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The synthesis and characterization of some binary and ternary zirconium iodides

Dennis Hugh Guthrie
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THE SYNTHESIS AND CHARACTERIZATION OF SOME BINARY AND
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The synthesis and characterization of
some binary and ternary
zirconium iodides

by

Dennis Hugh Guthrie

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
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GENERAL INTRODUCTION

Zirconium compounds were first discovered by Klaproth in 1789, while the metal itself was not isolated until 1824 by Berzelius. Zirconium, like many other transition metals, was first purified via the van Arkel-DeBoer process. Crude metal was transported from a $\sim 350^{\circ}\text{C}$ region to a filament of the particular metal resistively heated to $\sim 1500^{\circ}\text{C}$ by an iodide vapor phase transport reaction. The vapor phase species in the case of zirconium is ZrI_4 .

Zirconium was first employed in industry because of its strength, ductility, ease of fabrication and its resistance to acid and/or water corrosion. However, upon the birth of the nuclear age it was found to have one additional important property: a very low thermal neutron cross section (0.18 barns/atom). This combined with its high temperature stability and resistance to corrosion in hot water made it an excellent choice for containment of UO_2 fuel in water cooled reactors. The major problem then is that hafnium, which naturally occurs with zirconium, has a high (113 barns/atom) thermal neutron cross section, making the separation of these elements critical. Zirconium and hafnium are found together naturally in the ore zircon where hafnium is usually 2-3% of the zirconium content. Both metals have very similar physical and chemical properties which makes their separation difficult. Therefore, reactor grade zirconium (<100 ppm Hf) is produced via a long wet chemistry scheme (1). However, when zirconium is produced for commercial applications other than use in reactors, the relatively small hafnium

content is generally of no concern. In such cases the metal is obtained from the reduction of the tetrachloride with Mg to yield $MgCl_2$ and metal (the Kroll process).

The use of zirconium in nuclear reactors, usually in the form of Zircaloy-2 containing ~1.5% tin, has spurred research in the area of zirconium compounds. A lot of emphasis has been placed upon the binary Zr-ZrI₄ and ternary CsI-Zr-ZrI₄ systems because of the phenomenon of stress-corrosion-cracking (SCC). Many researchers in the field (2-4) believe SCC of Zircaloy-2 tubing is caused by iodine and/or cesium, both of which are fission products of UO₂. SCC of Zircaloy-2 occurs when fuel rods are exposed to a stress and reactor power increases after a sufficiently large fuel burn up. Therefore, in addition to the development of general information on transition metal halide chemistry it was hoped that this investigation into the binary Zr-ZrI₄ and ternary CsI-Zr-ZrI₄ systems might shed new light upon compounds perhaps important in SCC of Zircaloy-2.

When this work was initiated two binary iodides were well-known, ZrI₄ and ZrI₃. The first is an orange-red material obtained at ~350°C from the reaction of I₂ with Zr. Though its structure is similar to those of α-NbI₄ (5), ZrCl₄ (6) and β-ReCl₄ (7), it is unique in that the infinite chains of ZrI₆ octahedra share nonopposite edges to form a helical arrangement with a period of six octahedra along the chain (8).

Zirconium triiodide has been found to be nonstoichiometric over the range (775°C) $2.83(5) \leq I:Zr \leq 3.43(5)$ (475°C) (9). In the ideal stoichiometry one-third of the octahedral holes are filled between h.c.p.

iodine layers to form linear chains of ZrI_6 octahedra which share opposite faces. The zirconium atoms therefore form linear chains parallel to the c axis. The synthesis of " ZrI_2 " had also been reported by Sale and Shelton (10) from the disproportionation of ZrI_3 under a 360/390°C gradient in a sealed Pyrex tube. However, the powder pattern reported was found to agree well with that of the lower limit triiodide $ZrI_{2.8}$ (9). In addition to the known compounds ZrI_4 and ZrI_3 , Daake (11) prepared a phase assigned the composition " $ZrI_{1.8}$ ". This was obtained from the reaction of ZrI_3 or ZrI_4 with a large excess of zirconium at $\sim 750^\circ C$ for two weeks. The black platelet phase had a unique powder pattern; the composition was obtained from wet chemical analysis. In the present work the known binary zirconium iodides have been expanded to include two polymorphs of ZrI_2 (α, β). In addition, a discussion of the " $ZrI_{1.8}$ " phase will be presented.

Other published work in the Zr- ZrI_4 system agrees at least in part with that reported here and earlier by Daake and Corbett (9). Cubicciotti and coworkers report thermodynamic evidence for a nonstoichiometric triiodide from 3.4-2.8 as well as a diiodide from 2.0-1.9 ($\sim 420^\circ C$) (12). In addition, other more reduced phases such as $ZrI_{1.7}$, $ZrI_{1.0}$ and $ZrI_{0.16}$ (13) were also said to exist. These highly reduced phases were observed in extremely small quantities via a scanning electron microscope (SEM).

No previous work had been carried out in the CsI-Zr- ZrI_4 ternary system. However, work in the closely related CsCl-Zr- $ZrCl_4$ (14) system indicated that Cs_2ZrI_6 might be expected while work in CsCl-Nb- $NbCl_5$ (15)

indicated $\text{Cs}_3\text{Zr}_2\text{I}_9$ might be formed. In addition to these two ternary iodides a third, $\text{CsZr}_6\text{I}_{14}$, has been discovered as well as evidence for yet another phase.

The work in the binary and ternary systems is divided into PART I and PART II, respectively. Each part is then further subdivided according to individual compounds (to allow a more indepth look at each), each with a more specific introduction.

EXPERIMENTATION

Starting Materials

Zirconium metal. Within the Ames Laboratory zirconium can easily be acquired from Rick Schmidt as a crystal bar ~9-12 cm long and 1-2 cm in diameter. This reactor grade metal (<500 ppm Hf) has been obtained via the Van Arkel process. The bar was first cleaned with a metal cleaning solution (45% conc. HNO_3 , 45% H_2O and 10% HF by volume) and then rinsed with acetone. In order to cold-roll the metal with minimal cracking, the bar was melted into a loaf under vacuum and then cold-rolled into strips 0.4-0.5 mm thick. From this single strip, smaller strips were cut to 1/2 x 6 cm strips for isothermal or small gradient reactions or 1/2 x 10-12 cm for large gradient reactions. The next step was either to electropolish the strips or to clean them in acetone followed again by the metal cleaning solution. Finally, the strips were washed once more in acetone, dried, and stored under vacuum.

Zirconium tetraiodide. This is the only zirconium iodide which can easily be prepared from the reaction of metal and iodine. This was achieved by reacting gaseous I_2 (reagent grade, <0.005% Cl and Br) from a reservoir at ~150°C with excess metal heated to ~350°C in an evacuated and sealed Pyrex container. The orange-red tetraiodide was deposited in a section of the tube which protruded out of the furnace. The product was purified by vacuum sublimation (< 10^{-5} Torr) through a coarse-grade Pyrex frit at 400°C. As a precaution, ZrI_4 when initially sublimed was

sealed in several containers in 2-4 g quantities to avoid any large loss due to an accident and to avoid repeated exposure to the dry box atmosphere.

Cesium iodide. CsI (Alfa Products) was recrystallized from a 0.05 wt. % aqueous HI solution and then dried (350°C) and stored under vacuum.

Synthesis

When considering the synthesis of reduced early-transition metal or rare-earth metal halide compounds, several problems come to mind: 1) the air and moisture sensitivity of almost all compounds, 2) the high temperatures (600-100°C) often required to obtain these compounds, 3) the high pressures (up to 30 atm.) obtained when the more volatile reactants are heated to these high temperatures, 4) the reactivity of these reduced compounds with fused silica at high temperatures, 5) the low yields often obtained (1-15%). In many cases the combination of two or perhaps all five of these problems has made many reduced metal halides basically undiscovered until recently. A substantial break came with the use of tantalum, molybdenum or niobium tubing as reaction vessels. Problems 1-4 stated above can be overcome with the employment of these reaction vessels since they can be sealed under a vacuum or partial atmosphere of an inert gas, and they withstand both high temperatures and pressures, and standardly do not enter into the reaction. Problem 5 may in many cases be resolved by using vapor phase transport reaction conditions to produce single crystal materials on which single crystal

x-ray diffraction may be done. Therefore, the substitution of metal tubing for fused silica or Pyrex tubing has allowed the synthesis of several new metal halides.

Tantalum tubes 9.5 mm o.d. were exclusively used as reaction vessels in the zirconium binary and ternary systems. One end of a cleaned tube was first crimped and then welded within an evacuable Heliarc welder (16). The tube and starting materials (always sealed within evacuated Pyrex containers for long storage) were then taken into a dry box, the reactants loaded into the tube and the remaining end crimped via a small vise. To transfer the tube from the dry box to the Heliarc welder the tube was placed in a small container. The only direct contact with air was the 1/5 second transfer into the welder, which was immediately evacuated, and then back-filled with a partial atmosphere of helium. The tube was then welded. The tantalum tube was then sealed in an evacuated fused silica jacket before being placed in a furnace since tantalum is quickly oxidized upon heating in the air. Temperatures were monitored by a sheathed thermocouple attached to the outside of the fused silica jacket. Upon completion, the reaction was either allowed to cool slowly in the furnace by turning off the power, or quenched in air or water by removing the tube from the hot furnace.

Reaction tubes were opened within a dry box especially designed for crystal mounting and described in detail elsewhere (17). Identification of phases which have a distinctive reflectivity, color or crystal morphology was achieved by microscopic examination. Individual crystals were selected and picked up with a glass fiber dipped in Vaseline.

They were then inserted into 0.2 or 0.3 mm diameter thin-wall glass capillaries. These capillaries were then either sealed inside the dry box with the aid of a hot nichrome wire or plugged with Vaseline. These were then sealed outside the box with a gas torch and the ends capped with black wax (Apiezon W). Crystals successfully mounted were re-examined under higher magnification outside the box and the best further examined with oscillation photographs taken with a standard Weissenberg camera and Ni-filtered CuK_{α} -radiation. Samples for Guinier powder diffraction were mounted as described elsewhere (11). All remaining products were placed within Pyrex storage containers and sealed under vacuum.

Physical Measurements

X-Ray methods. A variety of x-ray cameras were used. Initially routine phase identification was made with Ni-filtered CuK_{α} radiation beam and a Phillips Debye-Scherrer camera having the standard 114.59 mm diameter. In the latter stages of this work an evacuable Model XDC-700 Guinier camera, IRDAB, Stockholm, was mainly used. This focussing camera yields excellent quality films by using a quartz monochromator to provide a nearly clean CuK_{α_1} incident beam in combination with single-emulsion film or double-emulsion film where only one side was developed. Weissenberg cameras, Charles Supper Co., were usually used in evaluation of possible single crystals and preliminary determination of unit cell constants, with a precession camera, Charles Supper Co., being used at times.

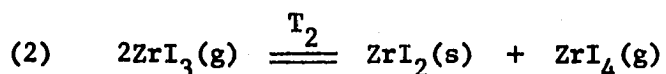
Single crystal x-ray diffraction data were collected on the Ames Laboratory four-circle diffractometer interfaced with a PDP-15 computer. MoK_α radiation monochromatized with a graphite single crystal ($\lambda = 0.70954 \text{ \AA}$) was used in all single crystal studies.

Resistivity measurements. Resistivity measurements were carried out by Dr. T. Hsiang by standard 4-probe techniques. The probes were attached to a single crystal with silver paste.

PART I. THE BINARY Zr-ZrI₄ SYSTEM

Initial reactions in the search for ZrI_x (x < 3) phases were transport-type reactions with ~150°C gradients, e.g. 600-750°C, 750-900°C. This provided a wide variety of temperatures to allow the formation of any possible phase. Then, when a phase was identified either by a crystal structure or powder pattern, attempts were made to determine the exact conditions needed to synthesize each particular phase in larger quantities.

From the reaction of ~1 g of ZrI₄ with a large stoichiometric excess (2-4 strips or 2-5 g or a surface area of 12-24 cm²) of zirconium in a 700-825°C gradient for approximately one month the products were: black blade-like crystals, a black powder, and ZrI₃. The crystals (~20% yield) were found growing on both the metal and walls of the tantalum tube in the ~750°C region. The black powder (~10% yield) coated the entire surface of the metal strips while the ZrI₃ (~70% yield) was in the cold end of the tube. Powder patterns of both the crystals and black material agreed with that of "ZrI_{1.8}" (11). However, the α-ZrI₂ data crystal was mounted from a reaction of this type (see the "ZrI_{1.8}" RESULTS). The hypothesized sequence of reactions needed to form crystals of diiodide (assuming, at least for this illustration, that "ZrI_{1.8}" is ZrI₂) are:



When T_2 and T_1 were 700 and 825°C, respectively, the blade-like crystals mentioned above were obtained. However, if T_2 and T_1 were increased to 800 and 900°C, respectively, gem crystals of β -ZrI₂ (Zr₆I₁₂) were deposited (~10% yield) in the 850°C region while a black layer of β -ZrI₂ (~5% yield) coated the entire metal surface and unreacted ZrI₃ (~85% yield) condensed in the cold zone on cooling. There appears to be an overlap in the stability regions for α and β -ZrI₂ since both blade and gem crystals have been observed together between 800 and 825°C.

The low yields of ZrI_x ($x < 3$) products are thought to be caused by blockage of the metal surface which prevents complete reduction of the more oxidized species. In a reaction such as that mentioned earlier, ~1 g ZrI₄ and 3-6 g Zr, as the temperature increases ZrI₄(g) is reduced to ZrI₃(g) with a layer of ZrI₃(s) being deposited on the metal surface. Then as the temperature increases the ZrI₃ may be directly reduced to form a layer of ZrI₂(s) (α , "ZrI_{1.8}" or β depending on the exact temperature). This less volatile ZrI₂(s) (the assumption that ZrI₂(s) has a low vapor pressure is not unfounded (18)) is thought to block the metal surface. At this point the transport reaction, equations 1 and 2, becomes predominant and crystals, up to 2-cm-long blades (700-825°C, α -ZrI₂, "ZrI_{1.8}") or 0.2-0.5 mm gems (800-975°C, β -ZrI₂), are slowly deposited upon the layer of diiodide coating the metal as well as the wall of the tantalum tube. Because the surface of the metal is blocked unreacted ZrI₃ remains and is condensed in the coldest zone of the tube. From this explanation it would seem that the addition of extra metal should result in higher yields. However, a little ZrI₂(s) seems to go

a long way so that even small quantities of ZrI_4 (0.02 g) reacted with 3-5 g of metal result in unreacted ZrI_3 ($T > 900^\circ C$).

In attempts to produce other reduced phases virtually every possible temperature region from 700-1000°C has been explored by either isothermal or gradient reactions. All temperatures above 900°C were explored by both small and large gradients, $\leq 50^\circ C$ and 100-200°C, respectively, while below 900°C most gradients were $> 50^\circ C$. Different starting materials such as ZrI_4 or ZrI_2 along with either metal strips or metal powder were used. In addition, the reaction times were varied from 1-6 weeks and different stopping techniques such as slow cooling (turning off the power to the furnace) or air and water quenching were employed. The use of different starting materials resulted in the same products although only a small amount of work has been done with the powdered metal. Both slow cooling and air quenching also produced the same products, the only difference being the first allows ZrI_3 to deposit in the cold end as crystals while the latter yields a fine powder of ZrI_3 throughout the tube. Water quenching in some cases produced, in addition to ZrI_3 , small quantities of ZrI_4 ($\sim 10\%$) presumably via some type of a disproportionation. Reactions generally proceeded for two weeks; if single crystals were desired via a transport-type reaction then they proceeded for 4-6 weeks.

Though not completely understood, blade-like crystals have been seen at unusually high temperatures in two reactions. Reactions 21 and 35 (19) were $\sim 870-950^\circ C$ gradient reactions which contained ~ 0.5 g of ZrI_4 and ~ 3 g of Zr strips. Each reaction proceeded for ~ 1 month.

Upon opening, ZrI_3 (80%) was found in the cold end of the tube along with β - ZrI_2 gem crystals, while the entire length of the metal strips was coated with a layer of β - ZrI_2 . Blade-like crystals (5%) were found in the hot end of the tube both on the layer of β - ZrI_2 and on the wall of the tantalum tube. One of the crystals mounted from reaction 21 was found to have an orthorhombic cell ($\underline{a} = 3.738(1)$, $\underline{b} = 6.817(2)$ and $\underline{c} = 14.860(4)$ Å) very similar to the monoclinic cell of α - ZrI_2 (see $ZrI_{1.8}$ section). No other phases have been seen or identified by either powder or single crystal x-ray diffraction. In addition, no phases are thought to be stable above $\sim 975^\circ\text{C}$ since only annealed metal strips and ZrI_3 have been obtained at such high temperatures.

THE SYNTHESIS AND STRUCTURE OF AN INFINITE CHAIN

FORM OF $ZrI_2(\alpha)$ ¹

¹In press: D. H. Guthrie and J. D. Corbett, J. Solid State Chem.
38 (1981).

INTRODUCTION

Several reduced zirconium halides with zirconium in an oxidation state less than three have recently been synthesized and characterized. Among the chlorides and bromides are the clusters Zr_6Cl_{15} (20) and Zr_6X_{12} (21), $ZrCl_2$ (3R-MoS₂-type) (22,23), and the double-metal-layered $ZrCl_2$ (17,24,25) and $ZrBr$ (26) compounds. Yet until recently the only well characterized zirconium iodides were ZrI_4 and ZrI_3 , both known for their importance in the purification of zirconium via the van Arkel process. The triiodide has been found to be nonstoichiometric over the range $ZrI_{2.83}$ (775°C) to $ZrI_{3.43}$ (475°C), with a recognizable superstructure to x-rays at the upper limit (9). The synthesis of a zirconium diiodide has been reported by Sale and Shelton (10) from the disproportionation of ZrI_3 under a 360/390°C gradient in a sealed Pyrex tube. However, the reported powder pattern has been found to correspond closely to that of the lower limit triiodide $ZrI_{2.8}$ (9). Lack of earlier evidence for zirconium iodides more reduced than the ZrI_3 phase appears to have originated mainly from the use of reaction times which were too short, temperatures which were too low and, probably, glass containers. Increases in these two parameters and the use of sealed tantalum containers have enabled the synthesis of the cluster Zr_6I_{12} (20), and the present article reports on a second polymorph of ZrI_2 , an infinite metal chain form. The new phase is stable at lower temperatures (775°C) than Zr_6I_{12} (875°C) and therefore is referred to as α - ZrI_2 .

EXPERIMENTAL SECTION

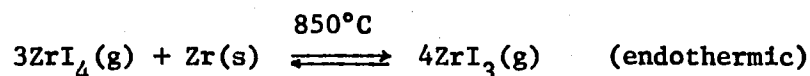
Materials and Synthesis

Materials. Reactor-grade crystal bar zirconium (<500 ppm Hf) was melted into a loaf under vacuum, cut into ~2 mm thick slices, and these were cold-rolled to strips 0.4 - 0.5 mm thick. The strips were then either electropolished or cleaned in acetone and then in a solution of 45% conc. HNO₃, 45% H₂O, 10% HF to remove any hydrocarbons and surface impurities picked up during cold rolling. The strips were then washed with acetone, dried, and stored under vacuum.

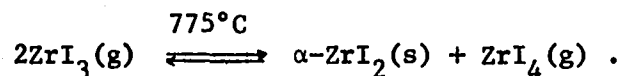
The tetraiodide was prepared by reaction of gaseous, reagent-grade iodine (<0.005% Cl and Br) from a reservoir at ~150°C with excess metal heated to 350-400°C within a sealed Pyrex container. The product was purified by vacuum sublimation (<10⁻⁵ Torr) through a coarse grade Pyrex frit at 400°C. Transfer and manipulation of all materials was done by standard vacuum-line or dry box techniques.

Synthesis. The use of sealed tantalum tubing as a reaction vessel for high temperature reactions involving lower halides of zirconium has proven very successful (9,17,23,24,26), and this approach was continued. The containers were induction cleaned (1800°C), arc welded under helium after filling, jacketed in fused silica tubes and sealed off under vacuum. Temperatures were monitored during the reaction with thermocouples fastened to the outside of the silica jacket. Any temperature difference between the Ta container and the outside of this jacket is considered small at the temperatures involved and fairly constant from reaction to reaction.

The initial synthesis used 0.1 g of ZrI_4 with a large excess of zirconium strips which extended the length of a 10-12 cm long, 0.95 cm o.d. tantalum tube. The reaction was carried out for four weeks under a 750/850°C temperature gradient after which the container was allowed to cool in the furnace. Long reaction times are required to overcome kinetic problems known in this and similar systems (23,27), and the temperature gradient allowed formation of phases which might be stable only in a limited temperature region. A 10-20% yield of lath-like crystals with a high metal-like luster were found growing in the 775°C region on the zirconium strip as well as the inside walls of the tantalum tube. These are thought to have been produced via the transport reactions



followed by



Subsequent reactions have indicated that the metal in the 775°C region first becomes coated with a powder and small crystals of $\alpha\text{-ZrI}_2$, presumably because of the presence of a large number of nucleation sites and a high P_{ZrI_4} in the early stages of the reaction. As the reaction proceeds larger crystals are formed, sometimes up to 2 cm long. A temperature zone <775°C (750°C) is necessary to allow separation of any ZrI_3 formed from $\alpha\text{-ZrI}_2$.

DATA COLLECTION

The Ta tube was opened in a dry box especially designed for crystal mounting, and suitable specimens selected under low magnification. These were sealed in the capillaries with the aid of a hot nichrome wire and later resealed outside the dry box with a gas flame. The single crystal selected for data collection was chosen with the aid of oscillation photographs and had extreme dimensions of 1.17 x 0.08 x 0.01 mm. Data for the indicated monoclinic unit cell were collected at ambient temperature on an automated four-circle diffractometer designed and built in the Ames Laboratory (28) using MoK_α radiation monochromated with a graphite crystal ($\lambda = 9,70954 \text{ \AA}$). All data within a sphere defined by $2\theta \leq 50^\circ$ were collected in the HKL , $\text{HK}\bar{\text{L}}$, $\text{H}\bar{\text{K}}\text{L}$, $\text{H}\bar{\text{K}}\bar{\text{L}}$ octants using an ω -scan mode. Peak heights of three standard reflections did not show any significant change over the period of data collection. A total of 1427 of the 1750 reflections checked were classed as observed by the criterion $I > 3\sigma(I)$. The observed intensities were corrected for Lorentz and polarization effects after which appropriate averaging of duplicate reflections yielded 669 independent data. Final monoclinic cell parameters and their estimated standard deviations were obtained from the same crystal by a least-squares fit to 2θ values of 12 reflections randomly distributed in reciprocal space ($27^\circ < 2\theta < 44^\circ$) which were tuned for both Friedel-related peaks; the result was $a = 6.821(2)$, $b = 3.741(1)$, $c = 14.937(3) \text{ \AA}$ and $\beta = 95.66(3)^\circ$. The edges of the crystals

lie parallel to the cell axes and the crystal dimensions are inversely related to the axial lengths.

STRUCTURE DETERMINATION

The unit cell was indicated to be centric based on a Howells-Phillips-Rogers test of the intensity distribution, and since no extinction conditions were noted the monoclinic space group $P2/m$ was chosen. Placement of all atoms on the mirror planes at $y = 0.0$ or 0.5 appeared likely based on the short b axis, 3.74 \AA , which is essentially the van der Waals diameter of iodine.

