | 2 0 1 | 0 | 0 | 1 |
| 0 | 0 | 8 | 2 0 2 | 0 | 11 | 3 |
| 17 | 30 | 1 | 2 0 4 | 18 | 0 | 0 |
| 2 | 5 | 19 | 2 0 5 | 0 | 38 | 19 |
| 3 | 5 | 11 | 2 0 7 | 1 | 11 | 7 |
| 13 | 20 | 0 | 2 0 8 | 12 | 0 | 0 |
| 2 | 5 | 10 | 2 0 10 | 3 | 13 | 11 |
| 3 | 5 | 3 | 2 0 11 | 2 | 1 | 2 |
| 2 | 0 | 1 | 2 0 13 | 0 | 0 | 3 |
| 2 | 5 | 3 | 2 0 14 | 5 | 0 | 0 |
| 7 | 10 | 4 | 2 0 16 | 4 | 1 | 2 |
|  | * |  | 2 0 17 | 0 | 2 | 9 |
| 3 | 5 | 0 | 2 1 1 | 0 | 1 | 2 |
| 0 | 0 | 11 | 2 1 2 | 0 | 5 | 4 |
| 24 | 40 | 1 | 2 1 4 | 23 | 0 | 0 |
| 3 | 5 | 27 | 2 1 5 | 0 | 29 | 26 |
|  | * |  | 2 1 7 | 2 | 6 | 10 |
|  | * |  | 2 1 8 | 20 | 0 | 1 |

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[a] Hexagonal fractional coordinates for the A-B-C structure calculations were obtained from the literature (11) and those for the A-C-B structure were derived as described in the text. The hhl reflections have been omitted here because of their total insensitivity to stacking sequence.

[b] Intensities estimated visually. For $I_{obs} = *$, $\theta > 45^{\circ}$.

[c] Integrated intensities from a microdensitometer film scan.

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Layer Type: | X | M | M | X | X | M | M | X | X | M | M | X |
| ZrCl (A-B-C): | $\underline{a}$ | b | c | $\underline{a}$ | $\underline{b}$ | c | a | $\underline{b}$ | $\underline{c}$ | a | b | $\underline{c}$ |
| ZrBr (A-C-B): | $\underline{a}$ | b | c | $\underline{a}$ | $\underline{c}$ | a | b | $\underline{c}$ | $\underline{b}$ | c | a | $\underline{b}$ |

The fact that a recent single crystal study in this laboratory has shown ScCl (58) to be isostructural with ZrBr raised suspicion about the structure type of HfCl. Izmailovich, Troyanov, and Tsirel'nikov (59) recently reported an indexed powder pattern for HfCl along with hexagonal lattice parameters of $\underline{a}$=3.377(2) Å and $\underline{c}$=26.65(2) Å and space group R$\bar{3}$m from which they inferred isostructuralism with ZrCl. Apparently the possibility of polytypism was not recognized; reflection intensities, although reported to be in good agreement with those of Struss and Corbett (22), were ignored in discussion of the structure. A comparison of powder diffraction intensities from the literature with calculated patterns for both polytypes of HfCl leads to the inescapable conclusion that this compound also adopts the ZrBr (A-C-B) structure. Interestingly, monochlorides of Gd and Tb have recently been shown by single crystal studies to adopt the ZrCl (A-B-C) structure (60).

### The non-existence of ZrI

Attempts to prepare ZrI at temperatures up to 900° by providing a large excess of Zr foil or turnings gave $ZrI_{1.8}$ as the most reduced product.

## Attempted intercalation of ZrX

The physical properties of ZrCl and ZrBr are reasonable manifestations of their crystal structures. For instance, their graphitic character is clearly related to the weak interslab (van der Waals X-X) interactions and suggests the possibility of intercalation with Lewis acids or bases.

Consideration of a short review of intercalation complexes of Lewis bases and layered sulfides (61) led to selection of ammonia, pyridine, and hydrazine as prime candidates for preliminary work. Heating ZrCl in a sealed Pyrex ampoule with pyridine (distilled from Molecular Sieve) for seven weeks at its boiling point of 115° failed to produce either the physical swelling or detectable lattice parameter changes associated with intercalative processes. A similar treatment of ZrBr for 6.5 weeks also gave negative results as did contact of ZrBr with $NH_3$(l) for eight days at 25° (P~10 atm) in a thick-wall Pyrex ampoule. Room temperature equilibration of ZrBr with hydrazine for four days in a stoppered vial produced no evidence of intercalation, nor did equilibration with liquid triphenylphosphine at 300° for ten days in a sealed tube.

Attempts to intercalate Na or K into ZrCl at 25° using dry ethylenediamine as a solvent resulted in complete dissolution of the metal after a few hours followed by a bronze coloration of a small portion of the ZrCl not covered by solvent. This bronze material may well be identical to the bronze ZrClH phase recently prepared in this laboratory by reacting ZrCl (even at 25°) with $H_2$(g) (62).

Intercalation of Lewis acids was also tried. ZrCl was heated at 120°

for 21 weeks in an evacuated, sealed tube with a $Al_2Cl_6(g)$ pressure of a few mm generated by excess $AlCl_3(s)$. X-ray powder data gave no evidence for any kind of reaction. Stirring ZrCl at 25° with a solution of $I_2$ in $CCl_4$ again gives negative results, although at 40° an amorphous red-brown product (believed to be $ZrI_4$) coats the ZrCl after a few hours.

## Electrical conductivity

Another physical property of ZrCl and ZrBr which deserves mention is electrical conductivity. Troyanov (48) using presumably single crystals of ZrCl (average size 4x4x0.1 mm), obtained by unspecified methods resistivities of roughly $10^3$ ohm·cm perpendicular to the platelets and $10^{-2}$ ohm·cm parallel to them. Although the values he gives are of questionable precision, the indicated electrical anisotropy is entirely consistent with the structural observation by Adolphson (10) that the metal bilayers in ZrCl parallel the platelet faces.

Further evidence for the high electrical conductivity of both ZrCl and ZrBr has been obtained in this work by two-probe measurements on 1-1.5 g pellets of these phases compressed at 7 $Mg/cm^2$ to 97% of the theoretical densities. Resistances measured between pellet faces with a VTVM were found to be less than 0.1 ohm for both ZrCl and ZrBr.

## X-ray photoelectron spectra of ZrX

X-ray photoelectron spectra of the valence region of these compounds give further evidence for extended delocalization of electrons. The results presented in Figures 2 (ZrCl) and 3 (ZrBr) show a well-developed metallic d band which extends to the Fermi level for both compounds. Data