Trial atom positions were obtained by a direct method using MULTAN (29). Several sets so produced were eliminated on the basis of chemical and structural common sense. After full-matrix least-square refinement of positional and isotropic thermal parameters for the best set, an $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.107$ was obtained. Closer inspection of the structure and data set at this point revealed the existence of a two fold screw axis ($0k0$, $k \neq 2n$ absent); therefore, the correct space group is $P2_1/m$ (No. 11) with all atoms on the special position $2e$. Refinement with anisotropic thermal parameters then produced a $R = 0.071$ and $R_w = 0.010$ where $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$ and $w = \sigma_F^{-2}$. Need for an absorption correction was indicated by elongation of the thermal ellipsoids along b , the shortest crystal axis. The correction utilized the program TALABS (30) and an absorption coefficient of $\mu = 190 \text{ cm}^{-1}$ (31) and the crystal was approximated as a rectangular box of extreme dimensions stated earlier. Because of the large differences in crystal dimensions, transmission coefficients varied from 0.25 to 0.82 and χ and ϕ settings for the faces were found to be critical.

After this was completed ($R = 0.065$, $R_w = 0.115$) the stronger reflections were observed to have larger values of $w||F_o|-|F_c||$. The data were therefore reweighted in groups sorted on F_o to give final converged residuals $R = 0.064$ and $R_w = 0.079$, with a final shift/error of < 0.001 for all atoms. The thermal ellipsoids were now more reasonably shaped, and the standard deviations were $\sim 15\%$ lower than before. A final Fourier difference synthesis map was flat to $\leq 1 \text{ e}/\text{\AA}^3$ at all points.

DESCRIPTION OF THE STRUCTURE

Final positional and thermal parameters for the structure of α - ZrI_2 are listed in Table I and significant distances and angles, in Table II. Structure factor results are in Appendix A.

An approximately [010] projection of the structure is shown in Figure 1. The iodine positions can be related to h.c.p. layers normal to c , with metal atoms (solid) occupying all octahedral sites between alternate layers to form slabs analogous to those in the CdI_2 structure. In the present case, however, the metal atoms are displaced 0.440 \AA from the centers of the octahedral sites toward shared edges of the polyhedra to form zig-zag chains parallel to b . This displacement of the metal atoms causes the iodine layers in each slab to buckle, and packing of these buckled layers in effect requires a second slab with independent atoms. Equivalent distances in the two independent slabs all differ by less than 3σ (Table II) except that the $\text{I4}^e - \text{I2}^b$ and $\text{I4}^a - \text{I2}$ distances differ by 6σ (0.016 \AA) in opposite directions.

The [001] projection in Figure 2 shows two iodine layers and the intervening metal layer which lies at $z \approx 0$. The two iodine octahedra outlined share a common edge (I2^b & I2) through which the presumed Zr-Zr bond passes. Edges of these polyhedra range between 3.74 and 4.47 \AA except for the shared edge $\text{I2}^b - \text{I2}$ which is 4.89 \AA . This elongation results when the adjacent shared edges of the occupied iodide octahedra are pushed apart to make room for the Zr-Zr bonds. Corresponding effects are observed in the zirconium-iodine distances.

Table I. Crystallographic data and atom parameters^a for α -ZrI₂.Composition: ZrI₂Cell: monoclinic, P2₁/m (no. 11), Z = 4Lattice parameters: $\underline{a} = 6.821(2) \text{ \AA}$, $\underline{b} = 3.741(1) \text{ \AA}$, $\underline{c} = 14.937(3) \text{ \AA}$,
 $\beta = 95.66(3)$ Refinement: R = 0.064, R_w = 0.079 (669 reflections, $2\theta \leq 50^\circ$)

	x	z	B ₁₁ ^b	B ₂₂	B ₃₃	B ₁₃
I1	0.6031(3)	0.6095(1)	1.13(6)	0.53(6)	1.42(7)	0.07(2)
I2	0.4498(3)	0.1473(1)	1.47(7)	0.62(6)	1.18(7)	0.02(2)
I3	0.8881(3)	0.3528(1)	1.34(7)	0.57(6)	1.30(7)	-0.05(2)
I4	0.0545(3)	0.8901(1)	1.17(7)	0.58(7)	1.39(7)	-0.02(2)
Zr1	0.1892(4)	0.5036(2)	0.93(9)	0.76(8)	1.44(9)	-0.00(3)
Zr2	0.6880(4)	0.9969(2)	0.95(9)	0.81(8)	1.26(7)	-0.01(3)

$$^a y = 0.25.$$

$$^b T = \exp [(-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^{*b^{*}} + 2B_{13}hla^{*c^{*}} + 2B_{23}k\ell b^{*c^{*}})];$$

$$B_{12} = B_{23} = 0 \text{ by symmetry.}$$

Table II. Important distances (Å) and angles (deg.) in the two independent units.

$a_{1-x, 1-y, 1-z}$, $b_{1-x, 1-y, -z}$, $c_{1-x, -y, 1-z}$, $d_{1-x, -y, -z}$,
 $e_{1+x, y, z-1}$, $f_{x, y, z-1}$, $g_{-x, 1-y, 1-z}$, $h_{x-1, y, z}$,
 $i_{2-x, 1-y, 1-z}$, $j_{-x, -y, 1-z}$

Distance

Zr-Zr, Intrachain

$2^f - 2^a$	3.183(3)	$1 - 1^g$	3.181(3)
$2^a - 2^c$	3.741(1)	$1^g - 1^j$	3.741(1)

Zr - Zr, Interchain

$2^f - 2^i$	4.642(4)	$1 - 1^a$	4.644(4)
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Zr-I

$2^f - 4^e$	3.096(2)	$1 - 1$	3.099(3)
$2^f - 2$	2.896(3)	$1 - 3^h$	2.895(3)
$2^f - 4^a$	2.973(2)	$1 - 1^a$	2.973(2)
$2^f - 2^b$	2.936(2)	$1 - 3^a$	2.933(2)

I - I, Intrasheet

$4^e - 2^b$	3.909(2)	$1 - 3^a$	3.925(2)
$4^a - 2$	3.950(2)	$1^a - 3^h$	3.934(2)
$4^a - 4^c$	3.741(1)	$1^a - 1^c$	3.741(1)
$2^b - 2^d$	3.741(1)	$3^a - 3^c$	3.741(1)
$4^e - 4^a$	3.911(3)	$1 - 1^a$	3.914(3)
$4^a - 2^b$	4.469(3)	$1^a - 3^a$	4.470(2)
$2^b - 2$	4.887(3)	$3^a - 3^h$	4.884(3)
$2 - 4^e$	5.904(3)	$3^h - 1$	5.902(3)

Table II (cont.)

I - I, Intersheet

$1^a - 2$	4.132(2)
$4^a - 3$	4.136(2)
$4^a - 1^a$	5.885(3)
$3 - 2$	4.068(2)
$2 - 3^h$	5.143(2)
$1^a - 4^g$	4.948(3)

Angles

I - Zr - I, Coordination Polyhedra

$4^a - 2^f - 4^c$	77.97(7)	$1^a - 1 - 1^c$	77.97(6)
$4^a - 2^f - 2^b$	98.26(4)	$1^a - 1 - 3^a$	98.35(4)
$2^b - 2^f - 2^d$	79.15(7)	$3^a - 1 - 3^c$	79.23(6)
$2^b - 2^f - 4^e$	80.15(7)	$3^a - 1 - 1$	81.13(6)
$4^a - 2^f - 4^e$	80.23(5)	$1^a - 1 - 1$	80.23(6)
$2^b - 2^f - 2$	113.85(6)	$3^a - 1 - 3^h$	113.84(6)
$4^a - 2^f - 2$	84.58(6)	$1^a - 1 - 3^h$	84.18(6)

I - I - I, Intrasheet

$2^d - 4^e - 2^b$	57.18(3)	$3^c - 1 - 3^a$	56.92(3)
$4^e - 2^b - 2^d$	61.41(2)	$1 - 3^a - 3^c$	61.44(2)
$4^c - 2 - 4^a$	56.54(3)	$1^c - 3^h - 1^a$	56.78(3)
$2 - 4^a - 4^c$	61.73(2)	$3^h - 1^a - 1^c$	61.61(2)

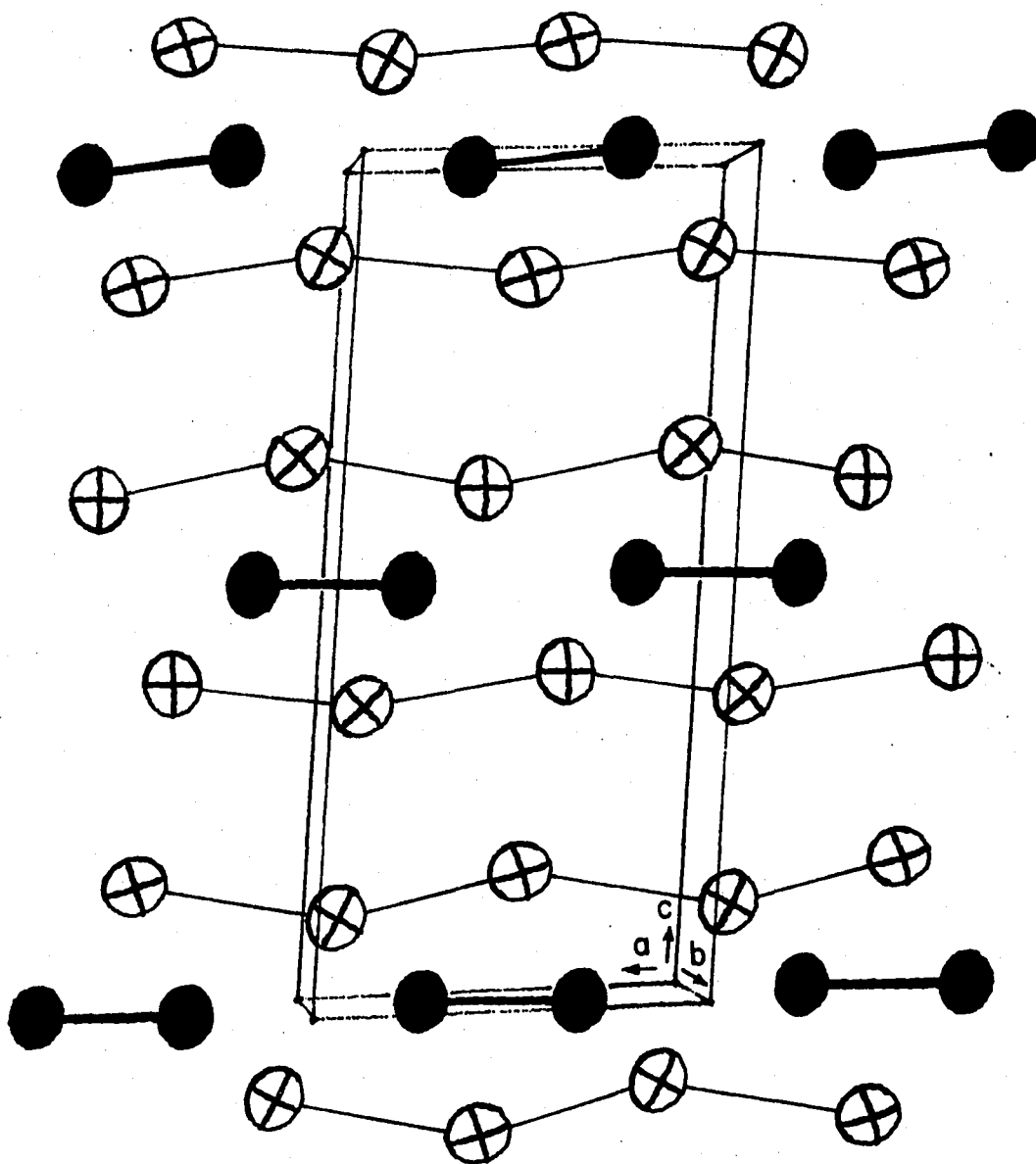


Figure 1. The $\alpha\text{-ZrI}_2$ structure viewed parallel to the zig-zag metal chains and the short b axis. Zirconium and iodine atoms are represented by solid and open ellipsoids, respectively.

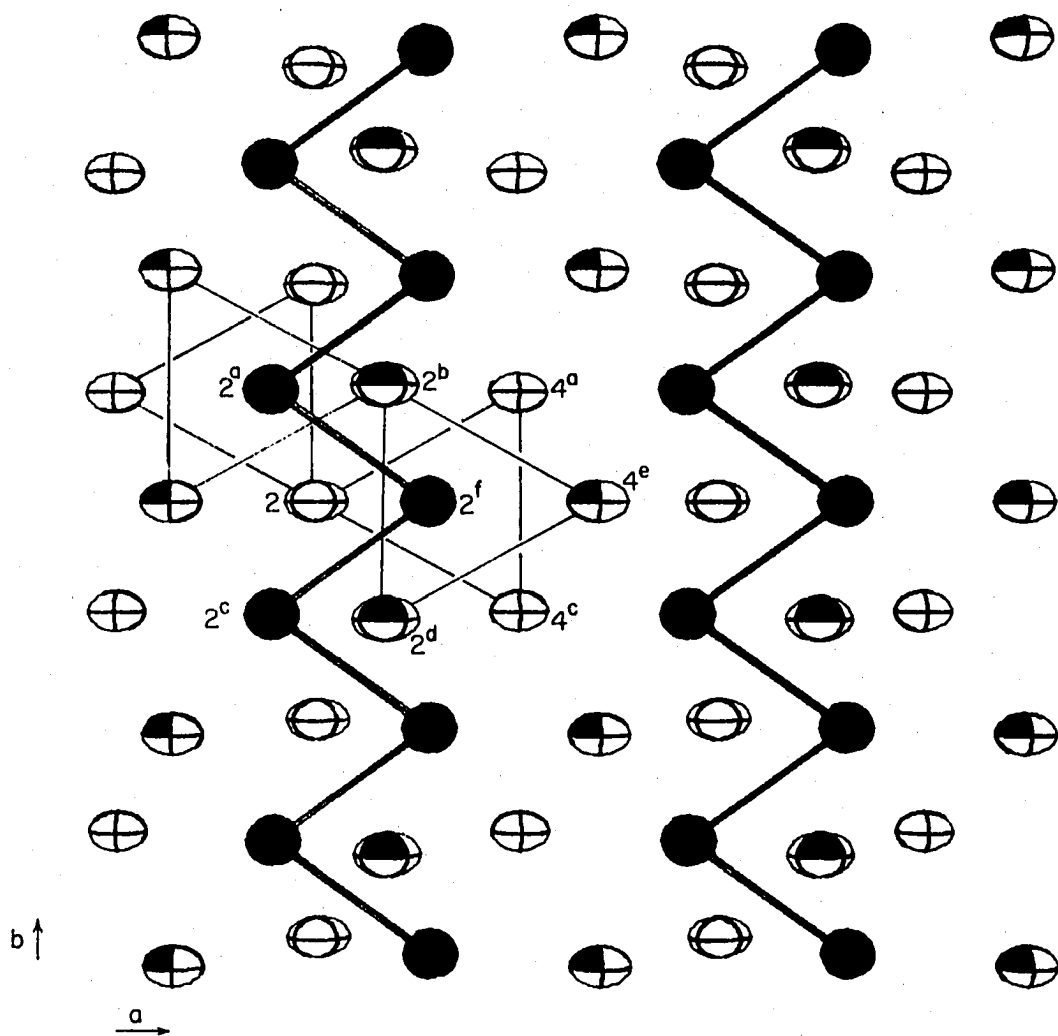


Figure 2. View of two iodine layers and the intervening zig-zag metal chains with two iodine octahedra which share a common edge outlined. All atoms lie on mirror planes at $y = 0.25$ and 0.75 . The iodine atoms partially darkened lie toward the viewer.

The metal-metal distances in α -ZrI₂ are closely comparable to those in the cluster Zr₆I₁₂ (β -ZrI₂) despite the lower number of metal neighbors in the former. The two Zr-Zr bonds per d² metal in α -ZrI₂ are formally single bonds but a substantial bonding restriction (matrix effect) is superimposed by the edge sharing of the distorted iodine octahedra, and the 3.182(2) Å distances observed corresponds to a Pauling bond order of only 0.31. In β -ZrI₂ each zirconium has pairs of metal neighbors in the Zr₆ octahedron at 3.195(1) Å and 3.204(2) Å. These are now formally bonded by half bonds and although repulsions between iodine atoms which bridge edges of the metal octahedron clearly restrict the approach of the metal atoms this is not as severe as in α -ZrI₂. Since the metal-bonding electrons do not screen the iodine atoms, the Zr-I distances are very similar throughout, 2.895(3) - 2.973(2) Å for the closer five in α -ZrI₂ vs. 2.860(2) - 2.947(2) Å for the closer four in β -ZrI₂, and 2.863 Å for the average in ZrI₄ (8). The transformation from α - to β -ZrI₂ at high temperatures involves a loss of two Zr-I bonds and a gain of two Zr-Zr bonds, and is thought to be largely entropically driven to the more open structure (the center of the Zr₆ cluster corresponds to a missing iodine atom in a close-packed layer).

The metal-metal interactions in the α -ZrI₂ chains still must be classed as "strong" since the 3.182 Å separation is less than the 3.204 Å average distance found in the (12-coordinate) metal. The result is a filled band semiconductor experimentally, with $\rho = 22$ ohm-cm and $E_g \approx 0.1$ eV at room temperature according to four probe measurements. No esr signal is observed at 94.7 Hz at either 20 or -196°C.

In a localized sense one can view the sigma bonds as generated by d_{xz} and $d_{x^2-y^2}$ orbitals, and these generate a filled band.

DISCUSSION

The α -ZrI₂ described here is isostructural and isoelectronic with β -MoTe₂ (32), and as such represents the first halide found with this particular structure. A considerable similarity also exists with the higher symmetry WTe₂ (space group Pnm2₁), the only difference being a smaller displacement of one slab with respect to another so that the β -angle, Fig. 1, decreases to 90° and an n-glide develops parallel to c. In fact an incipient n-glide in that direction is evident in the positional parameters in α -ZrI₂ except for the x-coordinates of the iodine atoms (Table I). In contrast with α -ZrI₂ however, MoTe₂ is a semi-metal with $\rho = 2 \times 10^{-3}$ ohm-cm at 25°C (33).

Structural similarities between reduced metal sulfides and selenides with those involving isoelectronic chloride and bromide anions are relatively rare. A direct relationship exists between MoS₂ and one polymorph of ZrCl₂ (23) as both have the 3R-MoS₂ type layered structure with trigonal prismatic coordination of the metals, while a lesser element of similarity occurs between Hf₂S (34) and HfCl₂ (26) where both contain infinite double metal layers but these are separated by a different number of nonmetal layers. The lack of more S vs. Cl and Se vs. Br structural similarities has been attributed to the greater covalency of the chalcide relative to that in the isoelectronic halide (35). Not surprisingly, iodine which bonds more covalently exhibits a larger number of isostructural relationships with the chalcides. Examples of these

include PrI_2 and MoS_2 (2H_1 and 3R types), GdI_2 and MoS_2 (2H_1) (36), ThI_2 and 4H-NbS_2 (37), and that seen here for $\beta\text{-MoTe}_2$ and $\alpha\text{-ZrI}_2$. Even so, mixing of iodide and metal valence orbitals is presumably less, making the bands narrower and metallic conduction less prevalent than in the chalcides.

An indication of the M-M bond strength in $\alpha\text{-ZrI}_2$ and similar distorted structures may be found in the magnitude of the lattice strain which accompanies M-M bond formation, specifically the amount of polyhedral distortion reflected in the ratio of the shortest to the longest M-X bonds (33). These ratios are 0.935, 0.959, and 0.962 for $\alpha\text{-ZrI}_2$, $\beta\text{-MoTe}_2$ and WTe_2 , respectively, indicating that $\alpha\text{-ZrI}_2$ has the strongest M-M bonds or the weakest M-X bonds. On the other hand, the metal-metal distances in both $\beta\text{-MoTe}_2$ and $\alpha\text{-ZrI}_2$ are comparable, being 10.5 and 10.7% greater than the corresponding single bond distances. Thus, relative to the semimetallic $\beta\text{-MoTe}_2$ the strong M-M bonding or greater distortion in $\alpha\text{-ZrI}_2$ combined with the greater separation of atomic orbital energies for zirconium and iodine causes a separation of a filled valence band and the empty conduction band and gives a semiconducting $\alpha\text{-ZrI}_2$.

The adoption of a distorted CdI_2 -type structure for these can easily be understood in terms of the extra stability obtained from the formation of two relatively short M-M bonds. The possibility of an $\alpha\text{-ZrI}_2 \rightarrow \beta\text{-ZrI}_2$ transition at an observable rate seems remote, as this would require more than a simple intralayer rearrangement of the metal atoms, although such a transition is thought to occur by a topotactic

path between the CdCl_2 -type structure of PrI_2 (IV) and the cluster $(\text{Pr}_4\text{I}_4)\text{I}_4$ (type V) form (36). The transition from the $\alpha\text{-ZrI}_2$ structure ($\text{P}2_1/\text{m}$) to an undistorted CdI_2 -type ($\text{P}\bar{3}\text{m}1$) structure, which requires only an intralayer displacement of the metal atoms, is allowed by Landau's theory of second order phase transitions (38) but is at present unknown. A similar transition has been observed between the MnP and NiAs -type structures of VS (39). In addition, there also exists the possibility of a low-temperature first-order phase transition in $\alpha\text{-ZrI}_2$ to the $\text{Pnm}2_1$ structure of WTe_2 . This has been observed for (metastable) $\beta\text{-MoTe}_2$ where the β angle varies discontinuously from 93.92° ($\text{P}2_1/\text{m}$) to 90° ($\text{Pnm}2_1$) within the temperature range $17^\circ\text{C} \rightarrow -40^\circ\text{C}$ (40), the low temperature orthorhombic structure thus being produced via a shear deformation of the nonmetal layers perpendicular to the \underline{c} axis. The pseudosymmetry relating atomic coordinates in the present structure (Table I) that was noted earlier reflects this potential.

A series of orthorhombic zirconium diiodides has recently been reported (41) which had cell parameters: $\underline{a} = 3.74 \text{ \AA}$, $\underline{b} = 6.93 \text{ \AA}$, $\underline{c} = n \times 14.85 \text{ \AA}$, where the $n = 24$ polytype was studied the most. These were obtained in the $760\text{--}780^\circ\text{C}$ temperature range and were thought to contain "alternating I-Zr-I double layers". Since the axial lengths are similar to those reported here, these may represent polytypes of a WTe_2 -type structure or, less likely, 2H-CdI_2 , with pairs of three layer slabs in the simple unit.

STRUCTURE OF β -ZrI₂: A M₆X₁₂ CLUSTER

INTRODUCTION

Binary halogen-bridged clusters of the early transition metals such as $M_6X_{12}^{n+}$ ($n = 2,3,4$) and $M'_6X'_8^{m+}$ ($m = 4$ principally) which contain an octahedral cluster of metal atoms have been well-known for several years (42). The transition metals usually associated with these compounds are $M = Nb$ and Ta and $M' = Mo$ and W . Recently, however, some newcomers have appeared on the scene: Zr_6Cl_{15} , Sc_7Cl_{12} and Zr_6I_{12} (20). This trio has facilitated a new trend of thinking: that six atom clusters can indeed be stable even though they may contain as few as 9 e/cluster, as is the case for Zr_6Cl_{15} and Sc_7Cl_{12} . Prior to this no clusters were known with fewer than 14 e/cluster and no discrete clusters of any sort had been made with elements earlier in the transition metal block than group V. Even now this trio has already been expanded to include Zr_6Cl_{12} and Zr_6Br_{12} (21) which are isostructural with Zr_6I_{12} as well as La_7I_{12} (43) which is isostructural with Sc_7Cl_{12} . The late arrival of metal clusters in groups III and IV is partly because suitable containers have only recently been known, but also it may be attributed to kinetic problems of formation rather than thermodynamic limitations of stability. A communication containing the original trio has appeared (20); Zr_6Cl_{15} and Sc_7Cl_{12} are discussed in more detail in Daake's (11) and Poeppelmeier's (44) theses, while a more-detailed discussion of Zr_6I_{12} will now be presented.

DATA COLLECTION

Gem crystals of $\beta\text{-ZrI}_2$ were sealed in 0.3 mm thin-wall glass capillaries under a dry nitrogen atmosphere. A single crystal, 0.25 x 0.35 x 0.45 mm, was selected via oscillation photos, indexed and diffraction data were collected on a rhombohedral cell with the hexagonal axes $\underline{a} = 14.502(2)$ and $\underline{c} = 9.996(2)$ Å based on tuned 2θ values for 12 reflections ($30 \leq 2\theta \leq 44^\circ$). Two octants of data, HKL and $\overline{H}\overline{K}\overline{L}$, ($2\theta \leq 50^\circ$) yielded 1119 observed ($I > 3\sigma(I)$) reflections which, when reduced and averaged in Laue symmetry $\overline{3}$, gave 609 independent reflections.

STRUCTURE DETERMINATION

Initial least-squares refinement on two iodine atoms and one zirconium atom (18-fold general positions) obtained via MULTAN (20) gave an $R = 0.14$. At this point a difference map indicated negative peaks at the atom positions. Examination of the data revealed low angle (2 θ) reflections had F_o 's significantly less than F_c 's and that the large intensity reflections ($F_c > 700$) also had $F_o < F_c$ indicating absorption and secondary extinction problems (45), respectively. Therefore, the raw data were corrected for absorption by TALABS (29) with a crystal shape defined by nine intersecting faces and a $\mu = 178 \text{ cm}^{-1}$ (31). The data were again reduced and averaged and input into EXTLSS (46) (a least-squares program which also allows correction for secondary extinction).

The isotropic full-matrix least-squares refinement converged at $R = \Sigma ||F_o| - |F_c|| / |F_o| = 0.150$. Final least-squares refinement with anisotropic thermal parameters, including reweighting (10 groups for 609 reflections, original $\omega\Delta^2$'s varied from 0.377 - 3.197) resulted in an $R = 0.109$ and $R_w = [\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega|F_o|^2]^{1/2} = 0.121$. A final difference map was flat to $\leq 1 \text{ e}/\text{\AA}^3$, even at the center of the cluster.

DESCRIPTION OF THE STRUCTURE

Final positional and thermal parameters for β -ZrI₂ are listed in Table III and important distances and angles, in Table IV. Structure factor results are available in Appendix B. In Figure 3 the cluster (Zr₆I₁₂) is viewed with the $\bar{3}$ axis vertical; approximately c.c.p. iodine layers stack vertically while zirconium atoms form a trigonal antiprism on either side of the middle iodide layer. The Zr-Zr inter-layer distances are slightly shorter than the intralayer bonds, 3.194(1) Å and 3.204(2) Å, respectively. The average Zr-Zr distance in this cluster is basically the same as those observed in α -Zr metal where the average Zr-Zr distance is 3.204 Å (6 neighbors each at 3.179 Å and 3.231 Å) (47).

In Figure 3 there are six zirconium atoms and eighteen iodine atoms yet the stoichiometry is Zr₆I₁₂. This is determined by the sharing of the iodines between different metal clusters. The six solid-black I2 atoms which bridge the edges of the two metal triangles, three above and below the cluster, bond only to the cluster shown and therefore are considered inner (i) iodines. The six striped I1 atoms about the waist of the cluster, bridging the two metal triangles, also occupy an exo position in a neighboring cluster and are referred to as inner-outer (i-a, a = aussen (42)). Finally, the six dotted I1 atoms in exo positions, three above and below the cluster, also bridge metal triangles in a neighboring cluster; that is to say they bond in the opposite manner as the striped iodine atoms just mentioned and are

Table III. Crystallographic data and atom parameters for Zr_6I_{12} .

Composition: Zr_6I_{12} , $Z = 3$

Cell: trigonal, $R\bar{3}$ (No. 148)

Lattice Parameters: $a = 14.502(2) \text{ \AA}$, $c = 9.996(2) \text{ \AA}$

Refinement: $R = 0.109$, $R_w = 0.121$ (609 reflections, $2\theta < 50^\circ$)

	x	y	z	B_{11}^a	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	
$I1^b$	0.35512(8)	0.10264(8)	0.33260(9)	2.14(6)	1.83(6)	1.5(1)	0.65(2)	0.23(2)	0.15(2)	∞
$I2^c$	0.12625(7)	0.17765(8)	0.3246(1)	1.64(6)	1.96(6)	1.2(1)	0.45(2)	-0.102(2)	-0.25(2)	
Zr1	0.1430(1)	0.0406(1)	0.1303(1)	1.07(6)	1.01(6)	0.7(1)	0.25(2)	0.02(2)	0.00(2)	

$$^a T = \exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^{*}b^{*} + 2B_{13}hla^{*}c^{*} + 2B_{23}k\ell b^{*}c^{*})].$$

^b Inner-outer (i-a) and outer-inner (a-i) iodine atoms.

^c Inner (i) iodine atoms.

Table IV. Important distances (Å) and angles (deg.) for Zr_6I_{12} .^a

<u>Distances</u>			<u>Bond angles</u>
<u>Zr-Zr</u>			
3-3 ^d	intralayer	3.204(2)	
3-3 ^b	interlayer	3.194(1)	
<u>Zr-I2</u>			<u>Zr-I2-Zr</u>
3 ^d -2		2.860(2)	67.96(5)
3-2		2.873(2)	
<u>Zr-I1</u>			<u>Zr-I1-Zr</u>
3-1 ^c		2.917(2)	66.02(4)
3 ^b -1 ^c		2.946(2)	
<u>Zr-I1</u>			
3-1 ^d		3.406(2)	

^aSuperscript letters are symmetry operations for atoms in Figure 3.

^b $y, y-x, -z$

^c $1/3-y, x-y-1/3, z-1/3$

^d $-y, x-y, z$

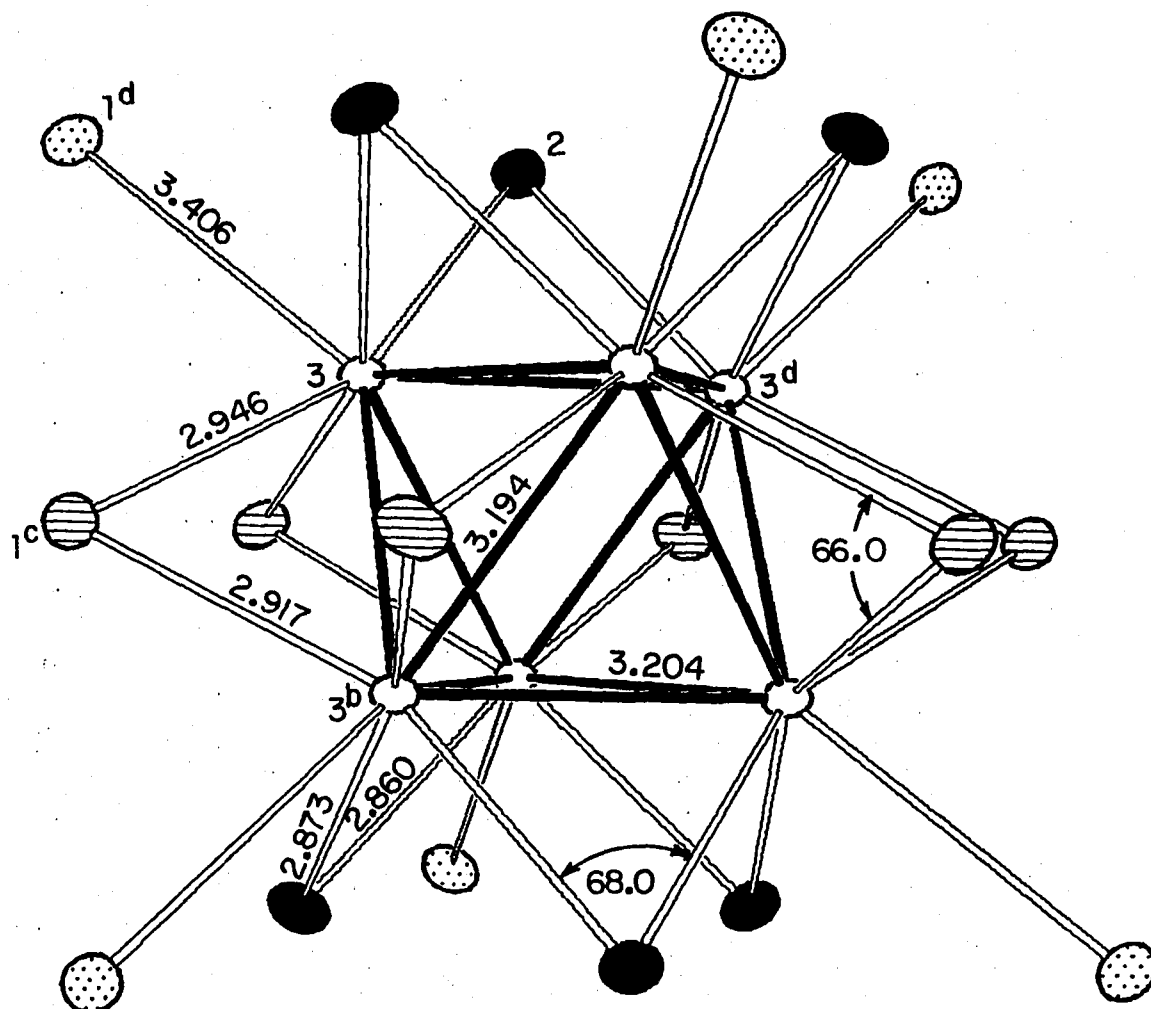


Figure 3. The Zr_6I_{12} cluster with the $\bar{3}$ axis of the cluster vertical and the zirconium atoms connected by heavy lines. The iodines are coded according to their bonding between clusters: solid I2 atoms are inner (i), striped I1 atoms are inner-outer (i-a) and dotted I1 atoms are outer-inner (a-i). Distances are in Angstroms and angles in degrees. The letters in atom identification refer to symmetry operations, Table IV.

designated as outer-inner (a-i) iodines. Therefore a more nearly precise description of the Zr_6I_{12} cluster is $Zr_6I_6^{i-i-a}I_{6.2/3}^{a-i}I_{6.1/3}$. The Zr-I distances agree with this bonding scheme: the Zr- I^i distances of 2.860 - 2.873 Å are shorter than the Zr- I^{i-a} distances, 2.917 - 2.946 Å, which are shorter than the Zr- I^{a-i} distances of 3.406 Å. The Zr_6I_{12} cluster can also be viewed as made-up of iodine and metal layers which stack in a cubic-closest packing sequence (ABC...). This is described elsewhere (44).

DISCUSSION

The two compounds Zr_6I_{12} and $Sc^{3+}ScCl_{12}^{3-}$ (Sc_7Cl_{12}) are closely related; the metal and halide atoms occupy the same positions except for the cation in the scandium compound. Figure 4 shows a $(11\bar{2}0)$ section of the Zr_6I_{12} structure. In the $R\bar{3}m$ space group the Sc^{3+} cation occupies the special $\bar{3}$ position $(0\ 0\ 1/2)$ which lies directly above and below the metal clusters along the three-fold axis. As of yet no binary or ternary zirconium compound with a cation of this position has been synthesized. However, it seems very plausible that a compound with a small cation such as Na^+ or K^+ , which would fit into an iodide octahedral hole, could indeed be made (see FUTURE WORK).

In addition to Zr_6I_{12} being isotypic with Sc_7Cl_{12} , both have properties which are similar to those of Zr_6Cl_{15} . All three have the same crystal morphology, gems with very well defined faces. There is also an interesting similarity in their synthetic habits: All have been observed to form crystals which either grow from a whisker-like crystal or have a whisker crystal attached to them. In the case of Sc_7Cl_{12} , this whisker is assumed to have the composition $ScCl_{1.45}$ and an explanation is given by Poepelmeier (44). The existence of such a whisker in the case of Zr_6I_{12} was observed earlier (19). Besides these similarities between Zr_6I_{12} , Zr_6Cl_{15} and Sc_7Cl_{12} there are at least two striking differences. First, in the final Fourier synthesis difference map no residual electron density is found at the center of the Zr_6I_{12} cluster, while there are ~ 7 and ~ 8 electrons/ \AA^3 at the center of the Zr_6Cl_{15} and

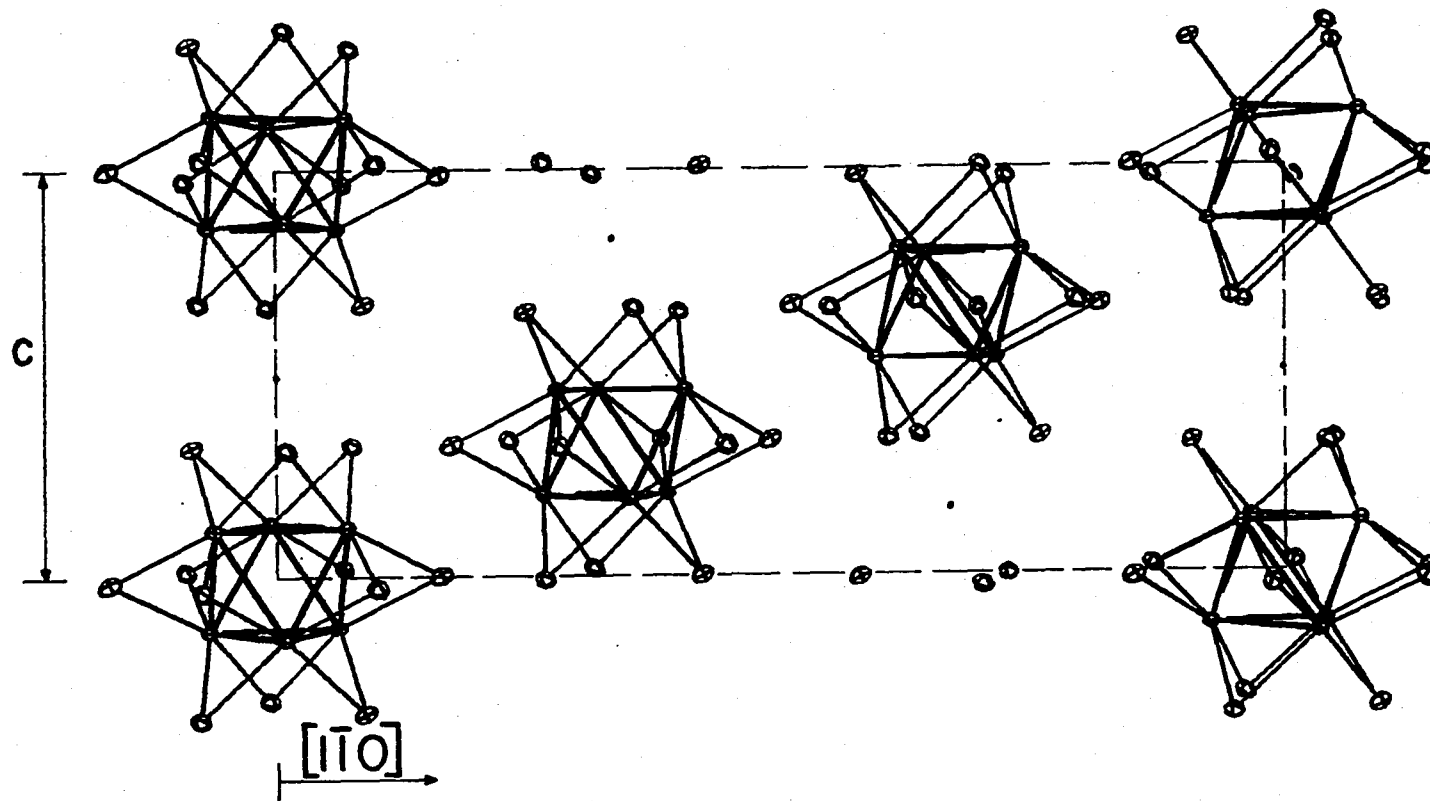


Figure 4. A $(11\bar{2}0)$ section of the Zr_6I_{12} structure which shows only the $Zr-I^{\frac{1}{2}}$ bonds. The dots just above and below the clusters are special positions with $\bar{3}$ symmetry which contain a Sc^{3+} cation in Sc_7Cl_{12} .

$\text{Sc}_7\text{Cl}_{12}$, respectively. The absence of residual electron density in a $\text{Zr}_6\text{Cl}_{12}$ cluster in $\text{K}_2\text{Zr}_7\text{Cl}_{18}$ (21) has been reported as well as the presence of the same in the La_7I_{12} (43) compound. Secondly, while $\text{Zr}_6\text{Cl}_{15}$ and $\text{Sc}_7\text{Cl}_{12}$ both have only 9 e/cluster, Zr_6I_{12} has 12. If a general molecular orbital bonding scheme is followed for an octahedral M_6X_{12} cluster with 12 electrons, they would occupy the a_{2u} and t_{1u} (xz, yz) bonding orbitals with the four remaining electrons going into a t_{1u} (z^2) level (48). Therefore this phase should be paramagnetic with two unpaired electrons. However, the point group symmetry is D_{3d} and not O_h since the iodides about the waist of the cluster differ from those above and below the cluster and since the interlayer Zr-Zr bonds are slightly shorter than the intralayer Zr-Zr bonds. Therefore, on going from $O_h \rightarrow D_{3h}$ the t_{1u} level splits into an e_u and an a_{2u} level. Now the four electrons pair up in the lower energy e_u level. This is consistent with the absence of any esr signal for this phase at either room or liquid N_2 temperatures.

THE "PHASE" $ZrI_{1.8}$

INTRODUCTION

A phase identified as $ZrI_{1.8}$ was first synthesized and its x-ray powder pattern reported by Daake (11). It was supposed to be the lowest limit in a composition range ZrI_x , $1.8 \leq x \leq 1.95$, obtained from the reaction of ZrI_3 or ZrI_4 with a large excess of zirconium at $\sim 750^\circ C$ for two weeks. The initial thrust of this research was to obtain single crystals of " $ZrI_{1.8}$ "; in that attempt the phases α - and β - ZrI_2 were synthesized and identified.

RESULTS

A problem developed, in that though $\alpha\text{-ZrI}_2$ had been well characterized and crystals could easily be obtained, a pure α -phase powder pattern had never been observed, but rather a " $\text{ZrI}_{1.8}$ " pattern. Subsequent Weissenberg work on some of the single $\alpha\text{-ZrI}_2$ crystals also revealed extra reflections, initially assumed to be due to a superstructure. Instead, a twinning mechanism was found which has shed new light on the powder pattern reported for " $\text{ZrI}_{1.8}$ ".

The Weissenberg photography contained extra reflections in the $h0l$ festoons. However, rather than occurring in an ordered fashion, where each festoon would have extra reflections in the same location, the extra reflections were spaced: None in the $00l$, $\sim 4/5$ in the $10l$, $\sim 1/2$ in the $20l$, $\sim 1/3$ in the $30l$, $\sim 1/6$ in the $40l$ and none in the $50l$.

The twinning was first assumed to be due to the intergrowth of monoclinic cells in different orientations. However, when a^*c^* reciprocal nets for two monoclinic cells were superimposed, the observed pattern for the extra reflections could not be obtained. Therefore, via trial and error an orthorhombic reciprocal net twinned with a monoclinic a^*c^* reciprocal net was found to produce the pattern seen in the Weissenberg. This twinning mechanism can be seen in Figure 5; the solid lined cell is the reciprocal a^*c^* net for the $\alpha\text{-ZrI}_2$ monoclinic cell; superimposed on that is a dashed reciprocal net for an orthorhombic cell with very similar dimensions. The points at which the orthorhombic cell intersects the $h0l$ festoons agrees very well with that observed in the Weissenberg

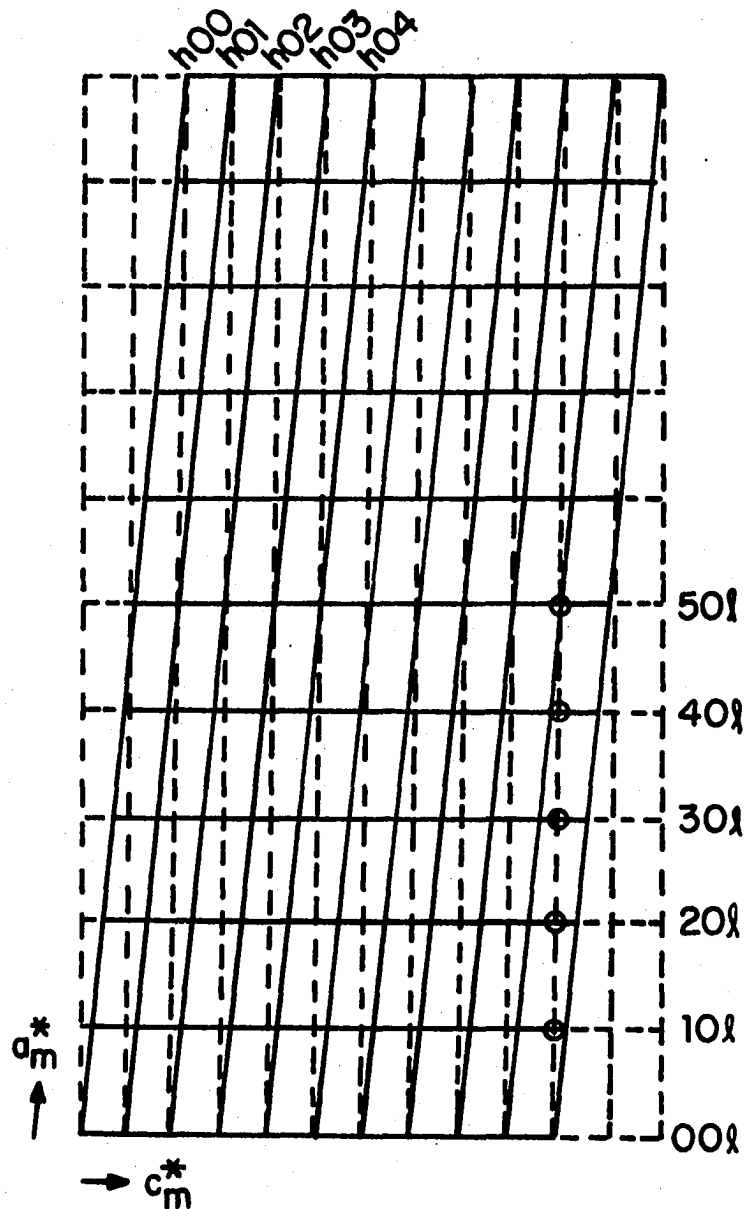


Figure 5. The twinning mechanism of a monoclinic and orthorhombic cell. The solid lined cell is the a^*c^* net from $\alpha\text{-ZrI}_2$ while the dashed cell corresponds to a reciprocal net for an orthorhombic cell of similar dimensions. The circles show the location of extra reflections on the $h0l$ festoons arising from the orthorhombic cell.

photographs, yielding no extra reflections on the 00ℓ line (a festoon in Weissenberg photography), while extra reflections were at $\sim 4/5$ on the 10ℓ , $\sim 1/2$ on the 20ℓ , $\sim 1/3$ on the 30ℓ , $\sim 1/6$ on the 40ℓ and no extra reflections on the 50ℓ line. Reflections higher than 50ℓ could not be verified.