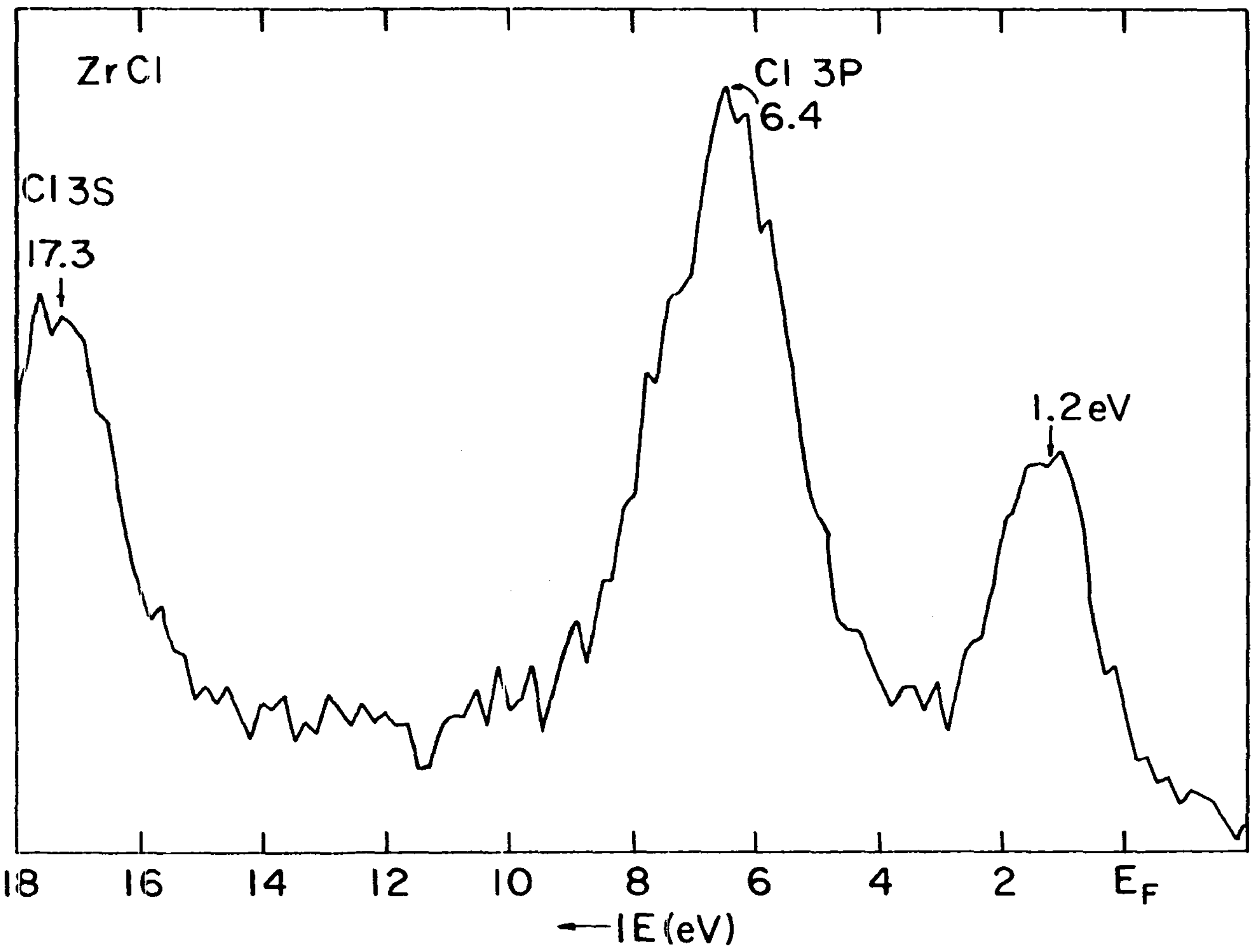

Figure 2. Valence region X-ray photoelectron spectrum of ZrCl

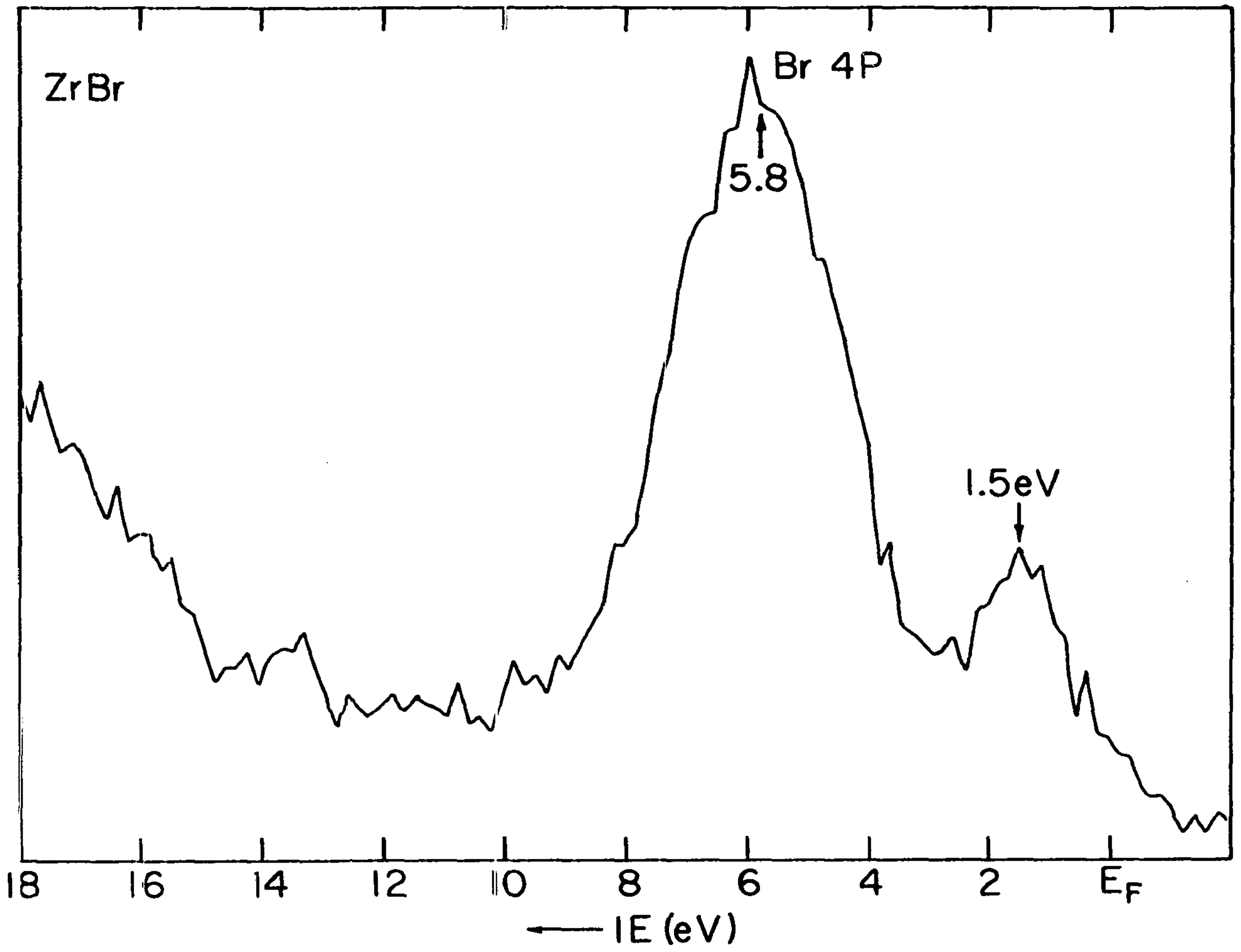

Figure 3. Valence region X-ray photoelectron spectrum of ZrBr

for the valence region are listed together with selected core energies in Table 7.

Both valence and core energies for Zr are slightly (0.3eV) higher in ZrBr than in ZrCl. This is opposite the trend predicted from electronegativity arguments alone, and may reflect the difference in interlayer coordination about halogen. Perhaps the Zr atoms in ZrBr can electrostatically "see" the halogen atoms in the nonadjacent but equivalently positioned second-nearest layer better than in ZrCl where the coordination about halogen is trigonal antiprismatic. It may in fact be this stronger interaction of Zr with second-layer halogen which makes ZrBr structurally less susceptible to grinding damage than is ZrCl (judged from line broadening in Guinier films). Perhaps the increased intralayer X-X distance (3.50 Å in ZrBr compared with 3.42 Å in ZrCl) gives the Zr atoms a larger "window" in ZrBr. In light of the "advantages" of the A-C-B structure, it is indeed puzzling that ZrCl adopts the A-B-C sequence in the first place.

As expected, the Zr valence and core energies in ZrCl are intermediate to those in $\alpha$-Zr metal and $ZrCl_4$. In the metal, each Zr is surrounded by six intralayer atoms at 3.23 Å (the hexagonal a parameter) and trigonal prismatically by three at 3.18 Å in two neighboring layers. The intralayer M-M distance in ZrCl is considerably greater (3.42 Å) than in the metal while the interlayer M-M separation is smaller (3.09 Å) and indicative of strong metal-metal bonding.

Interestingly, the Cl 2p peaks for ZrCl are significantly sharper than for $ZrCl_4$ while the Zr 3d peaks have a similar width for both compounds. This effect is easily understood from the fact that in $ZrCl_4$ there are

Table 7. X-ray photoelectron peaks (eV) for some zirconium halides

| | Zr | ZrBr | ZrCl | $ZrCl_4$[a] |
|---|---|---|---|---|
| Zr 4d | - | 1.5 | 1.2 | (5.0) |
| Br 4p | - | 5.8 | - | - |
| Cl 3p | - | - | 6.4 | (5.0) |
| O 2p | - | - | - | - |
| Cl $3s_{1/2}$ | - | - | 17.3 | 15.7 |
| Zr $3d_{5/2}$ | 177.6[b] | 179.6 | 179.3 | 182.8[c] |
| Zr $3d_{3/2}$ | 180.0 | 182.0 | 181.8 | 185.2 |
| Br $3p_{3/2}$ | - | 182.6 | - | - |
| Br $3p_{1/2}$ | - | 189.9 | - | - |
| Cl $2p_{3/2}$ | - | - | 199.6 | 198.5 |
| Cl $2p_{1/2}$ | - | - | 201.2 | 200.1 |

[a] Energies for this insulating phase have been corrected for charging effects relative to a few monolayers of a Au standard vaporized onto the sample surface.

[b] Given as 178.5eV in reference 63 relative to a hydrocarbon C1s standard.

[c] This band occurs at 182.6eV in $ZrO_2$ standardized against the C1s line (285.0eV) of surface deposited hydrocarbons (63).

three unique Zr-Cl distances (2.307 Å, 2.498 Å, and 2.655 Å) and eight different Cl-Cl distances (ranging from 3.30 Å to 3.81 Å) while the chemical environment for all Zr atoms is identical (64). In ZrCl, however, there is only one unique atom of each kind, hence sharp peaks for both Cl 2p and Zr 3d.

## Thermal stability of ZrX and reactions with glass

Uchimura and Funaki (39) have shown that up to 900° $ZrCl_4(g)$ is the only detectable $ZrCl_n(g)$ species in the Zr-Cl system. Unfortunately, measurements on the ZrCl/Zr equilibrium were done between 750° and 900° on samples which were directly in contact with glass and the results may therefore be somewhat in error. However, $ZrCl_4(g)$ pressures calculated from their data are within 30% of those determined here by a restricted volume decomposition of ZrCl in Ta at 975° ($P_{obs}$=2.9 atm, $P_{calc}$=2.8 atm) and at 1050° ($P_{obs}$=10.4 atm, $P_{calc}$=7.2 atm).

ZrCl remains a solid phase even at 1050°. If heated to 1100° (P=15-20 atm) there is still no evidence of melting. In an attempt to contain the $>50$ atm pressures expected at 1200°, a sealed 0.4 mm o.d. Ta tube containing ZrCl was placed inside a 6 mm o.d. capped tube along with sufficient ZrCl to produce an intertube pressure of 15 atm of $ZrCl_4(g)$ when completely disproportionated. Even with these precautions, the inner tube ruptured, resulting in the complete disproportionation of its contents. Hence it is only possible to conclude that ZrCl melts at greater than 1100°.

If either ZrCl or ZrBr is heated in a fused silica ampoule at 800-

850° for a few days, the ZrX turns from a blue-black to a bronze color with a considerable broadening of the powder pattern and a general line shift to lower angles. Furthermore, the glass becomes badly etched in areas where it directly contacts the ZrX phase. If however, the sample is first placed in an open Ta boat and heated under the same conditions the powder pattern remains virtually unchanged and the glass unetched.

If ZrX is heated with 0.33 mole fraction $ZrO_2$ (a net Zr 2+ oxidation state) at 850° for 8 days, fairly sharp powder patterns of $ZrX_{1-x}O_x$ are obtained (mixed with unconsumed $ZrO_2$) which are qualitatively identical to those obtained by heating ZrX in fused silica. From measurements on the shifted 110 and 001 lines the ZrCl lattice appears to have expanded by approximately 2% in <u>a</u> and 1% in <u>c</u>, whereas for ZrBr the lattice expansions were 1.76% and 1.45%, respectively. The powder pattern of $ZrX_{1-x}O_x$ is of considerable better quality for X=Br than for X=Cl and shows a direct correspondence (in number and intensity) with lines in the ZrBr powder pattern. Precise lattice constants (Appendix Table A-7) of <u>a</u>=3.5646(2) and <u>c</u>=28.479(5) were determined from 22 reflections for $ZrBr_{1-x}O_x$. From a qualitative comparison of $ZrO_2$ line intensities in powder patterns of the mixture before and after reaction, x is probably less than 0.1. In light of the fact that $O^{2-}$ is usually considered to be smaller than $Cl^-$, the expansion of both lattice parameters of $ZrX_{1-x}O_x$ relative to those of ZrX is probably the result of extraction of electron density from the Zr-Zr bilayer. X-ray photoelectron spectra of these materials would be very helpful in testing this hypothesis.