The existence of an orthorhombic zirconium iodide having cell parameters very similar to $\alpha\text{-ZrI}_2$ was not a surprise. Such a cell had been obtained from a blade-like crystal found in reaction 21 (19) with $\underline{a} = 3.738(1)$, $\underline{b} = 6.817(2)$ and $\underline{c} = 14.860(4)$ Å. Since $\alpha\text{-ZrI}_2$ is isoelectronic and isostructural with $\beta\text{-MoTe}_2$ (32), the assumption that this orthorhombic phase might have the closely related orthorhombic WTe_2 structure (32) was only logical, especially since $\beta\text{-MoTe}_2$ is known to transform into the WTe_2 structure at 250 K (40). Therefore, data were collected on the above mentioned cell and averaged in mmm Laue symmetry to yield 371 independent reflections ($2\theta \leq 50^\circ$). The extinctions observed were correct for WTe_2 (Pmn_2). Least-squares refinement of the atom positions from the WTe_2 structure along with isotropic thermal parameters ranging from 0.40-1.0 (in $\alpha\text{-ZrI}_2$, they were 0.65-1.4) resulted in an $R = 0.20$. Further refinement with anisotropic thermal parameters was attempted; however, the β_{22} 's on all the atoms went negative indicating a problem in the \underline{b} direction which has not yet been resolved. A Fourier difference synthesis map obtained earlier using isotropic thermal parameters held constant at 1.0 and at an $R = 0.20$ was flat to $\pm 2e/\text{Å}^3$ at all points except the atom positions which had 4-6 $e/\text{Å}^3$ (probably due to the slightly large thermal parameters). Examination of the data from

the diffractometer revealed that the reflection peaks were broad and the background count high, both being attributable to a poor single crystal. No other single crystals with an orthorhombic cell have been mounted and although a lot of work has been done above 900°C, these crystals were only observed in the gradient reactions 21 and 35 (19). References to other orthorhombic zirconium iodide phases have been made. Daake (11) reported such a phase with the cell parameters $a = 3.75$, $b = 6.85$ and $c = 15.0 \text{ \AA}$ obtained from Weissenberg work on a product of one of his "ZrI_{1.8}" reactions. In addition, a series of orthorhombic zirconium diiodides, obtained between 760-780°C, have recently been reported (41) with $a = 3.74$, $b = 6.93$ and $c = 14.85 \times n \text{ \AA}$, where the $n = 24$ polytype was studied the most.

The fact that an orthorhombic phase has been found to be twinned with $\alpha\text{-ZrI}_2$ sheds new light upon the powder pattern reported for "ZrI_{1.8}" (11). Figure 6 contains the graphed powder patterns of $\alpha\text{-ZrI}_2$, "ZrI_{1.8}" and an orthorhombic ZrI₂. The cell parameters for the last are those stated above while the atom positions used were from WTe₂ (32). It now appears that the "ZrI_{1.8}" pattern is a mixture containing $\alpha\text{-ZrI}_2$, ZrI₂ (WTe₂), probably intergrown, and a third unknown phase. The two strong doublets in the "ZrI_{1.8}" pattern at $\sim 29^\circ$ and $\sim 48^\circ$ as well as the singlet line at $\sim 12^\circ$ in 2θ differ in intensity from the calculated patterns because of known preferred orientation associated with mounting the sample. Three of the lines (those having dots above them) unaccounted for by the calculated patterns are observed to vary independent of the two calculated patterns in Daake's film data. These lines are stronger

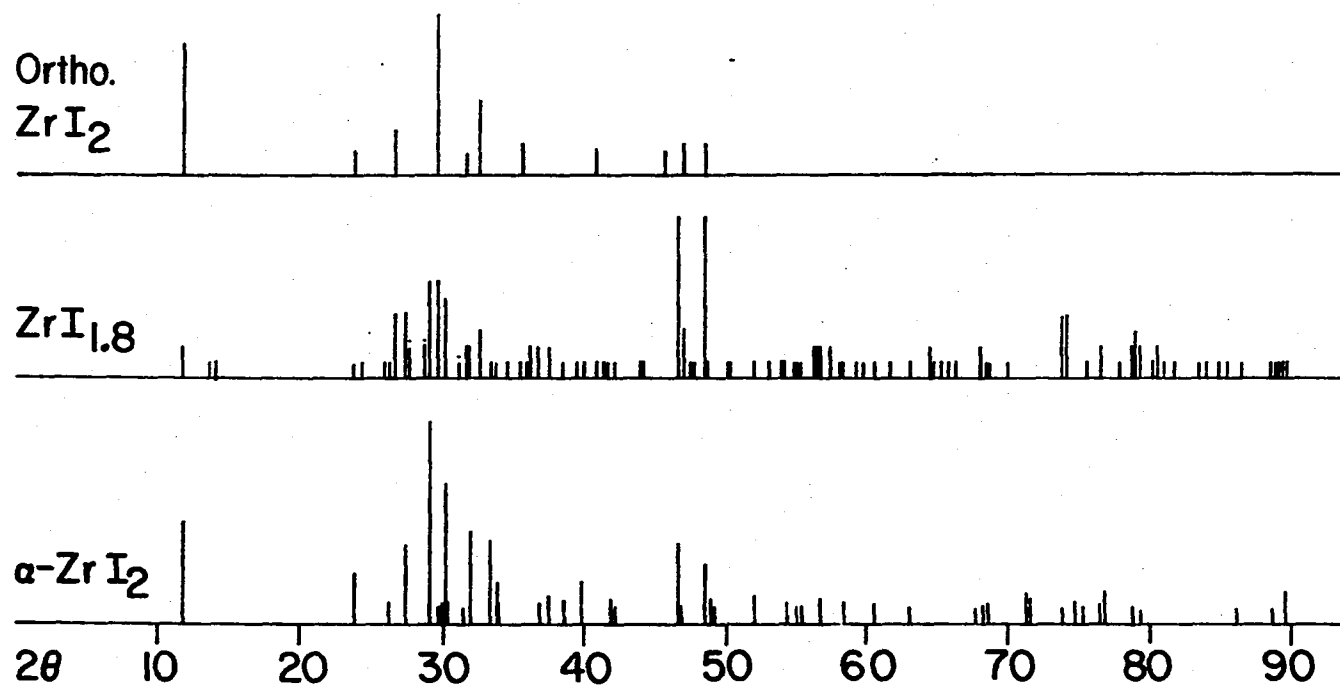


Figure 6. The Guinier x-ray powder diffraction patterns for α -ZrI₂ (calc.) ZrI_{1.8} (obs.) and an orthorhombic ZrI₂ (calc. using WTe₂ atom positions). The intensity of the two doublets at $\sim 29^\circ$ and $\sim 48^\circ$ along with the singlet at $\sim 12^\circ$ in 2θ in the ZrI_{1.8} graph differ from the patterns above and below because of preferred orientation problems. The three extra lines dotted in the ZrI_{1.8} pattern were observed to vary with composition.

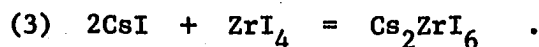
in powder patterns obtained from more reduced samples (I:Zr = 1.8) relative to more oxidized samples (I:Zr = 1.95). If this third phase were a reduced phase, ZrI_{2-x} , it would explain the low stoichiometries of 1.8 - 1.95 found by Daake rather than 2.0.

Finally, it is believed that the orthorhombic phase is formed at relatively high temperatures, above $900^{\circ}C$, while the monoclinic α - ZrI_2 phase is found between 700 - $825^{\circ}C$. Weissenberg and powder diffraction work has shown all α - ZrI_2 crystals to be twinned with varying amounts of the orthorhombic phase.

PART II. THE TERNARY CsI-Zr-ZrI₄ SYSTEM

No prior work in the CsI-Zr-ZrI₄ ternary system had been done. However, the compounds Cs₂ZrCl₆ (14) and Cs₃Nb₂Cl₉ (15) were well known and now the analogous zirconium iodides have been synthesized. In addition to these two compounds a third, CsZr₆I₁₄, has been discovered along with evidence for a fourth. As in the binary system, initial reactions in this ternary system were transport-type reactions with ~150°C gradients, e.g. 600-750°C or 750-900°C. This provided a wide variety of temperatures to allow the formation of any possible phase. Then when a phase was identified either by a crystal structure or powder pattern, attempts were made to synthesize each phase in larger quantities. Via this approach, virtually every temperature region from 600-975°C has been explored. Above 800°C, temperatures were explored by both small and large gradients, <50°C and 100-200°C, respectively, while below 800°C most gradients were >50°C. The starting materials were always ZrI₄, CsI (usually in a 3:1 ratio) and metal. The four new compounds mentioned above along with their apparent formation ranges have been found: Cs₂ZrI₆ (~600-700°C), Cs₃Zr₂I₉ (~700-900°C), CsZr₆I₁₄ (~900-950°C) and "Q" (~950-1000°C).

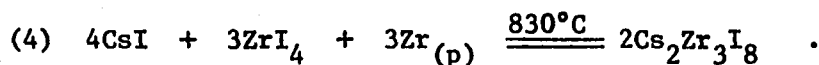
Cs₂ZrI₆ (see Appendix C) was obtained in ~600-700°C by reaction 3.



The orange Cs₂ZrI₆ crystals grind to a yellow-orange powder.

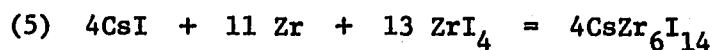
$\text{Cs}_3\text{Zr}_2\text{I}_9$ was obtained as black crystals, dark green when ground, between $\sim 700\text{--}900^\circ\text{C}$ from isothermal or gradient reactions of 0.4 g ZrI_4 (0.668 mmoles) and 0.058 g CsI (0.219 mmoles) (an $\sim 3:1$ molar ratio) with excess (2-4 g) zirconium strips. The CsI was generally completely consumed with the remaining ZrI_4 forming binary phases. Typical reaction times were 2-3 weeks.

As is often the case, $\text{CsZr}_6\text{I}_{14}$ was first obtained in an attempt to synthesize another phase. The original stoichiometry was that shown in reaction 4.



The proposed product would have $6e/\text{Zr}_3$ unit and therefore be isoelectronic and possibly isostructural with $\text{Zn}_2\text{Mo}_3\text{O}_8$ (49). (Hindsight being 20/20 enables one to say that a more reasonable attempt would have utilized NaI or KI since the smaller cation would probably fit better in an iodine octahedral hole relative to the larger Cs^+ (see FUTURE WORK).) Gem crystals of $\text{CsZr}_6\text{I}_{14}$ (crystals 1 actually $\text{CsZr}_6\text{I}_{14}\text{H}_x$, see DISCUSSION in $\text{CsZr}_6\text{I}_{14}$ section) resulted from this reaction along with $\text{Cs}_3\text{Zr}_2\text{I}_9$, ZrI_2 and ZrI_3 .

The balanced equation for the synthesis of $\text{CsZr}_6\text{I}_{14}$ is shown in reaction 5. However, when ZrI_4 and CsI



were reacted in an $\sim 3:1$ molar ratio (0.4 g ZrI_4 and 0.058 g CsI) with excess metal (~ 3 g) for 20 days in a $900\text{--}925^\circ\text{C}$ gradient, only ~ 10 mg

of $\text{CsZr}_6\text{I}_{14}$ (nonfibrous rod crystals, crystals 2) were obtained along with $\text{Cs}_3\text{Zr}_2\text{I}_9$, ZrI_2 and ZrI_3 . The problem with synthesizing larger quantities of $\text{CsZr}_6\text{I}_{14}$ appears to be that the metal surface becomes blocked as in the binary system. Under such circumstances most of the CsI goes into the cesium-rich $\text{Cs}_3\text{Zr}_2\text{I}_9$ compound while the remaining iodine from ZrI_4 forms more reduced binary phases.

The yet unidentified phase "Q" has generally been seen above 920°C . In reaction Cs 11 (19), fur or hair-like crystals (5%) were found in the $\sim 970^\circ\text{C}$ region of this $\sim 900\text{--}980^\circ\text{C}$ gradient reaction. However, similar crystals have also been seen at somewhat lower temperatures, $\sim 920^\circ\text{C}$, in Cs 18 (19), a $900\text{--}925^\circ\text{C}$ gradient reaction. In both cases the reactants were 0.4 g ZrI_4 , 0.058 g CsI and ~ 3 g Zr strips, while the products were $\text{Cs}_3\text{Zr}_2\text{I}_9$, $\text{CsZr}_6\text{I}_{14}$, ZrI_2 and the fur crystals. Thus far all phase "Q" crystals have been too frail for mounting and no powder pattern has been recorded because of the small quantities.

No other phases have been observed; however, in some ternary reactions the metal strips have been found to be very brittle. This usually occurs above 900°C . In such cases the metal can often be ground into a powder which yields a powder pattern the same as the metal itself. This has not been observed in all ternary reactions containing metal strips above 900°C nor has it been observed in any binary reactions.

THE STRUCTURE OF $\text{Cs}_3\text{Zr}_2\text{I}_9$
AND A COMPARISON WITH $\text{Cs}_3\text{Y}_2\text{I}_9$

INTRODUCTION

The collection of enneahalodimetallates(III), $A_3M_2X_9$, has been growing with the development of new techniques for their preparation (50,51). However, very little is known about iodides of this stoichiometry and little quantitative data, i.e., on their crystal structures, are available. Only $Cs_3Bi_2I_9$ (52,53) and $Cs_3Sb_2I_9$ (53,54) both crystallizing from aqueous solution, have been investigated by means of single crystal x-ray techniques. These have the $Cs_3Cr_2Cl_9$ -type structure (55) with $(chc)_2$ stacking of CsI_3 layers (alternative description: ABACBC). All the face-sharing I_6 -octahedra are filled with bismuth (or antimony) to yield 'isolated' confacial bioctahedra $Bi_2I_9^{3-}$ (or $Sb_2I_9^{3-}$). Coulomb repulsion between the tripositive metal atoms in these and other $M_2X_9^{3-}$ groups has been said (56) to lead to enlarged M-X distances and angles at the bridging anions compared with those to the terminal ones.

At first glance the synthesis of the title compound, $Cs_3Zr_2I_9$, may appear to be of no great significance since literally hundreds of these $A_3M_2X_9$ phases are known. However, the synthesis and characterization of $Cs_3Zr_2I_9$ along with $Cs_3Y_2I_9$ provides a view of a new trend: what happens when one electron per metal is added to a series $Cs_3M_2I_9$ to allow the formation of a metal-bonded species. A somewhat similar series has been studied in $Cs_3Cr_2Cl_9$, $Cs_3Mo_2Cl_9$ (57), $K_3W_2Cl_9$ (58), where the principal quantum number of the transition metal changes while the number of valence electrons (d^3) is held constant. Here the

metal-metal distance within the biotahedra was found to shorten from 3.12 (Cr) to 2.41 Å (W), indicating the presence of substantial metal-metal bonding in the latter case. Therefore a comparison of $\text{Cs}_3\text{Zr}_2\text{I}_9$ with $\text{Cs}_3\text{Y}_2\text{I}_9$, where the M^{3+} ions have a $4d^1$ and $4d^0$ configuration, respectively, was of interest and will be considered.

DATA COLLECTION

All reflection data within a sphere defined by $2\theta \leq 60^\circ$ in the HKL, $\bar{H}\bar{K}L$ and $H\bar{K}L$ octants were measured. The 3826 observed reflections ($I > 3\sigma(I)$) were corrected for Lorentz-polarization effects and averaged to 623 independent reflections. The extinction $hh2\bar{h}l$ with l odd was observed from which the trigonal space group $P31c$ was assumed. This was later converted to the hexagonal space group $P6_3/mmc$ when the positional parameters were observed to have the higher symmetry.

STRUCTURE DETERMINATION

One iodine and the zirconium position were obtained from a Patterson map and the remaining atom positions were located from a Fourier synthesis map. After full-matrix least-squares refinement of positional and isotropic thermal parameters R was 0.15. Refinement with anisotropic thermal parameters lowered this to a $R = 0.085$ and $R_w = 0.158$. The diffraction data were then reweighted in groups sorted on F_o to give final residuals $R = 0.083$ and $R_w = 0.075$, where the shift/error values were ≤ 0.001 for all parameters. A Fourier difference map computed at this point was flat to $\leq \pm 2e/\text{\AA}^3$ at the atoms and $\leq \pm 1e/\text{\AA}^3$ elsewhere.

DESCRIPTION OF THE STRUCTURE

The compound $\text{Cs}_3\text{Zr}_2\text{I}_9$ crystallizes in space group $P6_3/mmc$ with two formula units per cell and is isotypic with $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ (55). Final positional and thermal parameters are given in Table V. Distances and angles are listed in Table VI while the observed and calculated structure factors are available in Appendix D. The lattice constants determined from least-squares refinement of tuned 2 θ values from the data crystal are $a = 8.269(1)$, $c = 19.908(3)$ Å, $c/a = 2.408$, and the molar volume is 335.0 cm^3 .

In this structure, layers of close-packing atoms of the composition CsI_3 are stacked in the c lattice direction with relative ordering ABACBC or, alternatively, $(\underline{chc})_2$. Two-thirds of the octahedral interstices are filled with M^{3+} in pairs so that a confacial bioctahedron $\text{Zr}_2\text{I}_9^{3-}$ is formed, as shown in Figure 7. The structure is closely related to that of hexagonal BaTiO_3 (59) or CsCdCl_3 (60); in the latter all octahedral sites between CsCl_3^{2-} layers stacked in the same manner are occupied by Cd^{2+} to generate zig-zag chains of CdCl_6 octahedra in which single octahedra share corners with confacial bioctahedra. In the $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ -type defect structure the single octahedral sites are left vacant.

Table V. Crystallographic data and atom parameters for $\text{Cs}_3\text{Zr}_2\text{I}_9$.

Composition: $\text{Cs}_3\text{Zr}_2\text{I}_9$, $Z = 2$								
Cell: hexagonal, $P6_3/mmc$ (No.								
Lattice parameters: $a = 8.269(1) \text{ \AA}$, $c = 19.908(3) \text{ \AA}$								
Refinement: $R = 0.087$, $R_w = 0.075$ (623 reflections, $2\theta \leq 60^\circ$)								
Atom	Wyckoff Notation	x	y	z	B_{11}^a	B_{22}	B_{33}	B_{23}
Cs1	4f	1/3	2/3	0.0699(1)	4.28(6)	B_{11}	2.78(7)	0
Cs2	2b	0	0	1/4	3.60(7)	B_{11}	2.76(9)	0
Zr	4f	2/3	1/3	0.17128(9)	1.97(5)	B_{11}	1.45(6)	0
I1	12k	0.83187(8)	2x	0.08987(4)	3.82(4)	2.36(4)	2.46(4)	0.71(3)
I2	6h	0.4949(1)	2x	1/4	4.36(6)	2.75(6)	2.50(5)	0

$$a_T = \exp[4^{-1}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^{*b^{*}} + 2B_{13}hla^{*c^{*}} + 2B_{23}k\ell b^{*c^{*}})]$$

$$B_{12} = B_{22}/2; B_{13} = B_{23}/2.$$

Table VI. Bond Distances (\AA) and Angles (deg.) in $\text{Cs}_3\text{Zr}_2\text{I}_9$ and $\text{Cs}_3\text{Y}_2\text{I}_9$.^a

<u>$\text{Cs}_3\text{Zr}_2\text{I}_9$</u>		<u>$\text{Cs}_3\text{Y}_2\text{I}_9$</u>
3.134(4)	<u>Mc-Mc</u>	4.052(9)
2.828(1)	<u>Mc-I1A</u>	2.901(2)
2.917(1)	<u>Mc-I2B</u>	3.126(3)
4.098(1)	<u>I1A-I1A</u>	4.108(1)
4.313(1)	<u>I1A-I1C</u>	4.298(1)
3.999(1)	<u>I1A-I2B</u>	4.285(3)
4.008(1)	<u>I2B-I2B</u>	4.122(1)
4.154(1)	<u>Cs1A-I1A</u>	4.212(1)
3.964(3)	<u>Cs1A-I1C</u>	4.140(4)
4.268(3)	<u>Cs1A-I2B</u>	4.533(4)
4.135(1)	<u>Cs2B-I2B</u>	4.203(1)
3.995(1)	<u>Cs2B-I1A</u>	4.251(2)
91.21(5)	<u>I1A-Mc-I1A</u>	95.6(1)
87.47(3)	<u>I1A-Mc-I2B</u>	90.58(3)
93.84(5)	<u>I2B-Mc-I2B</u> (α)	82.52(9)
64.99(6)	<u>Mc-I2B-Mc</u> (β)	80.8(1)

^aItalicized letters refer to the different layers in the stacking sequence: \square AcBcA \square CaBaC \square ... (a, c: M; A, B, C: CsI_3 -layers).

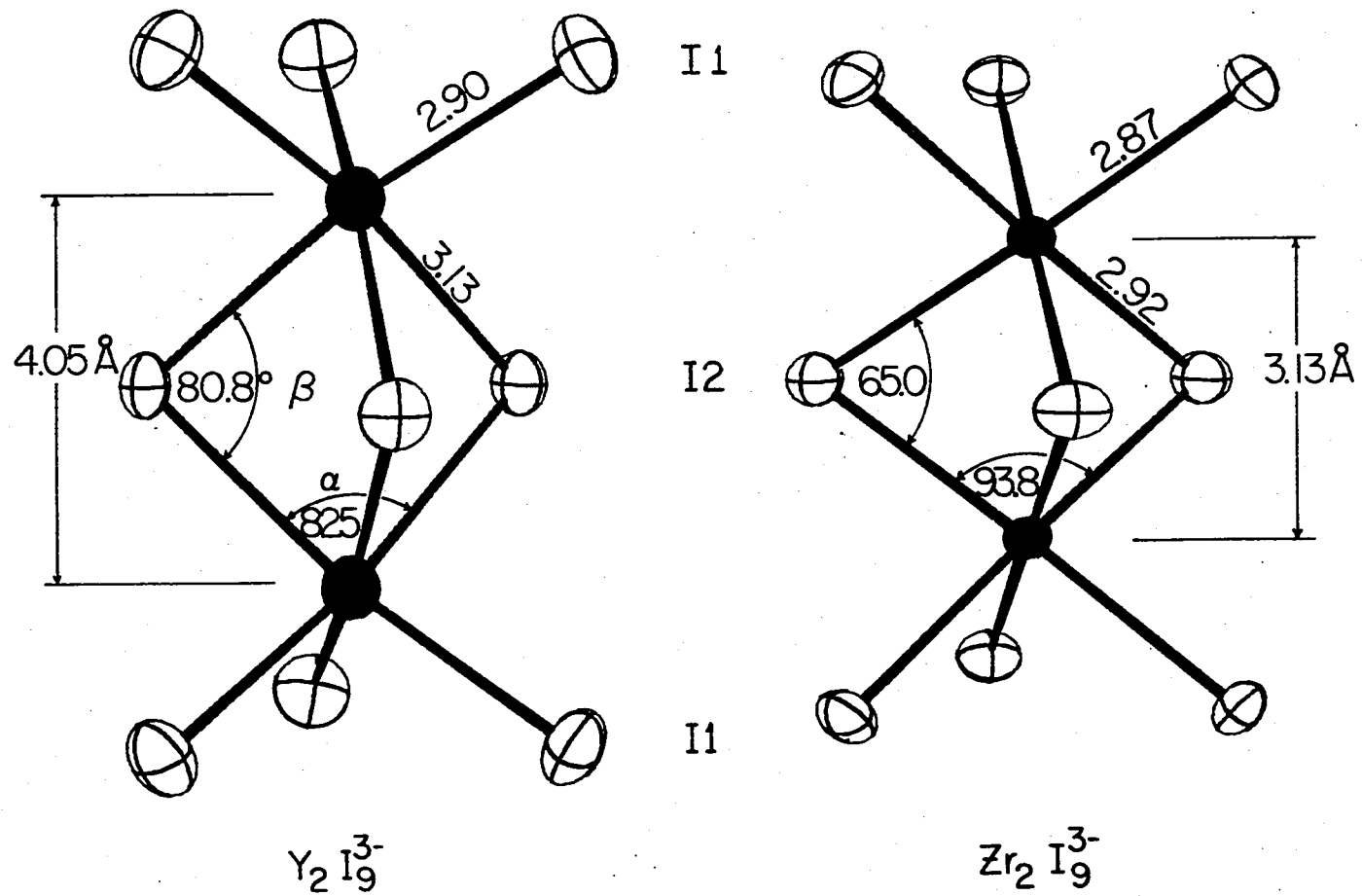


Figure 7. Perspective views of the $Y_2I_9^{3-}$ (left) and $Zr_2I_9^{3-}$ (right) groups in their $Cs_3M_2I_9$ salts. Drawn with the same linear scale, view distance and 50% probability thermal ellipsoids.