# THE CRYSTAL STRUCTURE OF $Zr_6Cl_{12}Cl_{6/2}$

## Structure Determination

Initial positions for one general (96-fold) Zr and two general Cl sets, Cl(I) and Cl(II), were obtained from the electron density map output by MULTAN (65) for input to ORFLS (66). Five cycles of least-squares refinement produced a conventional residual of 0.21.

Although a preliminary electron microprobe analysis[1] had suggested the composition $ZrCl_{2.2}$, examination of the electron density map generated by the program ALFF (67) revealed a new 48-fold set of Cl-size peaks belonging to special set g in the selected space group. Subsequent electron microprobe analyses on two very small (0.01-0.02 mm) gem crystals gave Cl/Zr=2.5(2).

Inclusion of this Cl(III) set among the atoms input to ORFLS yielded a residual of 0.137 after three cycles. Anisotropic refinement (with appropriate restrictions on the special set) resulted in R=0.113 and $R_W$=0.125. The program Omega (67) written locally by C. R. Hubbard was then used to reweight the dataset. The final refinement converged after

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[1] Only two of the 15-20 crystals of this transported phase were considered large enough (diameter > 0.03 mm) for single crystal work; both were mounted successfully. The crystal on which X-ray diffraction data had not been collected was demounted, washed with trichloroethylene to remove the silicone grease, and used for a preliminary electron microprobe analysis.

three cycles at R=0.111 and $R_W$=0.096 with no shift/error greater than 0.01. Final atomic parameters are given in Table 8 while a listing of observed and calculated structure factors appears in Table 9.

The final difference map was flat to ±1 electron/$A^3$ except for a peak of maximum height seven electrons/$A^3$ at the cluster center (16-fold special position a). The size and shape of this peak represents roughly 3-5 electrons per cluster and may simply be the result of program termination errors. It is interesting that small residual peaks are frequently observed at the center of phenyl rings in structure solutions of organic and organometallic compounds (68) as well as in metal cluster compounds (69). Although the final agreement factor can be improved by putting a carbon atom at the cluster center (refined B=2.2 $A^2$), there is no clear justification for doing so in this case. However, this possibility cannot be disproved from available data either since the electron microprobe analyses would not have detected elements lighter than sodium. Furthermore, the observation of this phase in only one of eight transport attempts (Table 5), and then in extremely small yields, does leave some suspicion that this compound could be an impurity stabilized phase.

## Interatomic distances and angles

Pertinent interatomic distances and angles with associated standard deviations were calculated by the program ORFFE (70) using as input the variance-covariance matrix from the final refinement cycle of ORFLS (66). These results are presented in Table 10 along with corresponding values for $TaCl_{2.5}$. It is unfortunate that the isostructuralism of these two

Table 8. Final atomic parameters for $Zr_6Cl_{15}$

A. Fractional coordinates for the independent atoms

| Atom | Ia3d Set | x | y | z |
|---|---|---|---|---|
| Zr | 96(h) | 0.06137(10) | 0.96548(11) | 0.08092(12) |
| Cl(I) | 96(h) | 0.15685(29) | 0.02965(31) | 0.05084(32) |
| Cl(II) | 96(h) | 0.10939(32) | 0.87617(30) | 0.01907(28) |
| Cl(III) | 48(g) | 0.57115(63) | 0.25-x | 0.12500 |

B. Anisotropic temperature factors (Å$^2$)

| Atom | $10^5\beta_{11}$ | $10^5\beta_{22}$ | $10^5\beta_{33}$ | $10^5\beta_{12}$ | $10^5\beta_{13}$ | $10^5\beta_{23}$ |
|---|---|---|---|---|---|---|
| Zr | 149(7) | 145(7) | 136(6) | 6.5(4.6) | 5.6(4.5) | 16(4) |
| Cl(I) | 133(17) | 228(18) | 225(19) | -20(12) | -35(12) | 66(14) |
| Cl(II) | 200(17) | 176(15) | 176(17) | 43(13) | -23(12) | 12(13) |
| Cl(III) | 182(15) | 182(15) | 209(25) | -78(18) | -35(12) | -35(12) |

Table 9. Observed and calculated structure factors for $Zr_6Cl_{15}$

H = 2

| K | L | FO | FC |
|---|---|---|---|
| 1 | 1 | 88 | 92 |
| 2 | 0 | 1730 | 1720 |

H = 3

| K | L | FO | FC |
|---|---|---|---|
| 2 | 1 | 262 | 267 |
| 3 | 2 | 274 | 282 |

H = 4

| K | L | FO | FC |
|---|---|---|---|
| 0 | 0 | 327 | 454 |
| 2 | 2 | 326 | 434 |
| 3 | 1 | 86 | 92 |
| 4 | 0 | 618 | 724 |
| 4 | 4 | 811 | 736 |

H = 5

| K | L | FC | FC |
|---|---|---|---|
| 3 | 2 | 372 | 391 |
| 4 | 1 | 532 | 580 |
| 5 | 2 | 962 | 1048 |

H = 6

| K | L | FO | FC |
|---|---|---|---|
| 1 | 1 | 124 | 156 |
| 2 | 0 | 560 | 699 |
| 3 | 1 | 323 | 334 |
| 3 | 3 | 760 | 815 |
| 4 | 0 | 189 | 209 |
| 5 | 3 | 804 | 863 |
| 5 | 5 | 630 | 673 |
| 6 | 4 | 705 | 688 |

H = 7

| K | L | FO | FC |
|---|---|---|---|
| 2 | 1 | 102 | 146 |
| 3 | 2 | 132 | 161 |
| 4 | 1 | 270 | 292 |
| 4 | 3 | 1145 | 1198 |
| 5 | 2 | 423 | 472 |
| 5 | 4 | 810 | 835 |
| 6 | 1 | 581 | 621 |
| 6 | 5 | 319 | 325 |
| 7 | 2 | 1013 | 1044 |
| 7 | 6 | 240 | 240 |

H = 8

| K | L | FC | FC |
|---|---|---|---|
| 0 | 0 | 983 | 1112 |
| 2 | 0 | 336 | 355 |
| 2 | 2 | 556 | 693 |
| 3 | 1 | 112 | 154 |
| 4 | 0 | 203 | 267 |
| 5 | 1 | 259 | 269 |
| 5 | 3 | 588 | 590 |
| 6 | 0 | 510 | 509 |
| 6 | 2 | 429 | 381 |
| 6 | 6 | 34 | 127 |
| 7 | 1 | 347 | 356 |
| 7 | 3 | 77 | 70 |
| 7 | 5 | 222 | 216 |
| 8 | 0 | 952 | 922 |
| 8 | 4 | 79 | 67 |
| 8 | 8 | 412 | 351 |

H = 9

| K | L | FO | FC |
|---|---|---|---|
| 2 | 1 | 419 | 458 |
| 3 | 2 | 423 | 443 |
| 4 | 1 | 468 | 483 |
| 4 | 3 | 396 | 405 |
| 5 | 2 | 114 | 155 |
| 5 | 4 | 421 | 416 |
| 6 | 1 | 274 | 269 |
| 6 | 5 | 110 | 135 |
| 7 | 2 | 76 | 88 |
| 7 | 4 | 463 | 432 |
| 8 | 1 | 619 | 612 |
| 8 | 3 | 127 | 163 |
| 8 | 7 | 617 | 539 |
| 9 | 2 | 767 | 736 |
| 9 | 6 | 368 | 304 |

H = 10

| K | L | FO | FC |
|---|---|---|---|
| 1 | 1 | 245 | 240 |
| 2 | 0 | 544 | 615 |
| 3 | 1 | 302 | 320 |
| 3 | 3 | 648 | 640 |
| 4 | 0 | 395 | 416 |
| 5 | 1 | 140 | 167 |
| 5 | 3 | 89 | 113 |
| 5 | 5 | 142 | 170 |
| 6 | 0 | 314 | 290 |
| 6 | 2 | 501 | 489 |
| 7 | 1 | 674 | 666 |
| 7 | 3 | 266 | 281 |
| 7 | 5 | 194 | 201 |
| 7 | 7 | 284 | 280 |
| 8 | 0 | 223 | 230 |
| 8 | 2 | 469 | 408 |
| 8 | 4 | 77 | 96 |
| 8 | 6 | 98 | 158 |
| 9 | 1 | 250 | 239 |
| 9 | 3 | 439 | 417 |
| 9 | 7 | 83 | 111 |
| 9 | 9 | 755 | 681 |
| 10 | 0 | 381 | 343 |
| 10 | 4 | 83 | 134 |

H = 11

| K | L | FO | FC |
|---|---|---|---|
| 3 | 2 | 812 | 825 |
| 4 | 1 | 551 | 561 |
| 4 | 3 | 118 | 139 |
| 5 | 2 | 228 | 225 |
| 5 | 4 | 238 | 246 |
| 6 | 1 | 325 | 313 |
| 6 | 3 | 434 | 400 |
| 7 | 2 | 244 | 260 |
| 7 | 6 | 91 | 99 |
| 8 | 3 | 299 | 280 |
| 8 | 5 | 366 | 342 |
| 8 | 7 | 79 | 51 |
| 9 | 2 | 85 | 125 |
| 9 | 4 | 432 | 410 |
| 9 | 6 | 128 | 159 |
| 9 | 8 | 211 | 212 |
| 10 | 1 | 331 | 316 |
| 10 | 3 | 90 | 119 |
| 10 | 7 | 617 | 531 |
| 10 | 9 | 66 | 62 |
| 11 | 2 | 265 | 243 |
| 11 | 6 | 706 | 650 |