DISCUSSION

The differences in configuration between $\text{Cs}_3\text{Zr}_2\text{I}_9$ and $\text{Cs}_3\text{Y}_2\text{I}_9$ (61) are very dramatic and can easily be seen in Figure 7. These are ascribed entirely to the formation of a zirconium-zirconium bond in the former through overlap of two d_{22}^1 orbitals through the shared face. This feature is reflected in many differences in the two structures even though they are formally isotypic. For example, the lattice constants themselves would ordinarily show a small and more or less uniform increase with decreasing atomic number in such a homologous series, but the 6.4% expansion in the c axis, 19.908 Å (Zr) to 21.280 Å (Y), parallel to the principal axis of the M_2X_9 bioctahedron on transition from zirconium to yttrium versus only a 1.6% increase in a , 8.269 Å (Zr) to 8.406 Å (Y), within the layers is noteworthy. Similar increases in molar volume (9.5%) and the c/a ratio (4.9%) are also diagnostic of the change in bonding (52). The marked differences of these compounds are also carried over to a macroscopic scale where the zirconium compound forms black crystals which grind to yield a dark green powder, while the yttrium compound is found as clear crystals. This is consistent with the metal-metal bonding in zirconium and the lack of the same in yttrium.

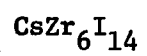
However, the most direct evidence for the change in bonding is also the most striking, a lengthening of the metal-metal distance across the shared face from 3.134(4) Å (Zr) to 4.052(9) Å (Y), a 22.6% increase. Such a large change naturally affects not only other distances and

angles in the $M_2I_9^{3-}$ bioctahedron but also positions of neighboring atoms as well. Internal angles defined by the metal atoms and I2 atoms in the shared face are affected most, a 15.8° increase from 65.0 to 80.8° in the angle β at the bridging iodine (M-I2-M) and an 11.3° decrease from 93.8 to 82.5° in the internal angle α at the metal (I2-M-I2) (see Figure 7). Small changes also occur in the external angles to atoms I1 and in the M-I distances.

In one sense the magnitude of the contraction in the M-M distances seems very remarkable since it is 0.2 \AA greater than that accompanying the transition from the paramagnetic $Cs_3Cr_2Cl_9$ to the diamagnetic $K_3W_2Cl_9$ and the formation of a triple bond. On the other hand the percentage decrease is nearly the same. But further interpretation and comparison with the latter series becomes complex owing to substantial changes in both halide and metal bonding radii let alone because of any restraints provided by the close packed M^IX_3 matrix.

A more complete and indepth look at the comparison of these two compounds can be found in a recent publication (61).

THE SYNTHESIS AND CHARACTERIZATION OF THE
FIRST TERNARY ZIRCONIUM IODIDE CLUSTER



INTRODUCTION

Ternary cluster species have been known for sometime, examples being $Zn_2Mo_3O_8$ (49), $CsNb_4X_{11}$ ($X = Cl, Br$) (62), $K_4Nb_6Cl_{18}$ (63), and $Mg_3Nb_6O_{11}$ (64). Until 1971 few other examples were known, then the discovery of the remarkable superconductivity properties of the Chervel phases (65) caused this list to literally explode with different combinations of the $M'Mo_6X_8$ ($X = S, Se, Te$) formula. In addition to the Chervel phases other ternary clusters have recently been synthesized such as $NaMo_4O_6$ (66), $CsNb_6I_{11}$ (67) and now $CsZr_6I_{14}$.

In the $CsI-Zr-ZrI_4$ ternary system no other cluster compounds are known to date and no other $M'M_6X_{14}$ phases have been reported. However, the analogous binary clusters Nb_6Cl_{14} (68) and Ta_6I_{14} (69) are known. The structural aspects of $CsZr_6I_{14}$ as well as its supposed hydride, $CsZr_6I_{14}H_x$, will be discussed. In addition, a comparison of these ternary $M'M_6X_{14}$ clusters will be made with the closely related binary M_6X_{14} clusters.

DATA COLLECTION

Data were collected on two different crystals (see the Discussion section). Data on crystal 1 were originally collected on a nonstandard monoclinic cell having $\underline{a} = 4.086(2)$, $\underline{b} = 3.973(2)$, $\underline{c} = 12.962(3)$ Å and $\gamma = 119.1(4)^\circ$. The space group $P2_1/m$ was originally chosen (\underline{c} unique) since the extinction $00l$ ($l \neq 2n$) was observed and a centric cell was predicted by an HPR plot. Because of the shortness of the \underline{a} and \underline{b} axes an iodine atom was placed at the origin.

The location of a second iodine in a Fourier electron density map indicated an acentric rather than a centric cell and therefore the space group $P2_1$ was selected and least-squares refinement of the two iodines resulted in an R equal to 0.21. The iodines were now observed to stack in an ABAC sequence along the long \underline{c} axis. Refinement of any possible zirconium positions increased R and it was therefore presumed that this cell was probably a subcell corresponding only to the iodine atoms which have the greater diffracting power. Reexamination of the indexing step revealed extra weak spots in the \underline{b} axial photo which would increase \underline{b} by a factor of four. When these new reflections were input along with the original set of reflections and reindexed, a new cell was obtained. Two octants of data, HKL and $\bar{H}\bar{K}L$, were collected ($2\theta \leq 60^\circ$) on the new orthorhombic cell with $\underline{a} = 14.275(4)$, $\underline{b} = 15.880(4)$ and $\underline{c} = 12.953(4)$ Å, which were obtained via LATT by tuning on the 2θ values of 14 reflections ($28 \leq 2\theta \leq 34^\circ$). After 1300 reflections had been checked, the C-centering restriction, $h + k \neq 2n$, was established

and added. The 3208 observed reflections were reduced and averaged in Laue symmetry mmm yielding 1640 independent reflections. Initially the space group C222 was used; this was later replaced with the correct space group Ccmb upon the discovery of the extinctions $0k\ell$ ($\ell \neq 2n$) and $hk0$ ($k \neq 2n$). Ccmb is a nonstandard setting of Cmca (No. 64).

All data in the octants HKL and $\bar{H}\bar{K}L$ were collected ($2\theta \leq 50^\circ$) on crystal 2. This second orthorhombic cell had $a = 14.300(3)$, $b = 15.833(2)$ and $c = 12.951(2)$ Å, again obtained via LATT by tuning on the 2θ values of 14 reflections ($28 \leq 2\theta \leq 47^\circ$). The 2263 observed reflections were reduced and averaged the same as crystal 1 yielding 1169 independent reflections.

STRUCTURE DETERMINATION

A value for R of 0.21 had been obtained from the refinement of two iodine atoms in the old (O) monoclinic cell for crystal 1. When the new (N) orthorhombic cell was found, an examination of the orientation matrices for the two cells, see Table VII, indicated that \vec{c}_O^* and \vec{c}_N^* were the same except opposite in direction. Since β_O is the only non-90° angle, the angles between c_O^* and a_O^* , c_O^* and b_O^* as well as c_N^* and a_N^* , c_N^* and b_N^* all must be 90°. Therefore, a_O^* , b_O^* , a_N^* and b_N^* all lie in the same plane since c_O^* and c_N^* differ only in direction. By using the equation $e \cdot f = |e||f| \cos \theta$, the angles between a_O^* and a_N^* as well as a_O^* and b_N^* were determined and found to be 0° and 90°, respectively. Therefore following the rules for converting reciprocal axes to real axes, b_O and b_N were found to lie in the same direction; however, they had different magnitudes. In the same manner a_N was found to be perpendicular to both c_N and b_N but not to lie along a_O . From this correlation between the old and new cells, six independent iodines were refined in the new orthorhombic cell (data set 1) and the zirconium positions located. Refinement of the six iodines and two zirconiums yielded an R equal to 0.25. At this point examination of the atom locations indicated, via chemical common sense, that one of the supposed iodines was truly a cesium. This was drawn from the fact that a cesium completely surrounded by iodines is more reasonable than an iodine in the same position. Further refinement yielded a residual equal to 0.12 using isotropic temperature factors.

Table VII. Orientation matrices for the old monoclinic and new orthorhombic cells.

<u>Old Monoclinic</u>		
<u>a₀[*]</u>	<u>b₀[*]</u>	<u>c₀[*]</u>
-0.1596	0.028915	0.05178
0.15763	0.28666	-0.00383
0.16140	-0.00704	0.05722
<u>New Orthorhombic</u>		
<u>a_N[*]</u>	<u>b_N[*]</u>	<u>c_N[*]</u>
-0.04160	0.027974	-0.051524
0.039194	0.051958	0.003892
0.040274	-0.021606	-0.057125

After the data sets from crystals 1 and 2 were corrected for absorption via a ϕ -scan program (70) and reweighted in fifty groups sorted on F_o , final R's and R_w 's with anisotropic temperature factors were $R = 0.090, 0.062$ and $R_w = 0.110, 0.083$, respectively. The structure of crystal 2 was refined with the atom positions from crystal 1. The final difference map for crystal 1 was flat to $\leq 1e/\text{\AA}^3$, while the same for crystal 2 had $+2$ and $+3e/\text{\AA}^3$ at the cesium and iodine positions, respectively, and $\leq 1e/\text{\AA}^3$ elsewhere. However, both clusters were observed to have a peak of $\sim 5e/\text{\AA}^3$ in the center of the zirconium cluster.

DESCRIPTION OF THE STRUCTURE

Final positional, thermal parameters and cell constants for $\text{CsZr}_6\text{I}_{14}$ crystal 1 and 2 are listed in Table VIII, and important distances and angles in Table IX, while structure factors are in Appendix E.

Both Zr_6I_{12} and $\text{Zr}_6\text{I}_{14}^-$ are based on M_6X_{12} clusters and a comparison of Figures 3 and 8 will show that they differ only in how the iodine atoms are shared between clusters. The exact sharing of iodines in Zr_6I_{12} , as stated earlier, is $\text{Zr}_6\text{I}_6^{\text{i-i-a}} \text{I}_{6 \cdot 2/3}^{\text{a-i}}$ while in $\text{Zr}_6\text{I}_{14}^-$ it is $\text{Zr}_6\text{I}_{10}^{\text{i-i-a}} \text{I}_{2 \cdot 2/3}^{\text{a-i}} \text{I}_{2 \cdot 1/3}^{\text{a-a}} \text{I}_{4 \cdot 1/2}^{\text{a-a}}$. The latter can be seen in Figure 8 by the coding of the iodines. The ten solid iodine atoms are inner (i) iodines bonded twice, only to the cluster shown. The two striped iodine atoms are bonded twice to the cluster shown but also once to neighboring clusters and are inner-outer (i-a) iodines. The two spotted iodine atoms bond once to the cluster shown and twice to neighboring clusters and are outer-inner (a-i) iodines, and finally the four open iodine atoms bond once to the cluster shown and once to neighboring clusters and are outer-outer (a-a) iodines. As seen in Zr_6I_{12} the Zr-I bond lengths in $\text{CsZr}_6\text{I}_{14}$ follow this bonding scheme where the Zr-I^{i} , $\text{Zr-I}^{\text{i-a}}$, $\text{Zr-I}^{\text{a-a}}$ and $\text{Zr-I}^{\text{a-i}}$ distances increase from 2.862-2.865, 2.923, 3.148 to 3.408 Å, respectively.

Table VIII. Crystallographic data for $\text{CsZr}_6\text{I}_{14}\text{H}_x$, crystals 1 and 2.

Composition: $\text{CsZr}_6\text{I}_{14}\text{H}_x$, $\text{CsZr}_6\text{I}_{14}$, $Z = 4$

Cell: Orthorhombic, Ccmb (nonstandard setting No. 64)

	(1)	(2)	Δ
Lattice Parameters:	$a = 14.275(4)$,	$a = 14.300(3)$	$.025(5)$
	$b = 15.880(4)$,	$b = 15.833(2)$	$-.047(5)$
	$c = 12.953(4)$,	$c = 12.951(2)$	$-.002(5)$
	$R = 0.090$	$R = 0.062$	
	$R_w = 0.110$	$R_w = 0.083$	
	1640 reflections, $2\theta < 59.9^\circ$	1169 reflections, $2\theta < 49.9^\circ$	

	x	y	z	B_{11}^a	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Crystal 1, $\text{CsZr}_6\text{I}_{14}\text{H}_x$									
I1	0.09821(8)	0.12549(7)	0.7509(1)	1.40(5)	1.56(5)	1.21(4)	0.11(3)	-0.031(3)	0.39(3)
I2	0.25619(8)	0.12574(7)	0.9936(1)	1.26(4)	1.65(5)	1.28(5)	0.32(3)	0.20(3)	0.29(3)
I3	0.6530(1)	0.25	0.25	1.53(6)	1.51(6)	1.39(6)	0.0	0.0	-0.40(4)
I4	0.1591(1)	0.0	0.2377(1)	1.53(6)	1.23(6)	1.22(6)	0.0	0.38(4)	0.0
I5	0.0	0.247(1)	0.0	1.80(6)	1.17(5)	1.21(6)	0.0	-0.27(5)	0.0
Cs	0.0	0.0	0.0	5.6(2)	3.9(2)	3.2(2)	0.0	-0.5(1)	0.0

Zr1	0.0660(1)	0.3920(1)	0.1101(1)	1.20(6)	1.64(6)	1.08(6)	-0.22(5)	0.27(5)	-0.23(5)
Zr2	0.3631(2)	0.0	0.1009(2)	1.78(9)	1.13(8)	1.21(9)	0.0	-0.44(7)	0.0

Crystal 2, CsZr₆I₁₄

I1	0.08991(9)	0.12535(6)	0.74989(8)	1.51(6)	1.34(6)	1.30(6)	0.10(3)	-0.27(3)	-0.41(3)
I2	0.25726(7)	0.12574(6)	0.99357(8)	1.26(5)	1.40(6)	1.38(5)	0.32(3)	0.17(3)	0.28(3)
I3	0.6512(1)	0.25	0.25	1.54(7)	1.24(7)	1.62(6)	0.0	0.0	-0.40(4)
I4	0.1581(1)	0.0	0.2382(1)	1.69(7)	1.10(7)	1.31(6)	0.0	0.39(4)	0.0
I5	0.0	0.24730(8)	0.0	1.92(7)	0.84(6)	1.40(6)	0.0	-0.28(5)	0.0
Cs	0.0	0.0	0.0	4.9(2)	3.4(1)	3.0(1)	0.0	-0.4(1)	0.0
Zr1	0.0643(1)	0.39420(9)	0.1078(1)	1.17(6)	0.99(6)	1.05(6)	-0.08(4)	0.06(4)	-0.09(4)
Zr2	0.3668(1)	0.0	0.0979(1)	1.29(8)	1.29(8)	1.13(7)	0.0	-0.19(6)	0.0

$$a_T = \exp\left[(-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^{*}b^{*} + 2B_{13}hla^{*}c^{*} + 2B_{23}k\ell b^{*}c^{*})\right].$$

Table IX. Selected bond distances (Å) and angles (deg.)

a $\frac{1}{2}+x, \frac{1}{2}+y, z$	b $\bar{x}, \bar{y}, \bar{z}$	c $\bar{x} y \bar{z}$	d $\frac{1}{2}-x, \frac{1}{2}, \bar{z}$
e $x, \frac{1}{2}-y, \frac{1}{2}-z$	f $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$	g $\bar{x}, \frac{1}{2}+y, \frac{1}{2}+z$	

	Distances	
	CsZr ₆ I ₁₄ H _x (Crystal 1)	CsZr ₆ I ₁₄ (Crystal 2)
<u>Zr-Zr intralayer</u>		
Zr1 ^b - Zr1 ^c	3.430(4)	3.350(3)
Zr1 - Zr2 ^a	3.368(3)	3.286(2)
<u>Zr-Zr interlayer</u>		
Zr1 - Zr1 ^c	3.418(4)	3.343(3)
Zr1 - Zr2 ^d	3.382(3)	3.298(2)
Zr1 - Zr1 ^b	4.842(4)	4.733(3)
Zr2 ^a - Zr2 ^d	4.704(2)	4.577(4)
<u>Zr - Iⁱ</u>		
Zr1 - I5	2.862(2)	2.864(2)
Zr1 ^c - I1 ^e	2.883(2)	2.888(2)
Zr1 ^b - I2 ^e	2.886(2)	2.887(2)
Zr2 ^d - I1 ^e	2.866(2)	2.863(2)
Zr2 ^a - I2 ^a	2.872(2)	2.871(2)

Table IX (cont.)

	Distances	
	CsZr ₆ I ₁₄ H _x (Crystal 1)	CsZr ₆ I ₁₄ (Crystal 2)
<u>Zr - I^{i-a}</u>		
Zr1 ^c - I4 ^g	2.932(2)	2.930 (2)
<u>Zr - I^{a-i}</u>		
Zr2 ^d - I4 ^d	3.409(3)	3.494(3)
<u>Zr - I^{a-a}</u>		
Zr1 ^b - I3 ^f	3.149(2)	3.186(2)
	Angles	
<u>Zr - I^{a-a} - Zr</u>		
Zr1 ^b - I3 ^f - Zr1 (adjacent cluster)	133.48(9)	134.08(7)
<u>Zr - Iⁱ - Zr</u>		
Zr1 - I5 - Zr1 ^c	73.32(8)	71.41(6)
Zr1 ^c - I1 ^e - Zr2 ^d	71.73(7)	69.68(5)
Zr1 ^b - I2 ^a - Zr2 ^a	71.95(7)	69.88(5)
<u>Zr - I^{i-a} - Zr</u>		
Zr1 ^b - I4 ^g - Zr1 ^c	71.62(8)	69.74(6)

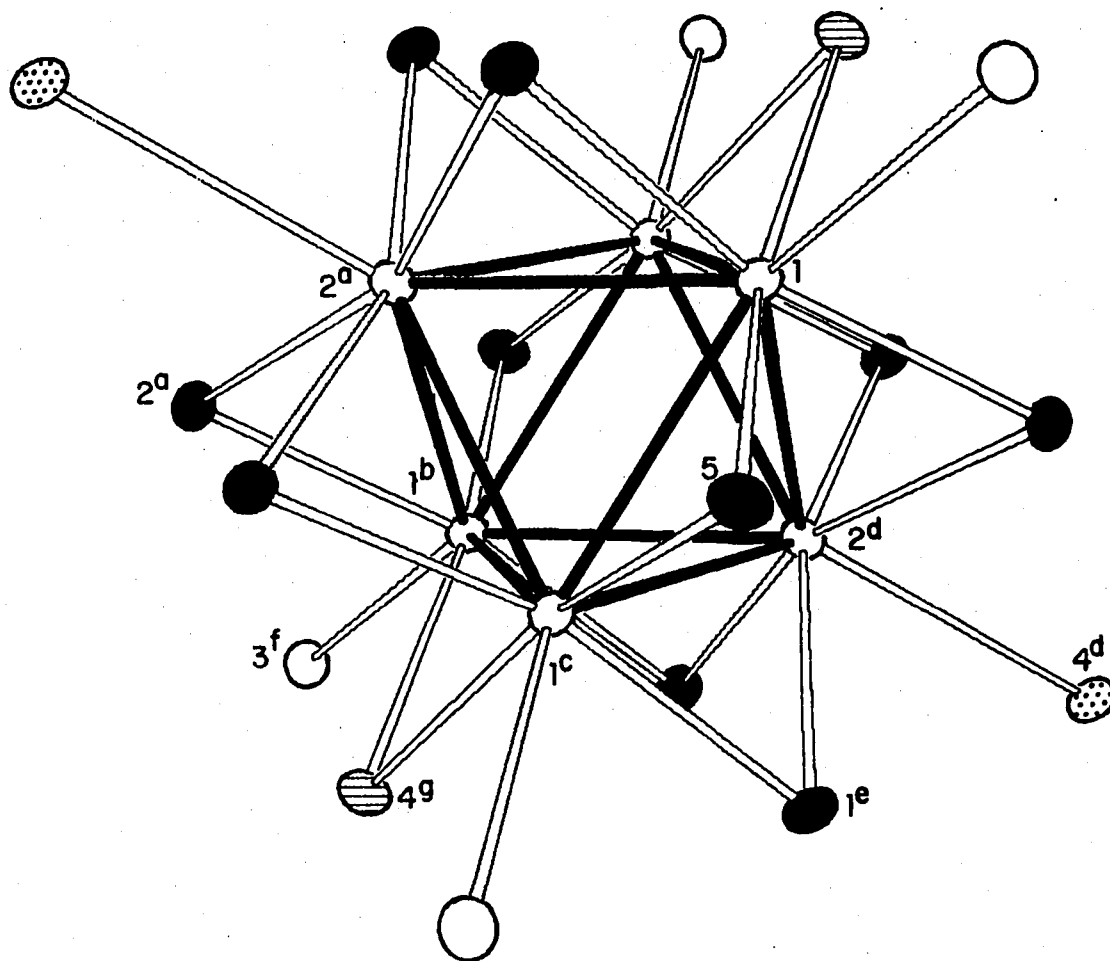


Figure 8. The $Zr_6I_{14}^-$ cluster (crystal 2) with the zirconium atoms connected by heavy lines. There is an inversion center at the center of the cluster and a mirror plane parallel to the paper which contains zirconium atoms 2^a and 2^d and iodine atoms 4^d and 4^g . The iodine atoms are coded according to their bonding between clusters: solid are inner (i), striped are inner-outer (i-a), dotted are outer-inner (a-i) and open are outer-outer (a-a). The letters in atom identification refer to symmetry operations, Table IX.

DISCUSSION

The Zr-Zr distances were expected to increase upon going from Zr_6I_{12} ($12 e/Zr_6$) to $Zr_6I_{14}^-$ ($11e/M_6$) since there are fewer electrons for metal-metal bonding. However, the observed increase from 3.194 - 3.204 Å in Zr_6I_{12} to 3.368 - 3.430 Å in $Zr_6I_{14}^-$, crystal 1, was much larger than expected. This is especially evident when compared with a somewhat analogous transition from $CsNb_6I_{11}$ ($20 e/M_6$) (67) to Nb_6I_{11} ($19 e/M_6$) (71) where the average Nb-Nb distance increases a mere 0.025 Å from 2.825(2) to 2.850(3) Å. Therefore, to verify the long Zr-Zr distances in crystal 1, data were collected on a second crystal. Several differences between crystal 1 and 2 were found but the most striking was that the Zr-Zr distances were ~ 0.08 Å longer in crystal 1 than in 2, 3.368 - 3.430 and 3.286 - 3.350 Å, respectively. The longer metal distances in crystal 1 are presumed to be indirect evidence for the presence of hydrogen in crystal 1 ($CsZr_6I_{14}H_x$) relative to crystal 2 ($CsZr_6I_{14}$). Crystal 1 was obtained from a reaction of CsI, ZrI_4 and metal powder while crystal 2 came from a similar reaction except metal strips were used. The powdered metal was obtained via the metal hydride, $\sim ZrH_{1.4}$, made at $\sim 450^\circ C$ from the direct reaction of hydrogen and metal. The brittle hydride was then ground into a powder and decomposed under a dynamic vacuum ($< 10^{-4}$ Torr) at $800^\circ C$; the H:Zr atomic ratio should be < 0.01 (72).