H = 12

| K | L | FC | FC |
|---|---|---|---|
| 0 | 0 | 355 | 376 |
| 2 | 0 | 107 | 141 |
| 2 | 2 | 475 | 425 |
| 3 | 1 | 616 | 629 |
| 4 | 0 | 394 | 347 |
| 4 | 4 | 532 | 502 |
| 5 | 1 | 452 | 428 |
| 6 | 2 | 75 | 57 |
| 6 | 4 | 167 | 197 |
| 6 | 6 | 255 | 273 |
| 7 | 1 | 87 | 131 |
| 7 | 3 | 73 | 97 |
| 8 | 4 | 323 | 343 |
| 8 | 6 | 166 | 177 |
| 8 | 8 | 430 | 421 |
| 9 | 1 | 461 | 435 |
| 9 | 3 | 152 | 212 |
| 9 | 5 | 143 | 170 |
| 10 | 0 | 75 | 89 |
| 10 | 2 | 336 | 338 |
| 10 | 8 | 106 | 131 |
| 10 | 10 | 175 | 163 |
| 11 | 1 | 217 | 246 |
| 11 | 7 | 84 | 100 |
| 11 | 9 | 149 | 198 |
| 12 | 0 | 544 | 521 |
| 12 | 8 | 539 | 442 |
| 12 | 12 | 127 | 120 |

H = 13

| K | L | FO | FC |
|---|---|---|---|
| 3 | 2 | 82 | 123 |
| 4 | 1 | 577 | 555 |
| 4 | 3 | 437 | 402 |
| 5 | 2 | 612 | 560 |
| 5 | 4 | 273 | 264 |
| 6 | 1 | 177 | 191 |
| 6 | 3 | 346 | 340 |
| 6 | 5 | 192 | 208 |
| 7 | 2 | 75 | 75 |
| 7 | 6 | 102 | 127 |
| 8 | 1 | 319 | 309 |
| 8 | 3 | 116 | 174 |
| 8 | 5 | 94 | 85 |
| 8 | 7 | 409 | 360 |
| 9 | 2 | 94 | 123 |
| 9 | 4 | 390 | 361 |
| 9 | 6 | 303 | 282 |
| 9 | 8 | 332 | 308 |
| 10 | 1 | 302 | 293 |
| 10 | 5 | 428 | 362 |
| 10 | 7 | 127 | 145 |
| 11 | 2 | 95 | 92 |
| 11 | 4 | 479 | 430 |
| 11 | 6 | 316 | 295 |
| 11 | 8 | 586 | 513 |
| 12 | 3 | 84 | 105 |
| 12 | 5 | 185 | 218 |
| 12 | 7 | 250 | 247 |
| 12 | 9 | 375 | 316 |
| 13 | 6 | 253 | 221 |
| 13 | 10 | 292 | 254 |

H = 14

| K | L | FO | FC |
|---|---|---|---|
| 1 | 1 | 256 | 247 |
| 3 | 1 | 287 | 297 |
| 4 | 0 | 431 | 419 |
| 4 | 2 | 470 | 419 |
| 5 | 1 | 84 | 84 |
| 5 | 3 | 207 | 224 |
| 6 | 0 | 105 | 177 |
| 6 | 4 | 315 | 329 |
| 7 | 1 | 166 | 209 |
| 7 | 3 | 91 | 131 |
| 7 | 7 | 202 | 223 |
| 8 | 2 | 166 | 218 |
| 8 | 6 | 260 | 271 |
| 9 | 5 | 493 | 428 |
| 9 | 7 | 120 | 134 |
| 10 | 2 | 329 | 301 |
| 10 | 6 | 284 | 265 |
| 10 | 8 | 76 | 71 |
| 11 | 3 | 292 | 261 |
| 11 | 9 | 135 | 153 |
| 11 | 11 | 99 | 104 |
| 12 | 0 | 78 | 113 |
| 12 | 2 | 89 | 133 |
| 12 | 6 | 401 | 326 |
| 12 | 8 | 112 | 147 |
| 12 | 10 | 130 | 147 |
| 13 | 1 | 88 | 98 |
| 13 | 3 | 88 | 98 |
| 13 | 5 | 82 | 88 |
| 13 | 7 | 271 | 263 |
| 13 | 11 | 99 | 107 |
| 14 | 0 | 392 | 368 |
| 14 | 4 | 181 | 207 |
| 14 | 8 | 371 | 284 |
| 14 | 12 | 106 | 175 |

H = 15

| K | L | FO | FC |
|---|---|---|---|
| 2 | 1 | 404 | 401 |
| 3 | 2 | 317 | 302 |
| 4 | 1 | 429 | 433 |
| 4 | 3 | 539 | 501 |
| 5 | 2 | 465 | 434 |
| 5 | 4 | 301 | 295 |
| 6 | 1 | 496 | 466 |
| 6 | 3 | 102 | 89 |
| 7 | 2 | 103 | 104 |
| 7 | 6 | 278 | 286 |
| 8 | 5 | 206 | 198 |
| 8 | 7 | 130 | 167 |
| 9 | 4 | 165 | 64 |
| 9 | 6 | 392 | 354 |
| 10 | 3 | 202 | 209 |
| 10 | 5 | 351 | 331 |
| 10 | 7 | 121 | 139 |
| 10 | 9 | 75 | 112 |
| 11 | 4 | 104 | 151 |
| 11 | 10 | 97 | 108 |
| 12 | 1 | 100 | 130 |
| 12 | 3 | 389 | 372 |
| 12 | 9 | 94 | 59 |
| 13 | 2 | 87 | 137 |
| 13 | 4 | 379 | 320 |
| 13 | 6 | 94 | 98 |
| 13 | 8 | 121 | 143 |
| 14 | 1 | 112 | 170 |
| 14 | 5 | 106 | 120 |
| 14 | 7 | 318 | 276 |
| 14 | 9 | 123 | 142 |
| 15 | 6 | 208 | 214 |
| 15 | 10 | 98 | 89 |

H = 16

| K | L | FO | FC |
|---|---|---|---|
| 3 | 1 | 77 | 114 |
| 4 | 2 | 248 | 250 |
| 4 | 4 | 336 | 330 |
| 5 | 1 | 145 | 188 |
| 6 | 0 | 600 | 530 |
| 6 | 4 | 102 | 133 |
| 6 | 6 | 396 | 385 |
| 7 | 1 | 123 | 181 |
| 8 | 0 | 354 | 319 |
| 8 | 8 | 95 | 154 |
| 9 | 1 | 309 | 301 |
| 9 | 3 | 187 | 193 |
| 9 | 7 | 255 | 236 |
| 10 | 0 | 512 | 445 |
| 10 | 2 | 241 | 247 |
| 10 | 6 | 83 | 80 |
| 10 | 8 | 246 | 237 |
| 11 | 1 | 289 | 279 |
| 11 | 5 | 372 | 315 |
| 11 | 9 | 101 | 133 |
| 12 | 2 | 459 | 393 |
| 12 | 6 | 372 | 314 |
| 12 | 8 | 190 | 180 |
| 12 | 12 | 165 | 217 |
| 13 | 1 | 106 | 144 |
| 13 | 5 | 91 | 74 |
| 14 | 0 | 131 | 176 |
| 14 | 2 | 100 | 139 |
| 14 | 6 | 306 | 262 |
| 14 | 10 | 94 | 96 |
| 16 | 0 | 121 | 159 |

H = 17

| K | L | FC | FC |
|---|---|---|---|
| 2 | 1 | 89 | 90 |
| 3 | 2 | 351 | 357 |
| 4 | 1 | 278 | 284 |
| 5 | 2 | 193 | 203 |
| 5 | 4 | 107 | 149 |
| 6 | 1 | 122 | 156 |
| 6 | 3 | 117 | 164 |
| 6 | 5 | 103 | 115 |
| 7 | 6 | 88 | 92 |
| 8 | 1 | 382 | 339 |
| 8 | 7 | 253 | 234 |
| 9 | 2 | 85 | 102 |
| 10 | 3 | 546 | 488 |
| 10 | 5 | 426 | 375 |
| 11 | 4 | 415 | 357 |
| 11 | 6 | 94 | 134 |
| 11 | 10 | 81 | 98 |
| 12 | 1 | 292 | 285 |
| 12 | 3 | 86 | 114 |
| 12 | 5 | 130 | 182 |
| 12 | 7 | 159 | 166 |
| 12 | 9 | 89 | 90 |
| 13 | 6 | 179 | 206 |
| 13 | 8 | 89 | 82 |
| 13 | 12 | 90 | 70 |
| 14 | 1 | 123 | 185 |
| 14 | 5 | 89 | 79 |
| 14 | 9 | 176 | 196 |
| 14 | 11 | 184 | 190 |
| 16 | 5 | 90 | 83 |
| 16 | 7 | 130 | 151 |
| 17 | 6 | 133 | 145 |

H = 18

| K | L | FO | FC |
|---|---|---|---|
| 2 | 0 | 92 | 138 |
| 3 | 3 | 94 | 120 |
| 4 | 0 | 103 | 121 |
| 5 | 5 | 96 | 141 |
| 6 | 0 | 367 | 292 |
| 6 | 2 | 511 | 449 |
| 6 | 4 | 99 | 140 |
| 7 | 1 | 90 | 104 |
| 7 | 3 | 120 | 181 |
| 8 | 0 | 282 | 270 |
| 8 | 2 | 240 | 235 |
| 8 | 4 | 261 | 257 |
| 9 | 1 | 301 | 296 |
| 9 | 9 | 203 | 202 |
| 10 | 0 | 204 | 222 |
| 10 | 2 | 175 | 192 |
| 10 | 6 | 380 | 337 |
| 11 | 1 | 173 | 208 |
| 11 | 7 | 184 | 183 |
| 11 | 11 | 125 | 129 |
| 12 | 0 | 417 | 390 |
| 12 | 8 | 212 | 203 |
| 14 | 0 | 86 | 120 |
| 14 | 2 | 278 | 282 |
| 14 | 6 | 107 | 151 |
| 14 | 8 | 93 | 52 |
| 14 | 10 | 146 | 151 |
| 15 | 5 | 108 | 144 |
| 16 | 0 | 143 | 168 |
| 16 | 2 | 85 | 67 |
| 16 | 4 | 113 | 126 |
| 17 | 3 | 270 | 262 |

H = 19

| K | L | FO | FC |
|---|---|---|---|
| 5 | 4 | 75 | 42 |
| 6 | 1 | 308 | 271 |
| 6 | 3 | 107 | 167 |
| 7 | 2 | 130 | 172 |
| 7 | 4 | 86 | 107 |
| 7 | 6 | 428 | 352 |
| 8 | 1 | 142 | 194 |
| 8 | 3 | 125 | 165 |
| 8 | 5 | 449 | 385 |
| 9 | 2 | 88 | 63 |
| 9 | 6 | 79 | 100 |
| 10 | 1 | 269 | 250 |
| 10 | 3 | 112 | 116 |
| 10 | 7 | 339 | 301 |
| 10 | 9 | 108 | 103 |
| 11 | 2 | 115 | 136 |
| 11 | 6 | 160 | 168 |
| 11 | 10 | 125 | 152 |
| 12 | 3 | 101 | 125 |
| 12 | 5 | 213 | 223 |
| 12 | 7 | 84 | 69 |
| 12 | 9 | 114 | 147 |
| 12 | 11 | 109 | 134 |
| 13 | 4 | 121 | 160 |
| 14 | 5 | 96 | 107 |
| 16 | 3 | 120 | 182 |

H = 20

| K | L | FO | FC |
|---|---|---|---|
| 0 | 0 | 642 | 551 |
| 2 | 0 | 120 | 142 |
| 2 | 2 | 85 | 130 |
| 3 | 1 | 469 | 459 |
| 5 | 1 | 493 | 441 |
| 6 | 0 | 155 | 188 |
| 6 | 2 | 86 | 86 |
| 6 | 4 | 166 | 167 |
| 6 | 6 | 103 | 81 |
| 7 | 1 | 106 | 141 |
| 7 | 5 | 308 | 292 |
| 8 | 0 | 109 | 125 |
| 8 | 2 | 86 | 107 |
| 9 | 3 | 169 | 199 |
| 12 | 6 | 89 | 105 |
| 13 | 7 | 123 | 124 |
| 14 | 0 | 91 | 125 |
| 14 | 4 | 119 | 154 |

H = 21

| K | L | FO | FC |
|---|---|---|---|
| 3 | 2 | 85 | 117 |
| 6 | 1 | 170 | 180 |
| 6 | 5 | 117 | 147 |
| 8 | 7 | 124 | 130 |
| 9 | 4 | 103 | 98 |
| 9 | 8 | 93 | 107 |
| 10 | 7 | 256 | 239 |
| 11 | 8 | 106 | 125 |
| 12 | 1 | 89 | 39 |
| 12 | 3 | 90 | 119 |

H = 22

| K | L | FC | FC |
|---|---|---|---|
| 2 | 0 | 96 | 178 |
| 4 | 0 | 131 | 184 |
| 5 | 1 | 420 | 388 |
| 5 | 5 | 295 | 302 |
| 6 | 2 | 95 | 91 |
| 6 | 4 | 83 | 91 |
| 7 | 3 | 177 | 173 |
| 7 | 7 | 165 | 240 |
| 8 | 4 | 134 | 172 |
| 9 | 5 | 149 | 204 |
| 11 | 5 | 95 | 104 |
| 12 | 0 | 97 | 134 |

H = 23

| K | L | FC | FC |
|---|---|---|---|
| 6 | 1 | 122 | 155 |
| 6 | 3 | 117 | 159 |
| 8 | 1 | 111 | 152 |
| 8 | 5 | 113 | 152 |

H = 24

| K | L | FC | FC |
|---|---|---|---|
| 4 | 0 | 105 | 121 |
| 4 | 2 | 86 | 78 |
| 6 | 0 | 140 | 193 |
| 6 | 4 | 102 | 127 |

H = 25

| K | L | FO | FC |
|---|---|---|---|
| 2 | 1 | 126 | 188 |

Table 10. Interatomic distances (Å) and angles for $M_6Cl_{15}$ (M=Zr,Ta)[a]

Intracluster interatomic distances

| Type | $Zr_6Cl_{15}$ | $Ta_6Cl_{15}$ | Type | $Zr_6Cl_{15}$ | $Ta_6Cl_{15}$ |
|---|---|---|---|---|---|
| M - M | 3.199(4) | 2.921(4)[b] | I - I | 3.529(12)[b] | 3.495(17) |
| | 3.215(4) | 2.928(4) | II - II | 3.518(6) | 3.408(17) |
| M - I | 2.506(6)[b] | 2.427(12)[b] | I - II | 3.462(9) | 3.275(17) |
| | 2.514(7) | 2.436(12) | | 3.609(10) | 3.454(17) |
| M - II | 2.494(6) | 2.413(12) | I - III | 3.306(12) | 3.217(28) |
| | 2.511(6) | 2.462(12) | | 3.510(10) | 3.353(28) |
| M - III | 2.588(5) | 2.564(25) | II - III | 3.359(7) | 3.163(28) |
| | | | | 3.572(7) | 3.393(28) |

Intracluster angles[c]

| | |
|---|---|
| Zr-I-Zr | 79.2(2)° |
| Zr-II-Zr | 79.9(2)° |
| Zr-Zr(trans)-III | 175.8(2)° |
| I-Zr-II | 169.1(2)° |

Intercluster M-III-M angle

| M | angle |
|---|---|
| Zr | 138.5(4)° |
| Ta | 142.0° |

[a] Results for $Ta_6Cl_{15}$ are from reference 14. Abbreviations: I=Cl(I); II=Cl(II); III=Cl(III).

[b] These pairs of distances are equal within given standard deviations.

[c] These angles are not available for $Ta_6Cl_{15}$.

compounds was not discovered until final stages of the $Zr_6Cl_{15}$ refinement.

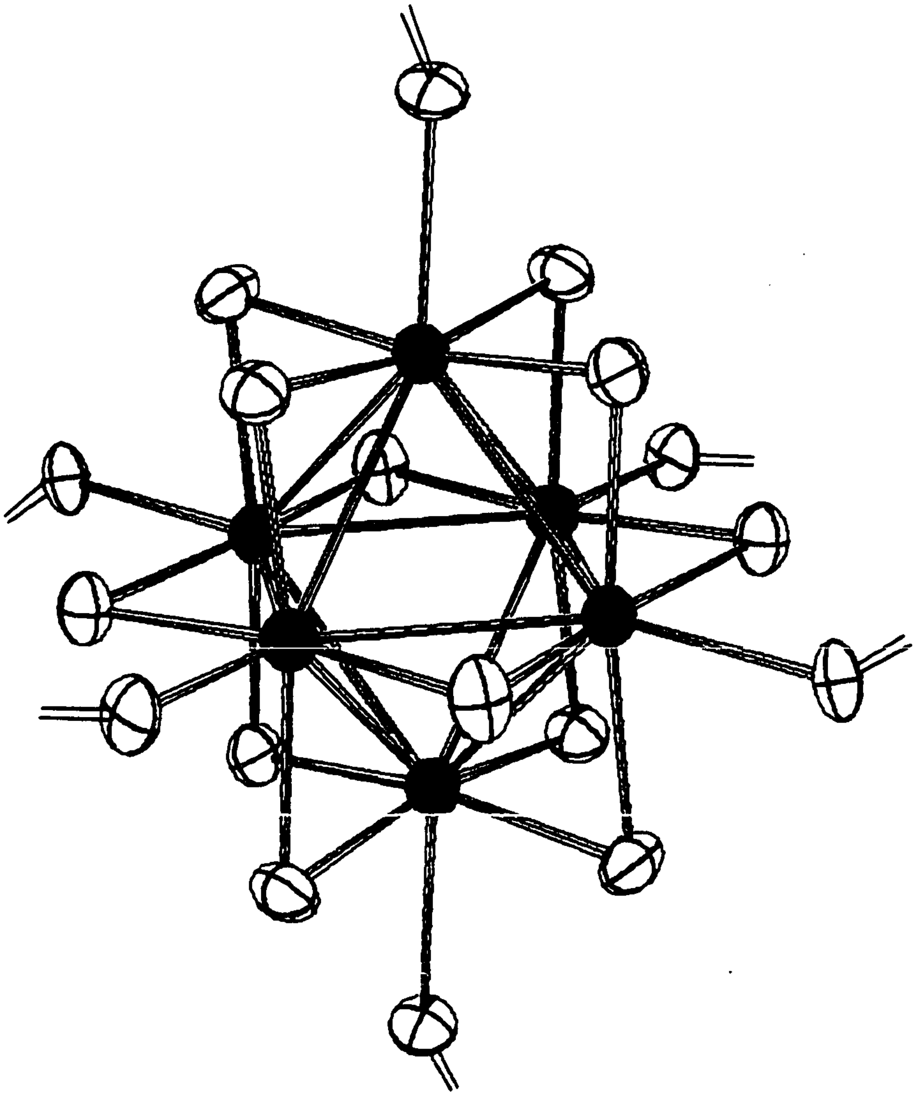
## Discussion

$Zr_6Cl_{15}$ is the first $M_6$ cluster compound reported for the Group IVB transition metals. Unlike the isostructural $Ta_6Cl_{15}$ (14) which has been shown by Kuhn and McCarley (71) and recently confirmed by Schäfer and Giegling (72) to be the most reduced compound in the Ta-Cl system, $Zr_6Cl_{15}$ is the middle of five compounds in the Zr-Cl system. Perhaps a very narrow stability range and/or extreme kinetic problems in forming this line compound contribute to its rare appearance. Even attempts to prepare this elusive phase stoichiometrically from ZrCl and $ZrCl_4$ or by a restricted volume decomposition of $ZrCl_3$ have not produced $Zr_6Cl_{15}$ observable in powder patterns.

Essentially the $M_6Cl_{15}$ (M=Zr,Ta) structure consists of an infinite 3-dimensional linkage of $M_6Cl_{12}{}^{3+}$ groups via intercluster bridging chlorides--in conventional symbolism, $(M_6Cl_{12}{}^{i})Cl_{6/2}{}^{a-a}$ (i̲ for German inser and a̲ for auser). In contrast to $Nb_6F_{15}$ (73) and $Ta_6I_{15}$ (74) both of which crystallize in space group Im3m with Z=2 and have six near neighbor clusters, $Zr_6Cl_{15}$ (Z=16) has eight near neighbor clusters but is bridge-bonded to only six of them. The $Nb_6F_{15}$ structure can be thought of as two interpenetrating and parallel cluster networks with all $M\text{-}X^{a-a}\text{-}M$ bond angles precisely 180°, whereas in $Ta_6Cl_{15}$ and $Zr_6Cl_{15}$ these angles are 142.0° and 138.5°, respectively, with all clusters linked into a single infinite network.