In $Nb_6I_{11}D$ the deuterium is known, via a neutron study (73), to lie in the middle of the niobium cluster. Therefore, in the similar clusters $CsNb_6I_{11}H$ (74) and now $CsZr_6I_{14}H_x$ the hydrogen is presumed to occupy a

similar position. The three systems Nb_6I_{11} - $\text{Nb}_6\text{I}_{11}\text{H}$, $\text{CsNb}_6\text{I}_{11}$ - $\text{CsNb}_6\text{I}_{11}\text{H}$ and $\text{CsZr}_6\text{I}_{14}$ - $\text{CsZr}_6\text{I}_{14}\text{H}_x$ show similar trends. All three show increases in the unit cell volumes, though quite small, of 0.2, 0.3 and 0.1%, respectively, with the uptake of hydrogen. In addition, the M-M distances in the latter two also increase with the uptake of hydrogen. In $\text{CsNb}_6\text{I}_{11}$ (67) to $\text{CsNb}_6\text{I}_{11}\text{H}$ (72), the Nb-Nb distances increase from 2.77(2), 2.795(2) and 2.940(2) to 2.817(2), 2.828(2) and 2.971(2) Å, amounting to 1.2, 1.1 and 1.7% increases. The increases in the Zr-Zr distances on going from $\text{CsZr}_6\text{I}_{14}$ to $\text{CsZr}_6\text{I}_{14}\text{H}_x$ are approximately twice as large, 3.286(2), 3.298(2), 3.343(3) and 3.350(3) to 3.368(3), 3.382(3), 3.418(4) and 3.430(4) Å which are 2.4, 2.5, 2.2 and 2.3% increases. The larger increases in the M-M distances in the case of the zirconium cluster can be attributed, at least in part, to the fact that the electron presumably removed by H is somewhat more bonding than in the niobium cluster, since the zirconium cluster contains only eleven electrons while the niobium cluster contains twenty electrons.

Since $\text{CsZr}_6\text{I}_{14}$ contains an odd number of electrons per cluster (11 e/ Zr_6) it presumably will be paramagnetic with at least one unpaired electron. Because only small quantities of this phase have been obtained esr measurements were carried out on two single crystals. The crystals were conservatively estimated as 0.1 mm cubes which corresponds to $\sim 10^{15}$ spins/crystal. A Bruker (ER 220 PSR) spectrometer interfaced with a Nicolet 1170 signal averager were used to make measurements at both room and liquid nitrogen temperatures. A conservative estimate was that 10^{11} spins or more should be detectable. However, no signal was observed

even at liquid nitrogen temperatures. The exact reason as to why a signal was not seen is not known, but it may be that this phase has a fast relaxation causing a broad signal so that even lower temperatures are required for detection. At the same time it may also be that the orientations of the single crystals produces a broad and perhaps anisotropic signal. In any case, when larger quantities of this phase are obtained, esr measurements should be repeated.

This $Zr_6I_{14}^-$ cluster is not the only M_6X_{14} cluster known, there are two binary analogs, Nb_6Cl_{14} (68) and Ta_6I_{14} (69). All three crystallize in the same space group $Cmca$ (No. 64). However, $Zr_6I_{14}^-$ was solved in $Ccmb$ while the niobium and tantalum clusters were solved in $Bbam$. If \vec{b} and \vec{c} are interchanged in the niobium and tantalum structures and the origin shifted by $\frac{1}{2} \frac{1}{2} \frac{1}{2}$, these structures may be compared directly. Figure 9 shows a 110 projection of the $CsZr_6I_{14}$ structure at \underline{c} approximately equal to $\frac{1}{2}$. The iodines (I^i) about the waist of the clusters lie at \underline{c} approximately equal to $\frac{1}{2}$ while metal triangles lie just above and below. The significance of this projection is that the cesium cation lies at $\frac{1}{2} 0 \frac{1}{2}$ and $0 \frac{1}{2} \frac{1}{2}$. This position is vacant in the Nb_6Cl_{14} and Ta_6I_{14} compounds and was not recognized by the earlier workers. It certainly seems feasible that the hole in the binary compounds could be filled with a cation, e.g. cesium, rubidium or potassium, thereby reducing the clusters. In addition, the cesium in $CsZr_6I_{14}$ or the hole in the binary clusters might also be replaced with a barium or lanthanum cation to reduce the clusters even further (see FUTURE WORK).

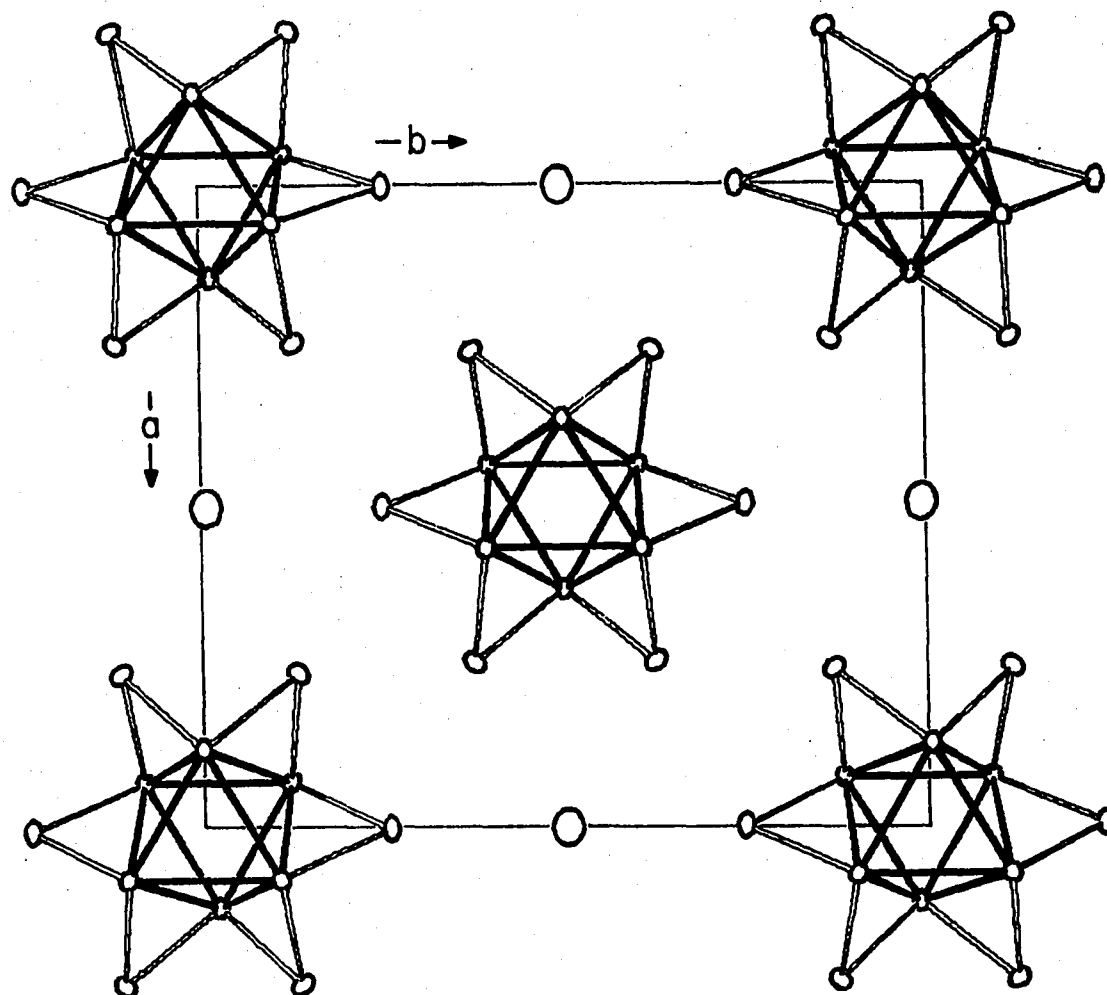


Figure 9. A (001) section of the CsZr₆I₁₄ structure (crystal 2) at $c \approx \frac{1}{2}$. Only the (inner) iodines which lie about the waist of a metal cluster are shown. The cesium atoms at $\frac{1}{2}00$ and $0\frac{1}{2}0$ lie within an octahedron of metal clusters.

FUTURE WORK

Concluding Remarks

This investigation has had at least a two-fold significance: the development of general information on transition metal halide chemistry and the consideration as to whether any of the new compounds found might have a bearing on SCC of zircaloy. The first has been achieved with the synthesis and characterization of the new compounds mentioned in the foregoing sections. The second is in many ways difficult since the research was directed more along the lines of chemical synthesis and characterization of new compounds rather than metallurgical correlations of these new compounds to SCC. However, some general comments can be made.

First of all, it is now considered fact that SCC of zircaloy is caused by a zirconium iodide. The question then is, which zirconium iodide? A ZrCl or ZrBr type would seem to be the prime candidate, mainly because of its easy basal cleavage (75). Unfortunately no such zirconium iodide has been positively identified. However, a zirconium monoiodide, of unknown structure, has reportedly been obtained from the disproportionation of a more oxidized phase, $ZrI_{2.4}$, in a 425-140°C gradient (76). A product analyzed as $ZrI_{1.2 \pm 0.1}$ remained in the 425°C region while ZrI_4 was deposited in the 140°C zone; an x-ray powder pattern for this phase has also been reported which does not correspond to the metal or any known binary phase. In any case, the next best candidate, at this time, would seem to be α - ZrI_2 which also has a layered structure with easy basal cleavage. Along these lines a study has been suggested which would

use single crystals of zirconium to grow $ZrCl$, $ZrBr$ and $\alpha-ZrI_2$ epitaxially. The results are hoped to lend support to a theory (75) that such phases may indeed be involved in SCC of zircaloy.

Secondly, although the required conditions (temperature, pressure of iodine, required stress, etc.) needed for iodine-induced SCC have been identified, no one has tried to isolate these phases. If contact with air and moisture could be avoided, studies such as SEM, XPS, and x-ray powder diffraction could be very informative especially in light of the new phases reported in this work.

Finally, though some work has been done to learn whether cesium may influence SCC more work may be needed, especially since zirconium strips have been observed to become brittle in some cesium ternary reactions above $900^\circ C$; this has never been observed in binary iodide reactions.

Binary work. Perhaps the most frustrating aspects of this work have been the lack of larger quantities of several of the new phases and the fact that a zirconium iodide more reduced than ZrI_2 has not been found, especially since $ZrCl$ (17) and $ZrBr$ (26) are well known. One reason for this may be that too much "heat and beat" chemistry has been done in the past. Recent work in the $La-LaCl_3$ system (77) has shown that at relatively low temperatures ($750-815^\circ C$) solid-solid reactions are a practical way to obtain reduced phases such as $LaCl$ in very large ($\sim 100\%$) yields. Earlier such phases had only been obtained at higher temperatures. Therefore perhaps more work should be done between $700-850^\circ C$ with either powdered metal or very large (10-20 g) quantities of metal

strips. The large quantities of metal are needed to overcome blockage of the surface which appears to prevent complete reaction.

If larger quantities of α -ZrI₂ and β -ZrI₂ could be obtained, studies such as XPS-UPS measurements along with other interesting chemistry could be done. It has been suggested that β -ZrI₂ might be soluble in a solvent such as pyridine or acetonitrile. If true, the solution would presumably contain discrete Zr₆I₁₂ clusters with solvent molecules most likely occupying the exo-positions about the clusters. If indeed the cluster were retained in solution, they perhaps could be reduced and isolated as a cation-anion pair, e.g., M⁺Zr₆I₁₂⁻. Likewise, if this were possible with the binary cluster it may also be possible with the ternary cluster CsZr₆I₁₄, which would allow reduction in solution rather than in the solid state (see future ternary work section). In addition, larger quantities of β -ZrI₂ would allow hydrogen absorption studies. The analogous Zr₆Cl₁₂ and Zr₆Br₁₂ clusters (21) are known not to take-up hydrogen yet CsZr₆I₁₄ is thought to form CsZr₆I₁₄H_x.

Larger quantities of α -ZrI₂ would allow an investigation into the transition from a distorted CdI₂-type structure (α -ZrI₂) to an undistorted or normal CdI₂ structure. Such a transition for α -ZrI₂ has been proven to be theoretically possible via a Landau second order phase transition (38,78). An experimental verification of this transition would, as has other work (39), lend support for studies into other systems where chemistry might first be predicted by theory prior to laboratory experiments.

An orthorhombic phase is now known to be involved in a twinning mechanism with $\alpha\text{-ZrI}_2$ (see $\text{ZrI}_{1.8}$ RESULTS). Crystals of this phase were seen in reactions 21 and 35 (19), with a pseudo single crystal mounted from the first. In both reactions ~ 0.5 g of ZrI_4 and a long metal strip (~ 13 cm, weighing ~ 2.5 g) were heated in an $\sim 850\text{--}950^\circ\text{C}$ gradient. The blade crystals, often observed to be forked at one or both ends (due to twinning), were obtained in only small quantities in the hot end of the tube. Future attempts to produce larger yields of this phase should use larger quantities of metal and/or smaller gradients ($900\text{--}950^\circ\text{C}$) with 1-2 month reaction times to allow larger crystals to form.

Work in this binary system has lacked in the fact that surface-sensitive techniques have not been employed in an attempt to identify phases which may exist in perhaps only a few monolayers. Techniques such as SEM, UPS-XPS, Auger and microprobe should be very helpful, especially in identification of zirconium iodides which might be important in the SCC of zircaloy.

Ternary work. A question which comes to mind is "why are extended chain structures such as Y_4Cl_6 (79), Sc_5Cl_8 (27), $\text{Sc}_7\text{Cl}_{10}$ (80), etc., so prevalent just to the left of group IV and isolated clusters such as Nb_3I_8 (81) and Nb_6I_{11} (71) just to the right, yet neither are known for zirconium?" (excluding Zr_6X_{12} (20,21) and ZrX (17,26)). One explanation may be that the correct M/X ratio has not or cannot be obtained in the binary. However, in light of all the work done in the Zr-ZrCl_4 , Zr-ZrBr_4 and Zr-ZrI_4 systems, it seems somewhat hard to believe that at least one

of these three doesn't have the correct M/X ratio. Therefore, perhaps the problem lies in electron count rather than M/X ratio. One such example is $\text{CsZr}_6\text{I}_{14}$. The M_6X_{14} structure is known for the binary compounds $\text{Nb}_6\text{Cl}_{14}$ (68) and Ta_6I_{14} (69), yet no such binary zirconium halide cluster is known. However, when one extra electron is added to the system $\text{CsZr}_6\text{I}_{14}$ is formed. Therefore, perhaps a whole host of new ternary zirconium halides could be synthesized, e.g., $\text{MZr}_6\text{X}_{12}$, $\text{M}_2\text{Zr}_3\text{X}_8$, $\text{MZr}_6\text{X}_{14}$, MZr_4X_6 , $\text{MZr}_8\text{X}_{16}$, etc. (where M = Na, K, Cs, Ba, La, etc.), if the correct electron count can be achieved. Then if these new compounds could be made, attempts to vary the number of electrons could be carried out, e.g., $\text{CsZr}_6\text{I}_{14}$, $\text{BaZr}_6\text{I}_{14}$ and $\text{LaZr}_6\text{I}_{14}$. If the proposed structures are studied some general observations can be made. In order to make $\text{M}_2\text{Zr}_3\text{X}_8$ ($\text{Zn}_2\text{Mo}_3\text{O}_8$ (49)) or $\text{MZr}_6\text{X}_{12}$ ($\text{Sc}_7\text{Cl}_{12}$ (20)), M must be small enough to fit in between the halide layers in octahedral and/or tetrahedral holes; therefore Na or K would be a good choice. In contrast in MZr_4X_6 (NaMo_4O_6 (66)) and $\text{MZr}_8\text{X}_{16}$ ($\text{Ba}_{1.13}\text{Mo}_8\text{O}_{16}$ (82)), M would lie in channels through the structure and the size may not be as critical. In $\text{MZr}_6\text{X}_{14}$ the hole is within the halide layer and therefore the best M would be one approximately the same size as X. From this point of view and in recognition of the recently discovered compounds $\text{CsNb}_6\text{I}_{11}$ (67), $\text{CsZr}_6\text{I}_{14}$, NaMo_4O_6 (66) and $\text{Ba}_{1.13}\text{Mo}_8\text{O}_{16}$ (82), the outlook for ternary zirconium halides as well as general ternary compounds seems extremely promising. In fact, one might go as far as to say a proverbial goldmine of new and very interesting ternary compounds awaits discovery.

The fur or hair-like crystal morphology of the unidentified ternary phase "Q" suggests a chain structure such as NaMo_4O_6 (66) or $\text{Ba}_{1.16}\text{Mo}_8\text{O}_{16}$ (81). At the same time this phase does not have to be ternary but could be a binary compound such as Y_4Cl_6 (79), Sc_5Cl_8 (27) or $\text{Sc}_7\text{Cl}_{10}$ (80). In any case the identification of phase "Q" may provide the first known extended chain structure for a zirconium halide. The best crystals were found growing on the metal in a 900-925°C gradient in reaction Cs18 (19) where the $\text{ZrI}_4:\text{CsI}:\text{Zr}$ molar ratio was 3:1:100. The same conditions with larger quantities of metal (6-10 g) may produce larger quantities. Since the cesium content is not known it's not possible to say whether the $\text{ZrI}_4:\text{CsI}$ ratio should be greater than or less than 3:1.

In this ternary system only one phase has not been seen which might be expected, CsZrI_3 with either the CsNiCl_3 (83) or CsMnF_3 (84) type structure. This compound would have a +2 zirconium and would complete the series Cs_2ZrI_6 , $\text{Cs}_3\text{Zr}_2\text{I}_9$, CsZrI_3 where 1/2, 2/3 and all the octahedra holes are filled, respectively. The most reasonable attempt to obtain this phase would seem to be the reduction of either Cs_2ZrI_6 or $\text{Cs}_3\text{Zr}_2\text{I}_9$ since attempts to react CsI and ZrI_4 with the metal have failed. In addition to completing the above mentioned series CsZrI_3 would also be the most reduced ternary phase known, since $\text{CsZr}_6\text{I}_{14}$ contains a zirconium in the oxidation state +2.16. It is noteworthy that although $\text{Cs}_3\text{Y}_2\text{I}_9$ is known (61), the analogous CsYI_3 compound has also not been synthesized (85).

Finally, as in the binary system larger quantities of some of the ternary phases are desired, especially $\text{CsZr}_6\text{I}_{14}$. Again, as in the binary system the best attempt would probably be a reaction of ZrI_4 and CsI (in an $\sim 3:1$ ratio) with very large, 10-20 g, quantities of metal so as to overcome problems associated with blockage of the surface. Larger quantities of this phase would allow the measurement of its magnetic susceptibility as well as better esr measurements. Most important, studies could be done on hydrogen uptake which would allow nmr studies of the presumed hydride $\text{CsZr}_6\text{I}_{14}\text{H}_x$.

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HALLELUJAH

APPENDIX A.

OBSERVED AND CALCULATED STRUCTURE FACTOR

AMPLITUDES (X10) FOR α -ZrI₂

K = 0				K = 1											
H	L	FO	FC	H	L	FO	FC								
-8	1	52	52	-3	10	48	50	1	9	145	139	5	8	33	39
-8	2	137	126	-3	11	66	68	1	10	22	24	5	9	161	169
-8	3	87	82	-3	12	170	175	1	11	41	41	5	10	79	82
-8	4	24	29	-3	13	42	43	1	12	74	69	5	12	39	37
-7	1	13	14	-3	14	36	37	1	13	182	171	6	0	46	48
-7	3	4	6	-3	15	31	34	1	14	54	53	6	1	25	24
-7	6	29	28	-3	16	115	120	1	15	55	53	6	2	194	192
-7	7	100	99	-3	17	37	37	1	16	72	68	6	4	103	103
-7	8	11	9	-2	1	124	133	1	17	87	83	6	5	7	9
-7	9	38	36	-2	2	35	30	2	0	86	91	6	6	61	62
-7	10	22	23	-2	3	228	242	2	1	243	270	6	8	6	9
-6	2	106	110	-2	4	220	232	2	2	139	151	6	9	12	13
-6	3	22	23	-2	5	109	110	2	3	97	98	6	10	63	64
-6	4	144	139	-2	6	102	96	2	4	204	210	7	0	5	5
-6	6	165	154	-2	7	126	126	2	5	172	186	7	1	6	7
-6	7	5	9	-2	8	21	4	2	6	31	31	7	2	19	20
-6	8	29	30	-2	9	79	78	2	7	27	25	7	3	61	60
-6	10	18	20	-2	10	46	44	2	9	104	97	7	4	17	17
-6	11	8	10	-2	11	55	54	2	10	76	71	7	5	95	95
-6	12	53	53	-2	12	65	62	2	11	15	14	7	6	25	27
-6	13	9	11	-2	13	6	0	2	12	56	52	7	7	37	37
-5	1	60	71	-2	14	38	36	2	13	6	8	8	0	64	61
-5	3	102	113	-2	15	24	25	2	14	42	42	8	1	77	75
-5	4	38	39	-2	16	49	51	2	16	49	49				
-5	5	69	65	-2	17	16	15	3	0	12	15				
-5	6	45	44	-1	1	27	31	3	1	96	97				
-5	7	39	39	-1	2	9	11	3	2	45	49				
-5	8	65	62	-1	3	30	33	3	3	80	89				
-5	9	74	68	-1	4	61	64	3	4	110	120				
-5	10	52	46	-1	5	146	148	3	5	67	102				
-5	11	175	163	-1	6	5	5	3	6	99	100				
-5	12	79	74	-1	7	163	169	3	7	73	79				
-5	13	21	19	-1	8	109	120	3	8	143	140				
-5	14	46	44	-1	9	95	94	3	9	77	77				
-5	15	56	56	-1	10	9	11	3	10	140	132				
-4	1	27	25	-1	11	88	92	3	11	55	54				
-4	2	68	61	-1	12	74	80	3	12	133	127				
-4	3	233	215	-1	13	142	149	3	13	35	35				
-4	4	86	94	-1	14	24	23	3	14	110	99				
-4	5	47	43	-1	15	92	97	3	15	37	37				
-4	6	48	42	-1	16	76	78	4	0	86	81				
-4	7	173	155	-1	17	65	71	4	1	222	225				
-4	8	56	53	0	2	132	123	4	2	78	73				
-4	9	11	13	0	4	214	198	4	4	64	63				
-4	11	44	40	0	6	153	139	4	5	175	173				
-4	12	19	20	0	7	14	1	4	6	52	49				
-4	13	16	16	0	8	281	273	4	7	4	6				
-4	16	6	7	0	9	6	1	4	8	22	23				
-3	1	97	99	0	10	60	61	4	9	53	57				
-3	2	18	20	0	12	37	34	4	10	22	25				
-3	3	90	94	0	14	60	52	4	11	13	16				
-3	4	98	106	1	0	3	4	4	13	6	7				
-3	5	74	95	1	1	8	10	5	1	98	110				
-3	6	65	64	1	3	10	13	5	2	36	41				
-3	7	66	94	1	4	60	66	5	3	52	59				
-3	8	164	166	1	5	173	185	5	4	32	36				
-3	9	73	76	1	6	38	39	5	5	33	36				
				1	7	123	120	5	6	65	69				
				1	8	121	118	5	7	75	84				