While the $M_6$ groups in $Nb_6F_{15}$ and $Ta_6I_{15}$ form a perfectly regular octahedron surrounded by a regular cube of $X^i$ atoms and a perfect $X^{a-a}$ octahedron, the precise local 4-fold symmetry is lost in $M_6Cl_{15}$ (M=Zr,Ta) while the 3-fold and lower symmetry is retained. Perhaps the most outstanding feature of the $M_6Cl_{15}$ structure is the presence of four sets of symmetry related but nonintersecting 3-fold axes on which all clusters are centered. Furthermore, near neighbor clusters which have no common bridging chlorine atoms always occur along a common 3-fold axis.

In all of the $M_6X_{15}$ cluster compounds, each X atom bridges two and only two metal atoms--either intracluster ($X^i$) over an $M_6$ pseudo-octahedral edge or intercluster ($X^{a-a}$)--while each M is bonded to four other intracluster M-atoms as well as to four $X^i$ and one $X^a$. All clusters in $Zr_6Cl_{15}$ are structurally identical and positionally interconvertible by symmetry. An ORTEP (75) generated drawing of the cluster centered at (0,0,0) is shown in Figure 4 as viewed down one of the three symmetry-equivalent cell axes. As in $Ta_6Cl_{15}$, the approximately octahedral $Zr_6$ group sits inside a distorted cube defined by the twelve $Cl^i$ atoms--one approximately centered on each cube edge--with a Zr atom displaced from the center of each face by approximately 0.24 Å toward the cluster center resulting in a $Cl_I$-Zr-$Cl_{II}$ angle of 169°. Whereas the $M_6$ group in $Ta_6Cl_{15}$ is precisely octahedral within the error limits given by Bauer and von Schnering (14), the $Zr_6$ group in $Zr_6Cl_{15}$ is slightly elongated along a unique three-fold axis. The average Zr-Zr distance of 3.207 Å is considerably longer than the Ta-Ta distance of 2.924 Å, but approximately equal to the average M-M distance of 3.205 Å in $\alpha$-Zr (6 neighbors at each 3.179 Å and 3.231 Å). It is especially interesting that $ZrCl_3$ has a much



$Zr_6Cl_{12}Cl_{6/2}$

Figure 4. Cluster centered at (0,0,0), viewed down [001]

shorter Zr-Zr separation (3.07 Å) than $Zr_6Cl_{15}$ but an almost identical crystallographic density.

An electron count shows the $M_6$ group of $Zr_6Cl_{15}$ to have nine bonding electrons as opposed to fifteen for $Ta_6Cl_{15}$. According to the molecular orbital scheme proposed by Cotton and Haas (76) for the isolated $M_6X_{12}^{n+}$ group, eight of these electrons would go into the $A_{1g}$ and $T_{1u}$ bonding molecular orbitals leaving one unpaired electron in either the $A_{2u}$ or $T_{2g}$ bonding molecular orbital, whichever is of lower energy. Bauer and von Schnering (14) have used magnetic measurements to confirm the presence of one unpaired electron per cluster in the 15-electron $Ta_6X_{15}$ (X=Cl,Br) compounds. Attempts in this laboratory to obtain sufficient quantities of $Zr_6Cl_{15}$ for similar measurements have been unsuccessful. Perhaps with six fewer bonding electrons per cluster than $Ta_6Cl_{15}$, $ZrCl_{2.5}$ may be stable with respect to disproportionation to $ZrCl_{1.8}$ and $ZrCl_3$ only under extremely limited conditions and may not even exist at temperatures where kinetic hindrance to preparation of this phase is not dominant.

# FUTURE WORK

In addition to determination of precise lattice constants for $ZrX_3$ (X=Cl,Br,I) and confirming the nonstoichiometry of these phases, the present work has resulted in the identification and X-ray characterization of several new, or hitherto poorly characterized zirconium subhalides. While the basic aims of this work have been accomplished, there remain a number of possibilities for future work on the Zr-X systems. Furthermore, some of the results obtained as well as techniques developed in the course of this work suggest possible research on related systems.

First, some long-term (perhaps many months) biphasic equilibrations are needed to determine composition limits for the $ZrBr_{1.8}$ phase and the upper composition limit of both the $ZrCl_{1.7}$ phase and the diiodide. A more precise determination of the triiodide lower limit and a more detailed study of the lattice parameter variation across the composition range of the triiodide are also needed.

Recent studies on the stress corrosion cracking of the nuclear fuel rod material Zircaloy-2 by fission-product iodine and cesium have suggested that chemical reactions can nucleate cracks in smooth specimens (77). Hence attainment of structural and thermodynamic data on the $ZrI_{1.8}$ phase is clearly essential for a better understanding of the nature of this chemical corrosion.

Second, perhaps transporting agents such as those employed by Schäfer (e.g., $AlCl_3$, $GaCl_3$, $FeCl_3$) (78) in growing crystals of various transition metal subchlorides can be used to improve yields of $ZrCl_{1.7}$ and $Zr_6Cl_{15}$. Other transition metals (e.g., Re, Nb, etc.) which are known to form gaseous subhalide molecules might also serve to provide more "reducing power" in the deposition zone. In either case, the object is to provide gaseous subhalide species which can either reduce $ZrCl_4$(g) or aid in disproportionation of $ZrCl_n$(g) species to $ZrCl_4$(g) and the depositing solid phase.

In the Zr-Br and Zr-I systems there has been no obvious transport of phases more reduced than the trihalides. However, a few (~0.05 mm diameter) gem-like crystals have been observed in a Zr-I system reaction when pacification of the metal prevented complete reduction to the diiodide lower limit ($ZrI_{1.8}$). The nearly perfect shape of these multi-faceted crystals implies growth from the gas phase. Although no analytical data are available, these "gems" may represent a cluster compound like $Ta_6I_{15}$ (74), $Ta_6I_{14}$ (71,79), or $Nb_6I_{11}$ (80,81). Since $Ta_6Br_{15}$ has been shown from powder data (14) to be isostructural with $Ta_6Cl_{15}$, perhaps $Zr_6Br_{15}$ can also be prepared under appropriate conditions.

Third, the inertness of Ta to Zr subhalides at temperatures where reaction with glass is troublesome, suggests that accurate static thermodynamic measurements on the ZrX/"$ZrX_2$" and Zr/ZrX equilibria can be carried out in glass providing the subhalides and/or metal are contained in Ta or some other suitably inert container. As noted earlier in this work, the powder patterns obtained for ZrX (X=Cl,Br) do not deteriorate when heated to 850° for several days in an open Ta boat sealed in fused silica, nor does the glass become etched. This simple modification of the apparatus employed by Uchimura and Funaki (39) in their thermodynamic study of the Zr-Cl system would not only increase the reliability of the data, but would also permit longer reaction times in order to obtain more crystalline products for X-ray identification.

Fourth, it may be possible to prepare ternary phases of the type $M_xZr_6X_{18}$ or $M_xZr_6I_{14}$ with isolated $Zr_6X_{18}^{n-}$ (X=Cl,Br) or $Zr_6I_{14}^{n-}$ cluster anions by appropriate choice of counter cation salts. Simon, von Schnering, and Schäfer (82) have reported easy preparation of up to 1 mm diameter gem-like crystals of $K_4Nb_6Cl_{18}$ in 1.5 g yields by reduction of $Nb_3Cl_8$ with Nb in a KCl/LiCl eutectic melt. They also have employed a stoichiometric solid-solid reaction by heating a pressed pellet of composition 4KCl + $Nb_6Cl_{14}$ and have similarly made the isostructural $K_4Nb_6Br_{18}$. In light of the fact that both Cs and I are $^{235}U$ fission products, the Cs-Zr-I ternary system should perhaps receive special attention.

Fifth, the easy preparation of ZrBr immediately suggests the probable existence of the hitherto unreported HfBr. If this compound can be prepared, it would also be of interest to determine whether it adopts the ZrCl (A-B-C) or the ZrBr (A-C-B) structure. Similar work on the Ti-X and Th-X systems might also prove fruitful.

Sixth, using the technique described in this work ($MX + MX_4$), it may be possible to prepare high purity $HfX_3$ (X=Cl,Br), a task which Dahl, et al. (15), found "unrewarding" when employing Hf powder. This $HfX_3$ could in turn be used to explore the intermediate region via biphasic equilibrations with HfX.

Seventh, "dissolution" of oxygen by ZrX (X=Cl,Br) to give $ZrX_{1-x}O_x$ products which evidently retains the ZrX structures, suggests the possible existence of $ZrX_{1-x}S_x$ and other ternary substitution compounds of ZrX, HfX, etc. Further research into the ternary Group IVB-halogen-chalcogen systems might well open some new doors for future work.

# APPENDIX

Table A-1. Guinier powder pattern of $ZrI_{1.8}$

| $d_{obs}$ | $I_{obs}$[a] | $d_{obs}$ | $I_{obs}$ | $d_{obs}$ | $I_{obs}$ |
|---|---|---|---|---|---|
| 7.45 | 2 | 2.054 | 1 | 1.4272 | 1 |
| 6.45 | 1 | 2.044 | 1 | 1.4186 | 1 |
| 6.22 | 1 | 2.205 | 1 | 1.4088 | 1 |
| 3.722 | 1 | 1.9428 | 10*- | 1.3769 | 2 |
| 3.631 | 1 | 1.9275 | 3*+ | 1.3688 | 1 |
| 3.418 | 1 | 1.9200 | Si | 1.3650 | 1 |
| 3.383 | 1 | 1.9072 | 1 | 1.3577 | Si |
| 3.328 | 4 | 1.9007 | 1 | 1.3438 | 1 |
| 3.243 | 4 | 1.8713 | 10*- | 1.3419 | 1 |
| 3.206 | 2 | 1.8641 | 1 | 1.2824 | 4*- |
| 3.137 | Si | 1.8145 | 1 | 1.2776 | 4 |
| 3.102 | 2 | 1.8095 | 1 | 1.2566 | 1 |
| 3.056 | 6*- | 1.7539 | 1 | 1.2456 | Si |
| 3.004 | 6*- | 1.7232 | 1 | 1.2430 | 2 |
| 2.949 | 5*- | 1.6969 | 1 | 1.2407 | 1 |
| 2.859 | 1 | 1.6903 | 1 | 1.2230 | 1 |
| 2.813 | 2 | 1.6716 | 1 | 1.2142 | 2 |
| 2.796 | 2 | 1.6684 | 1 | 1.2106 | 3*+ |
| 2.738 | 3 | 1.6631 | 2 | 1.2071 | 2 |
| 2.677 | 1 | 1.6573 | 1 | 1.1960 | 1 |
| 2.643 | 1 | 1.6372 | Si | 1.1912 | 2 |
| 2.591 | 1 | 1.6305 | 2 | 1.1862 | 1 |
| 2.522 | 1 | 1.6264 | 1 | 1.1773 | 1 |
| 2.514 | 1 | 1.6206 | 2 | 1.1574 | 1 |
| 2.487 | 1 | 1.6021 | 2 | 1.1509 | 1 |
| 2.475 | 2 | 1.5847 | 1 | 1.1415 | 1 |
| 2.438 | 2 | 1.5786 | 1 | 1.1347 | 1 |
| 2,388 | 2 | 1.5575 | 1 | 1.1241 | 1 |
| 2.331 | 1 | 1.5460 | 1 | 1.1088 | Si |
| 2.275 | 1 | 1.5433 | 1 | 1.1032 | 1 |
| 2.248 | 1 | 1.5261 | 1 | 1.1001 | 1 |
| 2.205 | 1 | 1.5012 | 1 | 1.0973 | 1 |
| 2.176 | 1 | 1.4721 | 1 | 1.0942 | 2 |
| 2.159 | 1 | 1.4447 | 2 | 1.0917 | 2 |
| 2.139 | 1 | 1.4383 | 1 | | |