-4 7 8 12	0 9 120 101	4 13 11 13	-4 6 40 35
-4 8 141 135	0 11 200 188	4 14 108 103	-4 7 146 131
-4 9 65 63	0 13 115 101	5 0 124 131	-4 8 48 45
-4 10 70 71	0 15 127 118	5 1 11 13	-4 9 9 12
-4 11 20 21	0 17 30 30	5 2 93 101	-4 10 8 12
-4 12 7 6	1 0 55 53	5 3 77 82	-4 11 35 36
-4 13 56 58	1 1 16 18	5 4 96 104	-4 12 12 17
-4 14 160 158	1 2 266 283	5 5 30 35	-4 13 13 14
-4 15 19 21	1 3 230 233	5 6 38 46	-3 1 80 81
-3 1 310 318	1 4 67 66	5 7 78 80	-3 2 15 16
-3 2 17 18	1 5 149 147	5 8 66 71	-3 3 75 76
-3 3 47 39	1 6 186 184	5 9 6 12	-3 4 80 86
-3 4 12 17	1 8 38 37	5 10 21 25	-3 5 58 62
-3 5 176 161	1 9 49 54	6 0 50 53	-3 6 50 51
-3 7 98 103	1 10 58 60	6 1 10 12	-3 7 51 54
-3 9 145 132	1 11 86 85	6 2 46 43	-3 8 134 141
-3 10 14 14	1 12 13 15	6 3 71 70	-3 9 62 63
-3 11 4 6	1 13 51 49	6 4 25 27	-3 10 40 43
-3 12 16 15	1 15 58 56	6 5 43 44	-3 11 56 58
-3 14 12 16	1 16 23 21	6 6 35 38	-3 12 143 152
-3 15 6 7	2 0 77 80	6 7 119 116	-3 13 35 37
-3 16 6 11	2 1 8 9	6 8 52 54	-3 14 29 32
-2 1 9 11	2 2 137 140	6 9 46 48	-3 15 27 29
-2 2 125 124	2 3 58 55	7 0 131 128	-2 1 108 101
-2 3 22 24	2 4 19 19	7 1 29 25	-2 3 164 188
-2 4 95 97	2 5 15 16	7 2 39 39	-2 4 177 188
-2 5 56 61	2 6 74 50	7 3 6 6	-2 5 89 87
-2 6 72 56	2 7 111 111	7 4 106 103	-2 6 83 78
-2 7 62 68	2 8 143 136	7 5 66 65	-2 7 102 105
-2 8 31 39	2 9 55 36	7 6 27 24	-2 8 20 20
-2 9 94 93	2 10 203 185		-2 9 66 63
-2 10 197 212	2 11 94 88	K = 2	-2 10 37 36
-2 11 56 55	2 12 50 47	H L FO FC	-2 11 46 46
-2 12 52 55	2 14 68 68	-7 1 10 12	-2 12 54 53
-2 13 53 59	2 15 85 83	-7 5 6 8	-2 14 27 31
-2 14 92 98	2 16 96 94	-6 2 103 96	-2 15 20 22
-2 15 62 63	3 0 44 10	-6 3 20 20	-1 1 21 32
-2 16 32 29	3 1 104 113	-6 4 119 120	-1 2 8 9
-2 17 50 49	3 2 18 20	-6 6 140 134	-1 3 23 12
-1 1 26 24	3 3 204 192	-6 7 7 8	-1 4 46 46
-1 2 273 293	3 7 167 175	-6 8 23 27	-1 5 111 120
-1 3 191 203	3 8 9 12	-6 10 17 18	-1 7 126 137
-1 4 17 18	3 9 30 32	-5 1 57 59	-1 8 89 96
-1 5 182 186	3 10 14 16	-5 2 4 5	-1 9 81 89
-1 6 197 202	3 11 10 14	-5 3 93 95	-1 11 75 79
-1 7 18 44	3 13 22 23	-5 4 34 33	-1 12 64 69
-1 9 31 39	3 14 9 12	-5 5 56 54	-1 13 122 129
-1 10 72 72	3 15 7 15	-5 6 37 38	-1 14 20 20
-1 11 92 85	4 0 74 84	-5 7 35 35	-1 15 81 85
-1 12 14 10	4 1 4 6	-5 8 56 54	0 0 418 411
-1 13 54 54	4 2 33 41	-5 9 60 56	0 1 4 0
-1 14 6 1	4 3 43 41	-5 10 41 40	0 2 100 111
-1 15 49 50	4 4 165 159	-5 11 150 142	0 4 167 115
-1 16 7 11	4 6 169 163	-5 12 69 65	0 6 121 114
-1 17 47 49	4 7 72 67	-4 1 22 21	0 8 228 204
0 1 33 27	4 8 53 51	-4 2 60 52	0 10 50 45
0 3 118 97	4 10 33 34	-4 3 202 181	0 12 28 28
0 5 137 119	4 11 66 64	-4 4 77 70	0 14 47 45
0 7 168 147	4 12 169 158	-4 5 37 35	1 3 10 3

1	4	57	49	5	10	71	72	0	3	66	62	-3	5	39	39
1	5	163	148	6	0	39	43	0	5	99	80	-2	1	61	64
1	6	36	31	6	1	19	20	0	7	115	107	-2	3	112	118
1	7	107	95	6	2	161	167	0	9	77	76	-2	4	105	112
1	8	107	93	6	4	87	89	0	11	159	141	-2	5	56	57
1	9	133	123	6	5	7	8	0	13	67	78	-2	6	49	49
1	10	15	20	6	6	53	55	1	0	33	34	-1	1	8	10
1	11	38	35	7	1	5	6	1	1	6	6	-1	2	5	4
1	12	59	60	7	2	16	17	1	2	182	184	-1	3	12	17
1	13	154	148					1	3	156	149	-1	4	29	31
1	14	46	46					1	4	45	45	-1	5	65	71
1	15	48	47					1	5	108	100	-1	7	78	88
2	0	77	48					1	6	134	128	0	0	270	235
2	1	198	206					1	8	25	28	0	2	54	47
2	2	116	130					1	9	36	35	0	4	108	99
2	3	82	77					1	10	42	44	0	6	77	65
2	4	164	169					1	11	63	62	1	3	6	7
2	5	158	150					1	12	9	11	1	4	35	33
2	6	14	14					2	0	49	50	1	5	95	91
2	7	23	25					2	1	5	5	1	6	20	19
2	9	67	82					2	2	98	93	1	7	64	61
2	10	63	59					2	3	41	38	2	0	47	47
2	11	13	12					2	4	11	10	2	1	126	130
2	12	46	45					2	6	55	56	2	2	75	70
2	14	34	37					2	7	83	79	2	3	55	50
3	0	9	12					2	8	102	98	2	4	106	105
3	1	81	79					2	9	39	25	2	5	99	98
3	2	39	40					2	10	143	139	2	6	5	7
3	3	70	68					2	11	68	67	3	0	6	8
3	4	102	98					3	0	52	8	3	1	48	48
3	5	59	56					3	1	68	73	3	2	24	26
3	6	87	85					3	2	12	13	3	3	40	41
3	7	63	61					3	3	158	148				
3	8	124	120					3	7	128	129				
3	9	69	65					3	8	6	9				
3	10	120	114					3	9	21	24				
3	11	47	46					3	10	10	12				
3	12	114	111					4	0	49	46				
3	13	32	31					4	2	23	23				
4	0	74	69					4	3	30	30				
4	1	197	189					4	4	123	115				
4	2	64	60					4	6	124	120				
4	4	53	53					4	7	52	50				
4	5	141	147					4	8	40	41				
4	6	43	42					5	0	97	98				
4	7	5	5					5	1	8	9				
4	8	18	20					5	2	74	76				
4	9	50	49					5	3	64	63				
4	10	20	22					5	4	76	79				
4	11	13	14					5	5	24	26				
5	1	87	93					5	6	34	36				
5	2	32	35					6	0	38	40				
5	3	50	49												
5	4	31	31												
5	5	31	32												
5	6	57	60												
5	7	72	72												
5	9	33	34												
5	9	145	148												

K = 3

H L FO FC

K = 4

H L FO FC

APPENDIX B.

OBSERVED AND CALCULATED STRUCTURE FACTOR

AMPLITUDES (X10) FOR β -ZrI₂

L = 0				L = 1				L = 2				L = 3			
H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
1	1	121	144	0	8	28	18	0	13	562	430	13-10	135	108	
1	4	219	266	0	14	173	143	0	13	6	3	13-7	251	207	
1	7	168	188	1	0	186	222	0	11	312	274	13-4	97	100	
1	10	206	208	1	12	301	267	0	6	68	83	13-1	128	161	
1	13	160	173	2	1	34	22	0	2	207	194	13	2	66	68
2	2	217	277	2	4	26	9	1	9	228	220	14-9	142	107	
2	5	1067	1466	2	7	124	118	1	11	189	168	14-6	230	231	
2	8	91	96	2	10	238	227	1	12	335	262	14-3	65	71	
2	11	147	141	2	13	88	93	1	1	1319	1873	14	0	84	90
3	0	182	246	3	1	142	177	1	3	4	65				
3	3	211	235	3	5	65	67	1	4	61	65				
3	6	257	295	3	8	173	143	1	7	61	65				
3	9	108	124	3	11	301	267	1	10	105	112				
4	1	345	428	3	14	186	222	1	11	38	62				
4	4	46	42	3	1	34	22	1	12	256	262				
4	7	74	79	3	4	26	9	1	2	159	163				
4	10	517	538	3	7	124	118	1	3	29	26				
5	2	168	203	3	10	238	227	1	4	114	125				
5	5	166	181	3	13	88	93	1	5	440	446				
5	11	70	85	3	1	142	177	1	6	162	201				
6	0	87	104	3	4	26	9	1	7	21	22				
6	3	188	220	3	7	124	118	1	8	794	878				
6	6	205	228	3	10	238	227	1	9	47	44				
6	9	81	88	3	13	88	93	1	10	535	392				
7	1	187	220	3	1	142	177	1	11	155	189				
7	4	191	188	3	4	26	9	1	12	250	262				
7	7	100	109	3	7	124	118	1	1	160	171				
8	2	236	261	3	10	238	227	1	2	17	17				
8	5	66	68	3	13	88	93	1	3	292	265				
8	8	128	141	3	1	142	177	1	4	57	69				
9	0	23	10	3	4	26	9	1	5	114	125				
9	3	653	712	3	7	124	118	1	6	440	446				
9	6	39	38	3	10	238	227	1	7	162	201				
10	1	152	158	3	13	88	93	1	8	21	22				
10	4	136	132	3	1	142	177	1	9	794	878				
10	7	74	76	3	4	26	9	1	10	47	44				
11	2	52	55	3	7	124	118	1	11	535	392				
11	5	154	160	3	10	238	227	1	12	155	189				
12	0	97	108	3	13	88	93	1	1	250	262				
12	3	134	144	3	1	142	177	1	2	160	171				
13	1	31	17	3	4	26	9	1	3	17	17				
				3	7	124	118	1	4	292	265				
				3	10	238	227	1	5	57	69				
				3	13	88	93	1	6	440	446				
				3	1	142	177	1	7	535	392				
				3	4	26	9	1	8	155	189				
				3	7	124	118	1	9	250	262				
				3	10	238	227	1	10	160	171				
				3	13	88	93	1	11	17	17				
				3	1	142	177	1	12	292	265				
				3	4	26	9	1	1	57	69				
				3	7	124	118	1	2	440	446				
				3	10	238	227	1	3	535	392				
				3	13	88	93	1	4	155	189				
				3	1	142	177	1	5	250	262				
				3	4	26	9	1	6	160	171				
				3	7	124	118	1	7	17	17				
				3	10	238	227	1	8	292	265				
				3	13	88	93	1	9	57	69				
				3	1	142	177	1	10	440	446				
				3	4	26	9	1	11	535	392				
				3	7	124	118	1	12	155	189				
				3	10	238	227	1	1	250	262				
				3	13	88	93	1	2	160	171				
				3	1	142	177	1	3	17	17				
				3	4	26	9	1	4	292	265				
				3	7	124	118	1	5	57	69				
				3	10	238	227	1	6	440	446				
				3	13	88	93	1	7	535	392				
				3	1	142	177	1	8	155	189				
				3	4	26	9	1	9	250	262				
				3	7	124	118	1	10	160	171				
				3	10	238	227	1	11	17	17				
				3	13	88	93	1	12	292	265				
				3	1	142	177	1	1	57	69				
				3	4	26	9	1	2	440	446				
				3	7	124	118	1	3	535	392				
				3	10	238	227	1	4	155	189				
				3	13	88	93	1	5	250	262				
				3	1	142	177	1	6	160	171				
				3	4	26	9	1	7	17	17				
				3	7	124	118	1	8	292	265				
				3	10	238	227	1	9	57	69				
				3	13	88	93	1	10	440	446				
				3	1	142	177	1	11	535	392				
				3	4	26	9	1	12	155	189				
				3	7	124	118	1	1	250	262				
				3	10	238	227	1	2	160	171				
				3	13	88	93	1	3	17	17				
				3	1	142	177	1	4	292	265				
				3	4	26	9	1	5	57	69				
				3	7	124	118	1	6	440	446				
				3	10	238	227	1	7	535	392				
				3	13	88	93	1	8	155	189				
				3	1	142	177	1	9	250	262				
				3	4	26	9	1	10	160	171				
				3	7	124	118	1	11	17	17				
				3	10	238	227	1	12	292	265				
				3	13	88	93	1	1	57	69				
				3	1	142	177	1	2	440	446				
				3	4	26	9	1	3	535	392				
				3	7	124	118	1	4	155	189				
				3	10	238	227	1	5	250	262				
				3	13	88	93	1	6	160	171				
				3	1	142	177	1	7	17	17				
				3	4	26	9	1	8	292	265				
				3	7	124	118	1	9	57	69				
				3	10	238	227	1	10	440	446				
				3	13	88	93	1	11	535	392				
				3	1	142	177	1	12	155	189				
				3	4	26	9	1	1	250	262				
				3	7	124	118	1	2	160	171				
				3	10	238	227	1	3	17	17				
				3	13	88	93	1	4	292	265				
				3	1	142	177	1	5	57	69				
				3	4	26	9	1	6	440	446				
				3	7	124	118	1	7	535	392				
				3	10	238	227	1	8	155	189				
				3	13	88	93	1	9	250	262				
				3	1	142	177	1	10	160	171				
				3	4	26	9	1	11	17	17				
				3	7	124	118	1	12	292	265				
				3	10	238	227	1	1	57	69				
				3	13	88	93	1	2	440	446				
				3	1	142	177	1	3	535	392				
				3	4	26	9	1	4						

10 1 21 8	8 1 34 53	5 9 130 148	4 1 459 370
10 4 166 158	8 4 136 126	6 -5 254 188	4 4 73 65
11 -7 141 115	8 7 498 528	6 -2 126 128	4 10 416 440
11 -4 189 177	9 -7 94 71	6 1 17 17	5 -4 86 69
11 -1 55 54	9 -4 331 290	6 4 98 94	5 -1 181 174
11 2 77 74	9 -1 248 263	6 7 109 115	5 2 282 262
11 5 61 69	9 2 113 121	7 -4 33 26	5 5 115 112
12 -9 966 773	9 5 130 128	7 -1 294 267	5 8 196 209
12 -6 216 166	10 -9 66 44	7 2 179 177	6 -3 51 45
12 0 99 104	10 -6 59 55	8 -6 1052 878	6 0 229 212
12 3 120 131	10 -3 364 303	8 -3 358 326	6 3 8 7
13-11 137 99	10 3 169 180	8 0 36 27	6 6 157 169
13 -8 37 29	10 6 72 77	8 3 142 136	7 -5 200 156
13 -5 121 115	11 -8 172 133	8 6 31 35	7 -2 945 900
13 -2 147 157	11 -5 923 723	9 -8 177 141	7 1 83 79
13 1 51 54	11 -2 182 177	9 -5 152 132	7 4 81 80
14-10 193 151	11 4 224 237	9 -2 339 276	7 7 205 236
14 -4 636 585	12-10 86 63	9 1 100 101	8 -7 181 149
	12 -7 59 46	9 4 105 99	8 -4 8 21
	12 2 136 140	10 -7 193 161	8 2 80 75
L = 4	13-12 21 27	10 -4 31 28	8 5 69 73
H K FO FC	13 -9 96 83	10 -1 812 643	9 -6 211 182
0 2 280 244	13 -6 120 100	10 2 93 92	9 -3 13 8
0 5 98 89	13 -3 138 126	10 5 104 106	9 0 170 141
0 8 187 180	13 0 540 530	11 -9 230 185	9 3 668 651
0 11 75 68	14-11 263 226	11 -6 38 30	10 -8 331 302
0 14 60 57	14 -8 35 33	11 -3 120 101	10 -5 173 162
1 0 514 428	14 -5 84 71	11 0 82 74	10 -2 32 17
1 6 180 169		11 3 167 176	10 1 56 47
1 9 759 720	L = 5	12 -8 112 100	11-10 107 99
1 12 40 37	H K FO FC	12 -5 95 83	11 -7 253 231
2 1 212 188	0 1 496 410	12 -2 111 103	11 -4 13 14
2 7 406 378	0 4 287 260	13-10 275 219	11 -1 216 191
2 10 84 77	0 7 134 133	13 -7 104 92	12 -9 551 445
2 13 37 36	0 10 76 69	13 -1 71 66	12 -6 71 70
3 -1 133 120	0 13 554 564	14 -9 83 82	12 -3 126 102
3 5 378 359	1 2 104 97	14 -6 166 156	12 0 258 230
3 8 141 143	1 5 72 72	14 -3 115 105	13 -5 44 38
3 11 75 79	1 8 52 47		13 -2 219 213
4 -3 1623 1483	1 11 149 152	L = 6	14 -7 214 205
4 0 65 72	2 0 336 276	H K FO FC	14 -4 555 443
4 3 40 46	2 3 152 128	0 0 1262 1203	
4 6 259 273	2 6 364 342	0 3 59 56	L = 7
4 9 101 99	2 9 30 3	0 6 80 72	H K FO FC
5 -2 80 82	2 12 80 89	0 9 148 143	0 2 74 87
5 4 86 88	3 -2 277 187	0 12 169 177	0 5 34 31
5 7 99 104	3 1 1108 990	1 1 89 70	0 8 96 94
5 10 89 92	3 4 343 306	1 4 67 64	0 11 39 41
6 -4 159 123	3 7 170 166	1 7 33 29	1 0 332 278
6 2 913 1086	3 10 65 68	1 10 26 25	1 3 194 179
6 5 78 80	4 -1 34 34	2 -1 40 33	1 6 212 187
6 8 50 56	4 2 225 195	2 2 174 148	1 9 674 626
7 -6 77 63	4 5 222 212	2 5 992 899	2 1 290 257
7 -3 136 130	4 8 78 82	2 8 78 76	2 4 64 53
7 0 135 145	4 11 102 111	2 11 106 122	2 7 146 144
7 3 129 129	5 -3 434 337	3 0 148 140	2 10 9 11
7 6 30 21	5 0 227 214	3 3 306 275	3 -1 127 101
7 9 10 1	5 3 119 105	3 9 45 47	3 2 495 434
8 -5 83 48	5 6 614 644	4 -2 45 18	3 5 164 143
8 -2 461 386			

3 8 22 13	4 8 33 35	8 -7 47 58
4 -3 1045 925	5 -3 165 162	8 -1 37 40
4 0 443 420	5 0 108 105	8 2 288 297
4 3 159 134	5 3 48 40	9 -6 83 105
4 6 41 37	5 6 546 550	9 -3 65 67
4 9 19 14	6 -5 208 217	9 0 55 46
5 -2 81 81	6 -2 169 157	10 -8 60 59
5 1 374 331	6 4 152 135	10 -5 56 64
5 7 198 210	7 -4 162 153	10 -2 102 114
6 -4 73 61	7 -1 50 12	11 -7 10 7
6 -1 75 69	7 2 198 177	11 -4 80 90
6 2 763 676	7 5 97 99	
6 5 170 155	8 -6 603 566	L = 10
7 -6 212 195	8 -3 12 25	H K FO FC
7 -3 125 120	8 0 14 14	0 2 104 112
7 0 14 9	8 3 221 226	0 5 133 147
7 3 24 24	9 -8 48 51	0 8 43 45
7 6 197 214	9 -5 11 15	1 3 72 72
8 -5 185 164	9 -2 116 112	2 1 49 44
8 -2 208 196	9 1 151 151	2 4 106 117
8 1 8 20	10 -7 79 88	3 -1 93 102
8 4 80 71	10 -4 232 236	3 2 67 75
9 -7 382 359	10 -1 621 552	3 5 43 43
9 -4 81 74	11 -9 130 148	4 -3 505 457
9 -1 16 4	11 -6 23 21	4 0 22 26
9 2 42 43	11 -3 21 30	4 3 56 61
10 -9 153 147	11 0 64 69	5 -2 61 78
10 -6 222 209	12 -8 93 92	5 1 68 71
10 -3 106 102	12 -5 71 70	5 4 100 109
10 0 179 157		6 -4 150 179
10 3 25 29	L = 9	6 -1 133 150
11 -8 93 93	H K FO FC	6 2 479 461
11 -5 729 625	0 0 1017 889	7 -6 125 146
11 -2 200 175	0 3 333 294	7 -3 22 25
11 1 91 87	0 6 105 116	7 0 48 51
12-10 48 48	0 9 41 42	8 -5 61 74
12 -7 88 89	1 1 52 44	8 -2 44 50
12 -1 295 256	1 4 208 195	9 -4 63 70
13 -9 12 22	1 7 36 39	
13 -6 9 14	2 -1 50 48	L = 11
	2 2 168 150	H K FO FC
L = 8	2 5 759 667	0 1 286 324
H K FO FC	2 8 84 88	0 4 58 70
0 1 84 70	3 0 148 141	1 2 9 20
0 4 173 156	3 3 54 48	1 5 135 149
0 7 24 34	3 6 73 75	2 0 119 141
1 2 54 49	4 -2 335 306	2 3 34 41
1 5 129 124	4 1 161 159	3 -2 52 57
1 8 201 204	4 4 8 13	3 1 615 667
2 3 154 143	4 7 122 129	4 -1 34 39
2 6 77 76	5 -4 443 435	4 2 117 124
2 9 43 41	5 -1 26 21	5 -3 57 75
3 -2 47 36	5 2 95 93	5 0 58 69
3 1 867 741	5 5 58 61	6 -2 116 140
3 4 83 72	6 -3 238 251	
3 7 141 150	6 3 252 270	
4 -1 160 141	7 -2 719 667	
4 2 108 98	7 1 237 238	
4 5 37 38	7 4 147 159	

APPENDIX C.

THE CALCULATED AND OBSERVED GUINIER
POWDER DIFFRACTION PATTERNS FOR Cs_2ZrI_6

A Guinier powder pattern of Cs_2ZrI_6 was measured by means of a mm scale placed on and developed with the film. Four NBS Si lines along with the zero line were refined to yield 2 θ standard deviations of 0.002. hkl and 2θ values for eleven of the strongest lines were refined in LATT to give, with a cubic restriction, $a = 11.659(2) \text{ \AA}$.