[a] Indication of pronounced attenuation (*-) or enhancement (*+) of certain reflections by preferred orientation was judged relative to a Guinier pattern of six macroscopic (0.5-1.5 mm diameter) platelets of this phase mounted in the same fashion as a powdered sample, but with special care taken to assure that all platelets were firmly affixed parallel to the tape.

Table A-2. Guinier powder pattern of $ZrBr_x$ mixed with unreacted ZrBr[a]

| d | $I_{obs}$ | $I_{ZrBr}$[b] | d | $I_{obs}$ | $I_{ZrBr}$ | d | $I_{obs}$ | $I_{ZrBr}$ |
|---|---|---|---|---|---|---|---|---|
| 7.31 | 8 | | 2.160 | 4 | | 1.4558 | 1 | |
| 6.81 | 3 | | 2.096 | 1 | | 1.4505 | 1 | 1 |
| 4.976 | 1 | | 2.061 | 2 | 3 | 1.4374 | 1 | |
| 4.322 | 4 | | 2.003 | 1 | | 1.4312 | 1 | |
| 4.010 | 2 | | 1.9738 | 1 | | 1.4234 | 1 | |
| 3.924 | 3 | | 1.9201 | Si | | 1.4185 | 1 | |
| 3.397 | 4 | | 1.8894 | 8 | | 1.4060 | 1 | |
| 3.211 | 3 | | 1.8818 | 8 | | 1.4017 | 2 | 2 |
| 3.136 | Si | | 1.7804 | 4 | | 1.3898 | 2 | |
| 3.095 | 2 | | 1.7529 | 6 | 5 | 1.3712 | 2 | |
| 3.077 | 6 | | 1.7222 | 1 | | 1.3597 | Si | |
| 3.021 | 2 | 2 | 1.7111 | 1 | | 1.3346 | 2 | 1 |
| 2.970 | 2 | 2 | 1.6408 | 1 | | 1.3327 | 4 | |
| 2.815 | 3 | | 1.6371 | Si | | 1.3234 | 1 | |
| 2.714 | 2 | | 1.6115 | 1 | | 1.3085 | 1 | |
| 2.670 | 10 | 10 | 1.6068 | 2 | | 1.2458 | Si | |
| 2.589 | 3 | | 1.6045 | 1 | | 1.2271 | 2 | |
| 2.566 | 3 | | 1.5782 | 1 | | 1.2237 | 2 | |
| 2.483 | 3 | | 1.5677 | 1 | | 1.2208 | 3 | |
| 2.459 | 1 | | 1.5560 | 1 | | 1.1939 | 5 | |
| 2.427 | 1 | | 1.5452 | 1 | | 1.1903 | 5 | |
| 2.422 | 1 | 2 | 1.5372 | 5 | | 1.1240 | 2 | 3 |
| 2.331 | 3 | | 1.5280 | 1 | | 1.1087 | Si | |
| 2.286 | 1 | | 1.5087 | 1 | | 1.0923 | 2 | |
| 2.278 | 2 | | 1.4875 | 2 | | 1.0880 | 2 | |
| 2.275 | 2 | | 1.4805 | 2 | | 1.0865 | 1 | |
| 2.263 | 1 | | 1.4652 | 2 | 4 | | | |

[a] Net composition: $ZrBr_{1.32}$; $1.4 < x < 1.6$ (estimated).

[b] Intensities for lines of pure ZrBr having $I_{calc} > 1$ (on a scale of 0-10) which may overlap lines of $ZrBr_x$.

Table A-3. Guinier powder pattern of $ZrBr_{1.8(2)}$[a]

| h k l | $I_{obs}$ | $d_{calc}$ | $d_{obs}$ | h k l | $I_{obs}$ | $d_{calc}$ | $d_{obs}$ |
|---|---|---|---|---|---|---|---|
| 0 0 1 | | 13.73 | | 1 0 8 | 1 | 1.4958 | 1.4959 |
| 0 0 2 | 4 | 6.86 | 6.88 | 2 0 2 | 1 | 1.4902 | 1.4898 |
| 0 0 3 | | 4.575 | | 1 1 5 | | 1.4833 | |
| 0 0 4 | 1 | 3.432 | 3.434 | 2 0 3 | 4 | 1.4482 | 1.4481 |
| 1 0 0 | 5 | 3.053 | 3.055 | 1 1 6 | 2 | 1.3964 | 1.3964 |
| 1 0 1 | | 2.980 | | 2 0 4 | | 1.3949 | |
| 1 0 2 | 1* | 2.790 | 2.790 | 0 0 10 | | 1.3726 | |
| 0 0 5 | | 2.745 | | 1 0 9 | | 1.3644 | |
| 1 0 3 | 8 | 2.540 | 2.541 | 2 0 5 | 1* | 1.3342 | 1.3344 |
| 0 0 6 | 1 | 2.288 | 2.288 | 1 1 7 | | 1.3110 | |
| 1 0 4 | 1 | 2.281 | 2.280 | 2 0 6 | 1 | 1.2699 | 1.2699 |
| 1 0 5 | 3 | 2.041 | 2.041 | 1 0 10 | | 1.2519 | |
| 0 0 7 | | 1.9609 | | 0 0 11 | | 1.2478 | |
| 1 0 6 | 1 | 1.8308 | 1.8307 | 1 1 8 | 2 | 1.2295 | 1.2295 |
| 1 1 0 | 10 | 1.7628 | 1.7633 | 2 0 7 | | 1.2046 | |
| 1 1 1 | | 1.7485 | | 1 0 11 | | 1.1551 | |
| 0 0 8 | 1 | 1.7157 | 1.7159 | 2 1 0 | 2 | 1.1541 | 1.1541 |
| 1 1 2 | 2 | 1.7074 | 1.7074 | 1 1 9 | | 1.1534 | |
| 1 0 7 | | 1.6499 | | 2 1 1 | | 1.1500 | |
| 1 1 3 | | 1.6450 | | 0 0 12 | 1* | 1.1438 | 1.1436 |
| 1 1 4 | 1 | 1.5680 | 1.5676 | 2 0 8 | 1 | 1.1405 | 1.1405 |
| 2 0 0 | 3 | 1.5267 | 1.5267 | 2 1 2 | 1 | 1.1381 | 1.1380 |
| 0 0 9 | | 1.5251 | | 2 1 3 | 5 | 1.1190 | 1.1192 |
| 2 0 1 | | 1.5173 | | 2 1 4 | | 1.0939 | |

[a] Based on a primitive hexagonal cell with a=3.5257(2) and c=13.726(2) computed by the CDR program from all 23 non-ZrBr lines in a powder pattern of $ZrBr_{1.42}$(Table 4, text). The three indicated (*) reflections are of uncertain intensity because of overlap with ZrBr lines.

Table A-4. Indexed Guinier powder pattern of $ZrCl_{1.6}$[a]

| h | k | l | $\theta_{obs}$ | $\theta_{calc}$ | $d_{calc}$ | $I_{obs}$ |
|---|---|---|---|---|---|---|
| 0 | 0 | 3 | 6.83 | 6.84 | 6.463 | 10 |
| 0 | 0 | 6 | 13.79 | 13.79 | 3.232 | 1 |
| 1 | 0 | 0 | 15.25 | 15.24 | 2.930 | 1 |
| 1 | 0 | 1[b] | 15.42 | 15.42 | 2.897 | 6 |
| 1 | 0 | 2 | 15.94 | 15.94 | 2.804 | 6 |
| 1 | 0 | 4[b] | 17.89 | 17.89 | 2.507 | 8 |
| 0 | 0 | 8 | 18.55 | 18.53 | 2.424 | 2 |
| 1 | 0 | 5 | 19.23 | 19.24 | 2.338 | 8 |
| 0 | 0 | 9 | 20.95 | 20.95 | 2.154 | 5 |
| 1 | 0 | 7 | 22.50 | 22.50 | 2.013 | 5 |
| 1 | 0 | 8 | 24.36 | 22.36 | 1.868 | 4 |
| 1 | 0 | 9 | 26.32 | 26.35 | 1.736 | 4 |
| 1 | 1 | 0 | 27.09 | 27.09 | 1.6915 | 8 |
| 1 | 1 | 3 | 28.07 | 28.08 | 1.6364 | 5 |
| 0 | 0 | 12 | 28.47 | 28.47 | 1.6158 | 4 |
| 1 | 0 | 11 | 30.66 | 30.66 | 1.5104 | 2 |
| 1 | 1 | 6 | 30.94 | 30.93 | 1.4986 | 2 |
| 2 | 0 | 0* | 31.70 | 31.73 | 1.4649 | 1 |
| 2 | 0 | 1[b] | 31.83 | 31.83 | 1.4607 | 3 |
| 2 | 0 | 2 | 32.13 | 32.13 | 1.4484 | 3 |
| 2 | 0 | 4[b] | 33.33 | 33.32 | 1.4023 | 4 |
| 2 | 0 | 5 | 34.21 | 34.20 | 1.3704 | 4 |
| 1 | 1 | 9 | 35.39 | 35.38 | 1.3304 | 7 |
| 2 | 0 | 7 | 36.51 | 36.50 | 1.2950 | 3 |
| 2 | 0 | 8 | 37.91 | 37.91 | 1.2537 | 2 |
| 1 | 0 | 14 | 37.95 | 37.97 | 1.2521 | 2 |
| 1 | 1 | 12* | 41.24 | 41.24 | 1.1686 | 7 |
| 2 | 0 | 10* | 41.24 | 41.24 | 1.1686 |  |
| 2 | 0 | 11 | 43.14 | 43.14 | 1.1266 | 2 |
| 1 | 0 | 16 | 43.47 | 43.46 | 1.1199 | 3 |
| 2 | 1 | 1[b] | 44.17 | 44.17 | 1.1055 | 3 |
| 2 | 1 | 2 | 44.44 | 44.44 | 1.1002 | 3 |

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[a] All reflections except those indicated (*) were used for a final least squares lattice refinement to give hexagonal cell parameters of *a*=3.3829(2) and *c*=19.390(1).

[b] Products prepared at temperatures above 600° show an increasing tendency toward broad bands in these regions.

Table A-5. Calculated Guinier powder pattern of $Zr_6Cl_{15}$[a]

| $d_{calc}$ | $I_{calc}$ | N[b] | h | k | l[c] | $d_{calc}$ | $I_{calc}$ | N | h | k | l |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 7.47 | 1000 | 1 | 2 | 2 | 0 | 1.8263 | 73 | 4 | 11 | 3 | 2 |
| 5.650 | 61 | 1 | 3 | 2 | 1 | 1.7996 | 35 | 2 | 11 | 4 | 1 |
| 4.315 | 35 | 1 | 4 | 2 | 2 | 1.7496 | 55 | 4 | 9 | 8 | 1 |
| 3.737 | 41 | 1 | 4 | 4 | 0 | 1.7262 | 47 | 3 | 10 | 7 | 1 |
| 3.430 | 49 | 2 | 5 | 3 | 2 | 1.7036 | 38 | 2 | 12 | 3 | 1 |
| 3.343 | 73 | 1 | 6 | 2 | 0 | 1.6409 | 38 | 3 | 9 | 9 | 2 |
| 3.262 | 91 | 1 | 5 | 4 | 1 | 1.5178 | 52 | 4 | 9 | 8 | 7 |
| 2.877 | 176 | 3 | 5 | 5 | 2 | 1.5024 | 38 | 4 | 13 | 5 | 2 |
| 2.527 | 113 | 1 | 6 | 5 | 3 | 1.3061 | 39 | 2 | 10 | 9 | 9 |
| 2.492 | 38 | 2 | 8 | 2 | 2 | 1.2962 | 31 | 5 | 13 | 9 | 4 |
| 2.458 | 212 | 3 | 7 | 4 | 3 | 1.2866 | 34 | 4 | 11 | 10 | 7 |
| 2.394 | 31 | 1 | 7 | 5 | 2 | 1.2165 | 31 | 3 | 14 | 9 | 5 |
| 2.280 | 110 | 3 | 7 | 6 | 1 | 1.1236 | 43 | 3 | 13 | 11 | 8 |
| 2.228 | 102 | 3 | 7 | 5 | 4 | 1.0597 | 54 | 5 | 17 | 10 | 3 |
| 2.136 | 70 | 2 | 8 | 5 | 3 | 1.0518 | 41 | 3 | 16 | 12 | 2 |
| 2.093 | 67 | 2 | 7 | 7 | 2 | 1.0441 | 54 | 4 | 20 | 3 | 1 |
| 2.073 | 40 | 2 | 10 | 2 | 0 | 1.0390 | 43 | 5 | 17 | 10 | 5 |
| 1.9462 | 30 | 3 | 10 | 3 | 3 | 1.0243 | 85 | 6 | 20 | 5 | 1 |

[a] Lines are omitted from this listing if the combined intensity for all reflections at a given d value is less than 30 relative to $I_{calc}$=1000 for (2 2 0).

[b] N=the number of reflections contributing to $I_{calc}$ at a given d.

[c] The representative hkl listed when $N > 1$ is the one with greatest $I_{calc}$.

Table A-6. Powder diffraction data for ZrBr[a]

| h k l | $d_{calc}$[b] | $I_{obs}$ (Guin.) | $I_{obs}$ (D.S.) | h k l | $d_{calc}$ | $I_{obs}$ (Guin.) | $I_{obs}$ (D.S.) |
|---|---|---|---|---|---|---|---|
| 0 0 3 | 9.357 | 14 | 20 | 1 0 17 | 1.4503 | 8 | 20 |
| 0 0 6 | 4.678 | 8 | 20 | 2 0 7 | 1.4188 | 11 | 5 |
| 0 0 9 | 3.119 | 0 | 0 | 1 1 12 | 1.4021 | 21 | 25 |
| 1 0 1 | 3.016 | 15 | 5 | 2 0 8 | 1.3924 | 0 | 0 |
| 1 0 2 | 2.965 | 17 | 25 | 0 0 21 | 1.3367 | 0 | 20 |
| 1 0 4 | 2.785 | 9 | 5 | 2 0 10 | 1.3345 | 13 | |
| 1 0 5 | 2.669 | 100 | 100 | 1 0 19 | 1.3283 | 0 | 0 |
| 1 0 7 | 2.419 | 19 | 30 | 2 0 11 | 1.3039 | 1 | 0 |
| 0 0 12 | 2.339 | 8 | 35 | 1 1 15 | 1.2788 | 17 | 25 |
| 1 0 8 | 2.295 | 0 | 0 | 1 0 20 | 1.2738 | 1 | 0 |
| 1 0 10 | 2.060 | 30 | 40 | 2 0 13 | 1.2412 | 0 | 0 |
| 1 0 11 | 1.9529 | 3 | 5 | 2 0 14 | 1.2097 | 0 | 0 |
| 0 0 15 | 1.8714 | 5 | 28 | 1 0 22 | 1.1762 | 4 | 20 |
| 1 0 13 | 1.7592 | 3 | 5 | 0 0 24 | 1.1696 | 0 | 0 |
| 1 1 0 | 1.7515 | 50 | 40 | 1 1 18 | 1.1647 | 4 | 10 |
| 1 1 3 | 1.7216 | 8 | 5 | 2 0 16 | 1.1475 | 1 | 0 |
| 1 0 14 | 1.6727 | 0 | 0 | 2 1 1 | 1.1457 | 1 | 0 |
| 1 1 6 | 1.6404 | 11 | 5 | 2 1 2 | 1.1429 | 5 | 5 |
| 0 0 18 | 1.5595 | 1 | 10 | 1 0 23 | 1.1323 | 2 | 0 |
| 1 1 9 | 1.5272 | 0 | 0 | 2 1 4 | 1.1317 | 0 | 0 |
| 1 0 16 | 1.5188 | 5 | 5 | 2 1 5 | 1.1235 | 29 | 20 |
| 2 0 1 | 1.5147 | 0 | | 2 0 17 | 1.1171 | 2 | 5 |
| 2 0 2 | 1.5081 | 11 | 5 | 2 1 7 | 1.1025 | 6 | 5 |
| 2 0 4 | 1.4826 | 0 | 0 | 2 1 8 | 1.0899 | 0 | 0 |
| 2 0 5 | 1.4644 | 38 | 25 | | | | |

[a] Guinier intensities are from a microdensitometer film scan while Debye-Scherrer intensities were visually estimated.

[b] All observed reflections are within ±0.02° of $\theta_{calc}$ for lattice parameters of *a*=3.5031(3) and *c*=28.071(3).

Table A-7. Hexagonal lattice constants for $\alpha$-Zr, some indexed zirconium halides, and HfCl

| Phase Composition | N[a] | a (Å) | c (Å) | Preparative Method |
|---|---|---|---|---|
| $\alpha$-Zr | 11 | 3.2328(4) | 5.1505(9) | $ZrCl \xrightarrow{1054^\circ} Zr^\circ + ZrCl_4(g)$ |
| ZrCl | 9 | 3.4212(3) | 26.693(3) | Equilibration with Zr (975°) |
| | 10 | 3.4233(5) | 26.692(4) | Equilibration with Zr (1054°) |
| ZrBr | 23 | 3.5031(3) | 28.071(3) | Stoichiometric prep (825°) |
| $ZrBr_{1-x}O_x$ | 22 | 3.5646(2) | 28.479(5) | ZrBr + xs $ZrO_2$ (850°,6d) |
| HfCl[b] | 24 | 3.3697(3) | 26.582(6) | $HfCl_{1.3}$+ xs Hf (650°,6d) |
| $ZrCl_{1.6}$ | 28 | 3.3830(2) | 19.390(1) | $ZrCl_3$ + xs ZrCl (600°,35d) |
| $ZrBr_{1.8}$ | 21 | 3.5257(2) | 13.726(2) | ZrBr + xs $ZrBr_3$ (600°,28d) |

[a] The number of unambiguously assigned reflections input to the CDR program.

[b] Based on a Debye-Scherrer film read and corrected for shrinkage by A.W. Struss and reported in an earlier publication (22).

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## ACKNOWLEDGMENTS

The author especially wishes to express his appreciation to Professor John D. Corbett for his helpful suggestions and creative feedback during the course of this work. He also wishes to thank Professor H. F. Franzen and Dr. Mirtha Umaña for acquiring the XPS data presented here, and Professor R. A. Jacobson for providing the diffractometer and programs for collection of single crystal data. The author is grateful to Bob Daake for taking vacation time to write the Guinier Film Measuring Program which has saved tedious hours of repetitive calculations, and he cannot overlook the patience of his typist wife who invested many tiring days in preparing this typewritten manuscript.

Since joining Physical and Inorganic Chemistry Group IX of the Ames Laboratory, the author has enjoyed both serious and humorous discussions with other Group members, and is particularly grateful to Art Struss and A. V. Hariharan for their constructive criticisms and friendly encouragement during the course of this research.