The A_2MX_6 compounds of the type K_2PtCl_6 (14) crystallize in the cubic space group $\text{Fm}\bar{3}\text{m}$ with $Z = 4$; the cations and metals lie on the special position $1/4, 1/4, 1/4$ and $0,0,0$, respectively, while the halide is at $x,0,0$. The parameter x was approximated from the average of the Zr-I distances (2.87 and 2.92 Å) in $\text{Cs}_3\text{Zr}_2\text{I}_9$ (2.895 Å). Using $a = 11.659 \text{ Å}$ and $x = 0.246$, the powder on the following page was calculated. The observed powder agrees quite well in both intensity and 2θ verifying that Cs_2ZrI_6 is isotypic with K_2PtCl_6 as well as Cs_2ZrCl_6 .

Calculated and observed Guinier powder patterns for Cs₂ZrI₆

hkl	¹ 2θ _{obs.}	² 2θ _{calc.}	I _{obs.}	I _{calc.}
111	13.22 ³	13.14	1	0.7
200	15.26 ³	15.19	1/2	0.3
220	21.56 ³	21.54	1/2	0.3
311		25.31		0.3
222	26.50 ³	26.46	10	10
400	30.69 ³	30.65	8	7.3
333	40.20 ³	40.15	1/2	0
440	43.80 ³	43.89	6	5
622	52.01 ³	51.98	4	4
444	54.53 ³	54.48	2	1.6
800	63.86	63.81	1/2	0.7
662	70.38	70.33	1/2	1.4
840	72.45 ³	72.44	1/2	1.8
844	80.66 ³	80.68	1/2	1.3

¹ Standard deviations of 2θ values are ±0.02.

² All 2θ with I_{calc.} ≥ 0.3/10 are listed.

³ Eleven lines used in LATT.

APPENDIX D.

OBSERVED AND CALCULATED STRUCTURE FACTOR

AMPLITUDES (X10) FOR $\text{Cs}_3\text{Zr}_2\text{I}_9$

1/2

Cs₃Zr₂I₉

M	L	FD	FC
0	0	0	0
0	2	555	-945
0	4	979	-682
0	6	6505	-8816
0	8	223	-26
0	10	215	-111
0	12	6623	7142
0	14	1674	-1764
0	16	220	-93
0	18	2694	-2538
0	20	696	786
0	24	1659	1559
0	26	1331	-1306
M = 1			
K	L	FD	FC
0	0	689	-755
0	1	1131	1185
0	2	165	67
0	4	146	-95
0	5	1770	-1696
0	6	694	-608
0	7	119	-59
0	8	1090	994
0	9	540	-562
0	10	758	829
0	11	504	319
0	12	210	-370
0	13	2011	1987
0	14	339	-271
0	15	248	237
0	16	689	-655
0	17	1057	-1007
0	18	495	-431
0	19	549	-582
0	20	614	570
0	21	732	-672
0	22	438	426
0	23	238	251
0	24	87	-9
0	25	874	856
0	26	98	-10
0	27	119	108
1	0	1517	1271
1	2	435	-322
1	4	464	321
1	6	1142	1234
1	8	1667	-1678
1	9	69	-0
1	10	1687	-1676
1	11	120	0
1	12	424	463
1	14	374	391
1	15	77	0
1	16	1412	1276
1	18	1802	961
1	20	1130	-1035
1	22	913	-829

M	L	FD	FC
1	24	92	-99
1	27	102	0
M = 2			
K	L	FD	FC
0	0	1014	-631
0	1	2105	2109
0	2	4843	-4692
0	3	5416	5788
0	4	4640	5114
0	5	3125	3107
0	6	469	-655
0	7	3449	-3371
0	8	3788	3996
0	9	3781	-3686
0	10	3399	-3462
0	11	644	-534
0	13	1135	1110
0	14	1791	-1865
0	15	2227	2220
0	16	2330	2332
0	17	495	488
0	18	885	-772
0	19	1614	-1490
0	20	1304	1234
0	21	552	-537
0	22	1435	-1356
0	23	388	352
0	24	388	341
0	25	327	317
0	26	299	-243
0	27	376	345
1	0	316	-417
1	1	1090	1148
1	2	71	154
1	3	298	-315
1	4	124	-98
1	5	1256	-1134
1	6	823	-864
1	7	240	-206
1	8	761	772
1	9	226	-260
1	10	654	705
1	11	331	240
1	12	63	-55
1	13	1782	1790
1	14	123	-72
1	15	168	-34
1	16	546	-563
1	17	854	-823
1	18	544	-529
1	19	494	-512
1	20	399	392
1	21	468	-434
1	22	426	389
1	23	193	192
1	24	106	102
1	25	829	803
1	26	122	67

2	0	8582	8660
2	2	428	-573
2	3	154	-0
2	4	801	-593
2	5	261	-0
2	6	5624	-5428
2	7	291	0
2	8	194	-196
2	9	634	0
2	10	91	2
2	11	190	0
2	12	5621	4949
2	14	1335	-1336
2	15	122	-0
2	16	171	-147
2	18	1748	-1860
2	19	94	0
2	20	568	571
2	22	179	125
2	24	1234	1217
2	26	1046	-1040
M = 3			
K	L	FD	FC
0	0	1394	1223
0	1	292	-338
0	2	387	-289
0	3	68	102
0	4	385	247
0	5	341	-388
0	6	833	972
0	7	204	239
0	8	1436	-1680
0	10	1369	-1344
0	11	331	354
0	12	480	445
0	13	117	-163
0	14	224	246
0	16	1842	1854
0	17	262	-267
0	18	823	772
0	19	85	117
0	20	883	-863
0	22	699	-688
0	23	148	167
0	24	86	-36
0	25	95	-86
1	0	397	-461
1	1	842	-868
1	2	76	167
1	3	185	-185
1	5	1181	1301
1	6	561	-644
1	8	752	699
1	9	535	554
1	10	644	662
1	11	307	-304
1	12	170	-140
1	13	1486	-1482

1	14	221	-154
1	15	219	-230
1	16	512	-539
1	17	888	775
1	18	355	-345
1	19	484	391
1	20	446	442
1	21	582	557
1	22	385	356
1	23	161	-199
1	25	683	-709
2	0	511	-632
2	1	542	653
2	2	135	-23
2	3	282	228
2	4	119	186
2	5	1053	-1175
2	6	341	-338
2	7	226	261
2	8	820	769
2	9	556	-554
2	10	389	410
2	11	265	312
2	12	288	-275
2	13	1860	1846
2	14	297	-287
2	15	276	277
2	16	324	-341
2	17	655	-682
2	18	169	-208
2	19	132	-160
2	20	491	499
2	21	597	-572
2	22	289	216
2	23	184	149
2	24	186	-97
2	25	533	543
3	0	464	352
3	2	341	-277
3	4	233	289
3	6	895	993
3	8	932	981
3	10	920	-954
3	12	111	70
3	13	194	0
3	14	160	173
3	16	759	782
3	18	662	780
3	20	693	-689
3	22	581	-528
M = 4			
K	L	FD	FC
0	0	696	-647
0	1	1454	-1141
0	2	2919	-2966
0	3	3833	-3870
0	4	1379	3498
0	5	2115	-2329

0	6	320	-519
0	7	2589	2550
0	8	2882	2884
0	9	2684	2573
0	10	2461	-2582
0	11	419	438
0	12	81	-48
0	13	848	-835
0	14	1387	-1328
0	15	1669	-1666
0	16	1693	1742
0	17	368	-362
0	18	562	-561
0	19	1121	1208
0	20	894	930
0	21	388	393
0	22	1824	-1844
0	23	278	-296
0	24	221	227
0	25	236	-254
1	0	886	865
1	1	225	240
1	2	344	-358
1	4	238	170
1	5	271	291
1	6	794	849
1	7	154	-188
1	8	1818	-1884
1	10	1873	-1822
1	11	274	-277
1	12	284	253
1	13	115	127
1	14	154	162
1	16	817	828
1	17	194	215
1	18	629	675
1	19	186	-95
1	20	683	-711
1	21	86	-49
1	22	510	-552
1	23	118	-138
1	24	97	-34
2	0	513	-484
2	1	949	923
2	2	2163	-2134
2	3	2957	2886
2	4	2349	2460
2	5	1510	1554
2	6	278	-328
2	7	1841	-1843
2	8	1918	2011
2	9	1924	-1923
2	10	1814	-1836
2	11	279	-268
2	13	615	604
2	14	986	-931
2	15	1264	1303
2	16	1302	1316
2	17	271	263

2	18	427	-435
2	19	889	-967
2	20	644	688
2	21	288	-314
2	22	780	-885
2	23	216	253
3	0	77	-94
3	1	712	678
3	2	93	188
3	3	319	-388
3	5	473	-460
3	6	491	-477
3	7	88	-128
3	8	266	282
3	9	86	47
3	10	277	267
3	11	89	13
3	12	86	55
3	13	924	981
3	14	86	72
3	15	135	-182
3	16	232	-232
3	17	386	-396
3	18	378	-396
3	19	175	-221
3	20	118	163
3	21	125	-144
3	22	139	183
4	0	3665	3399
4	1	280	-0
4	2	253	-232
4	4	352	-337
4	6	2079	-2155
4	8	99	-94
4	10	97	92
4	12	2854	2151
4	14	658	-653
4	16	112	-174
4	18	748	-778
4	20	236	228
M = 5			
K	L	FD	FC
0	0	189	-156
0	1	786	-797
0	2	73	50
0	3	526	520
0	4	92	91
0	5	668	642
0	6	588	-567
0	7	94	133
0	8	423	425
0	9	112	-158
0	10	281	283
0	13	1160	-1191
0	14	89	39
0	15	238	267
0	16	263	-255
0	17	481	496

0	18	583	-482
0	19	243	249
0	21	137	139
0	22	198	282
0	24	144	145
1	0	94	-185
1	1	764	757
1	2</		

2/2

3 16	288	-382
3 17	394	379
3 18	147	-190
3 19	122	189
3 20	142	223
4 0	255	-235
4 1	187	154
4 4	114	115
4 5	584	-492
4 6	98	-134
4 7	303	274
4 8	353	389
4 9	296	-298
4 11	124	64
4 12	131	-182
4 13	350	365
4 14	147	-151
4 15	184	141
4 17	239	-288
5 2	151	-192
5 4	184	182
5 6	619	583
5 8	315	-329
5 10	367	-486
5 14	88	16

M = 6		
K	L	FO FC
0 0	4752	4521
0 2	388	-384
0 4	461	-391
0 6	2918	-2938
0 7	755	31
0 8	99	-89
0 9	252	-3
0 10	96	82
0 12	2774	2881
0 14	839	-819
0 16	198	-178
0 18	1824	-1826
0 20	322	388
0 22	184	147
1 0	257	-256
1 1	488	-371
1 3	328	-314
1 4	88	-34
1 5	614	688
1 6	289	-239
1 7	99	-124
1 8	419	482
1 9	462	478
1 10	323	318
1 11	86	-115
1 12	155	-174
1 13	713	-716
1 14	87	-125
1 15	211	-238
1 16	278	-256
1 17	423	426

1 18	185	-135
1 19	99	107
1 20	268	319
1 21	361	486
2 0	358	-316
2 1	538	-588
2 2	1286	-1142
2 3	1524	-1524
2 4	1418	1367
2 5	968	-923
2 6	135	-153
2 7	1151	1151
2 8	1288	1136
2 9	1882	1843
2 10	1874	-1832
2 11	99	188
2 12	98	-117
2 13	382	-368
2 14	538	-586
2 15	747	-754
2 16	783	788
2 17	145	-155
2 18	289	-226
2 19	641	662
3 0	363	336
3 1	178	188
3 2	153	-283
3 5	249	228
3 6	485	481
3 7	186	-138
3 8	383	-375
3 10	383	-488
3 11	228	-238
3 12	126	176
3 13	95	182
3 16	298	317
3 17	135	198
4 0	164	-213
4 1	184	233
4 2	719	-619
4 3	977	937
4 4	848	791
4 5	561	542
4 6	117	-189
4 7	696	-784
4 8	643	639
4 9	639	-649
4 10	597	-682
4 11	287	-16
4 12	91	-84
4 14	237	-245
5 1	318	292
5 3	116	-147
5 5	97	-151
5 6	183	-232

M = 7			
K	L	FO	FC
0 0	344	-386	

0 1	99	133
0 2	117	-156
0 3	111	123
0 4	286	192
0 5	664	-648
0 6	113	-145
0 7	412	369
0 8	588	521
0 9	342	-385
0 11	86	114
0 12	227	-224
0 13	489	411
0 14	139	-214
0 15	135	143
0 17	312	-346
0 20	299	346
1 0	113	136
1 1	98	121
1 2	239	-223
1 4	88	128
1 5	115	146
1 6	677	652
1 7	84	-89
1 8	473	-459
1 10	513	-538
1 11	115	-146
1 16	368	428
1 17	182	128
1 18	482	437
2 0	97	-48
2 1	444	-372
2 3	387	341
2 4	114	123
2 5	194	258
2 6	333	-314
2 7	84	-36
2 8	181	177
2 9	143	-175
2 11	91	67
2 13	489	-488
2 15	175	248
3 1	431	398
3 2	116	168
3 3	99	128
3 4	113	-181
3 5	112	-184
3 6	196	-251
3 7	93	-82
3 9	141	-288
3 10	234	231
3 11	97	-39
3 13	497	538
4 0	347	368
4 1	147	-139
4 2	184	-135
4 5	166	-172
4 6	96	123
4 7	99	182
4 8	117	-198

Cs₃Zr₂I₉

M = 8			
K	L	FO	FC
0 0	244	-235	
0 1	383	387	
0 2	918	-823	
0 3	1414	1247	
0 4	1135	1831	
0 5	729	677	
0 7	897	-861	
0 8	875	824	
0 9	984	-873	
0 10	832	-786	
0 11	128	-35	
0 12	98	-71	
0 13	168	239	
0 14	351	-324	
0 15	648	661	
0 16	589	684	
1 1	481	438	
1 2	185	141	
1 5	148	-193	
1 6	322	-298	
1 7	115	-88	
1 10	148	193	
1 13	554	569	
2 0	1665	1568	
2 2	114	-115	
2 4	178	-218	
2 5	94	-58	
2 6	932	-982	
2 7	188	31	
3 0	184	-113	
3 1	185	-148	
3 3	168	-176	
3 5	285	232	

M = 18			
K	L	FO	FC
0 0	187	-187	
0 1	139	-158	
0 2	437	-378	
0 3	918	-823	

M = 9			
K	L	FO	FC
0 0	579	518	
0 1	221	-174	
0 3	84	34	
0 5	215	-213	
0 6	116	75	
0 7	132	128	
0 8	154	-229	
0 10	118	-197	
0 11	193	219	
0 12	252	319	
1 0	115	-88	
1 1	199	-232	
1 2	92	-82	
1 3	266	-234	
1 4	186	-93	
1 5	194	215	
1 6	185	-142	
1 8	188	137	
1 9	289	286	

APPENDIX E.

OBSERVED AND CALCULATED STRUCTURE FACTOR

AMPLITUDES (X10) FOR $\text{CsZr}_6\text{I}_{14}$ (CRYSTALS 1 AND 2)

CoZr₆L₁₄ (Crystal I) F_oF_c x 10

H = 1				H = 2				H = 3																			
K	L	FO	FC	K	L	FO	FC	K	L	FO	FC																
12	14	386	368	5	8	2301	2225	15	9	707	749	4	10	8613	7962	12	12	2370	2036	3	4	3474	3171				
14	14	2079	1853	5	9	3042	3445	15	10	406	388	4	11	8574	8679	12	13	2948	2743	3	11	2517	2489				
14	2	1352	1281	5	10	3373	3209	15	13	462	409	4	12	3710	3311	12	14	4494	4686	3	13	2156	1777				
14	6	592	751	5	12	1547	1398	17	1	352	299	4	13	3912	3299	12	15	2534	2596	3	14	608	715				
14	8	1778	1881	5	13	447	272	17	2	381	348	4	14	8460	7356	14	0	3613	3312	3	16	2185	2040				
14	10	2309	2761	5	14	2561	2453	17	3	1013	1013	4	15	3890	2923	14	1	1956	1931	3	17	904	951				
14	12	830	1012	5	16	1436	1100	17	5	2600	2442	4	16	1675	1652	14	2	1623	1713	5	1	2859	3623				
16	2	873	892	5	17	1566	1635	17	7	381	102	4	17	4090	4189	14	3	2351	2356	5	2	4696	4720				
16	4	9922	9591	7	1	708	178	17	8	1551	1522	6	0	4038	4151	14	5	330	278	5	4	893	846				
16	6	1420	1493	7	2	1369	1401	19	1	1333	1399	6	1	2607	2620	14	6	344	498	5	5	3208	3400				
16	8	4570	4595	7	3	513	974	19	3	423	529	6	2	2037	2077	14	7	2800	2693	5	6	4193	5093				
16	12	5900	6152	7	4	308	194	19	5	1837	1788	6	3	3264	3099	14	8	2457	2223	5	7	1755	1860				
18	0	1172	1184	7	5	2239	2095	19	6	492	559	6	4	321	125	14	10	2223	2283	5	8	4365	4297				
2	2	935	876	7	6	698	750	19	9	977	1061	6	6	639	267	14	11	1127	1188	5	9	954	1092				
2	4	4594	4665	7	8	3112	2887	21	2	921	982	6	7	3422	3610	14	12	465	612	5	10	988	817				
2	6	3381	3352	7	11	1135	864	21	3	471	520	6	8	2725	2466	14	13	1275	1517	5	11	2660	2916				
2	8	791	585	7	12	1141	1143	21	5	749	972	6	9	364	344	16	0	1119	1113	5	12	715	686				
2	10	1269	1139	7	13	1103	1092	21	8	1221	1082	6	10	2479	2559	16	1	591	547	5	13	2262	1889				
2	12	1814	1801	7	14	590	397	21	11	1221	1082	6	11	1221	1082	16	2	1007	1001	5	14	715	709				
2	14	1662	1605	7	16	1873	1940	21	14	1502	1637	6	12	748	637	16	3	1302	1263	5	16	2819	3256				
2	16	2199	2293	9	2	2097	3082	21	16	1502	1637	6	13	2096	1967	16	6	573	612	5	17	599	733				
2	18	533	450	9	4	998	897	21	18	1100	1163	6	15	1332	1338	16	7	1129	1086	7	1	2127	2619				
4	0	3968	3655	9	6	2512	3249	21	20	1688	1743	6	16	412	609	16	8	432	544	7	2	1166	1236				
4	2	1774	1793	9	8	998	897	21	22	3	913	838	6	18	262	361	16	10	2	359	527	7	3	1693	1291		
4	4	369	212	9	10	5755	5697	21	24	3660	3858	6	20	286	229	16	12	1632	1676	7	4	1070	1192				
4	6	655	657	9	12	2285	2124	21	26	5	1028	1020	6	22	1485	1453	20	0	2112	1916	7	5	1340	1404			
4	8	3062	3493	9	14	1441	1706	21	28	6	2949	3074	6	24	2220	2638	20	1	3361	3591	7	6	626	699			
4	10	790	928	9	16	1195	1151	21	30	7	863	985	6	26	5	830	688	20	2	4966	4929	7	7	1423	1637		
4	14	1259	1176	9	18	2284	1495	21	32	8	960	1223	6	28	6	2025	2014	20	3	3904	3931	7	8	846	914		
4	16	2057	1922	9	20	13422	3157	21	34	11	1678	1695	6	30	8	376	173	20	4	4218	1152	7	9	2573	2030		
6	0	1835	1792	11	2	1295	947	21	36	12	1803	940	6	32	10	424	569	20	5	3110	3312	7	10	1167	1200		
6	2	1431	1473	11	4	1295	947	21	38	13	1048	966	6	34	12	478	687	20	6	4153	4082	7	11	870	806		
6	4	984	914	11	6	1297	1153	21	40	14	2397	2179	6	36	13	1197	1080	20	7	2732	2953	7	12	1466	1408		
6	6	1523	1493	11	8	1297	1153	21	42	17	715	822	6	38	14	1262	1442	20	8	1515	1410	7	13	465	540		
6	8	2445	2216	11	10	3	970	1043	21	44	1985	1775	6	40	16	438	209	22	0	1467	1582	7	14	511	635		
6	10	523	701	11	12	1080	1195	21	46	2	1080	1195	6	42	18	324	459	22	1	671	799	7	15	1475	2017		
6	12	639	743	11	14	2	1089	1491	21	48	3	1347	1467	6	44	1	500	483	22	2	848	981	7	16	2836	2520	
6	14	1635	1656	11	16	2	1089	1491	21	50	4	2105	2169	6	46	10	2	688	696	22	3	1908	2251				
6	16	2354	2560	11	18	1551	1304	21	52	2	1578	1520	6	48	4	2925	2808	22	4	790	964	7	17	2562	2493		
8	2	554	496	11	20	11204	1130	21	54	2	1663	1952	6	50	5	510	530	22	5	1204	1130	7	18	1902	2030		
8	4	16151	13971	11	22	11204	1130	21	56	2	1326	1156	6	52	6	1747	1746	22	6	2136	1901	7	19	2136	1901		
8	6	3581	3694	11	24	11204	1130	21	58	2	1140	1147	6	54	7	328	223	22	7	1807	1941	7	20	2661	2567		
8	8	817168	16446	11	26	11204	1147	21	60	2	1186	1135	6	56	8	332	256	22	8	2315	2943	7	21	461	360		
8	10	1791	1424	11	28	13	2042	1953	21	62	12	1186	1135	6	58	9	953	936	22	9	5	775	126	7	22	1553	1453
8	12	4724	4509	11	30	13	2220	2373	21	64	13	1711	1427	6	60	10	12	1126	1164	22	10	1104	1282	7	23	1104	1282
8	14	2363	2409	11	32	13	2220	2373	21	66	14	1248	1270	6	62	11	13	662	697	22	11	1840	2016				
8	16	5934	5985	11	34	13	4	703	632	21	68	15	432	544	6	64	12	14	1557	1564	22	12	441	543			
10	0	3241	3922	11	36	13	7	1068	1784	21	70	16	471	615	6	66	12	15	2194	2273	22	13	354	400			
10	2	548	354	11	38	13	8	1724	1435	21	72	17	479	746	6	68	12	16	2405	1974	22	14	815	433			
10	4	5746	5583	11	40	13	9	2093	1935	21	74	18	3036	3225	6	70	12	17	3072	2960	22	15	4	815	433		
10	6	3951	3728	11	42	13	10	2237	2351	21	76	19	4567	9332	6	72	12	18	1428	1721	22	16	5	1916	1556		
10	8	2029	1795	11	44	13	11	2596	2308	21	78	20	215057	16855	6	74	12	19	1529	1270	22	17	7	459	493		
10	10	2039	2224	11	46	13	12	590	757	21	80	21	3148581	6769	6	76	12	20	1914	1911	22	18	8	622	657		
10	12	2260	2456	11	48	13	13	1759	1945	21	82	22	41088	8947	6	78	12	21	829	898	22	19	9	473	578		
10	14	1916	2116	11	50	15	1	336	476	21	84	23	511619	11319	6	80	12	22	1981	2030	22	20	10	936	926		
12	0	334	383	11	52	15	2	1564	1473	21	86	24	6139201	15456	6	82	12	23	3803	2924	22	21	11	1152	1260		
12	2	843	875	11	54	15	3	402	556	21	88	25	7	4905	3758	6	84	12	24	4	489	345	22	22	12	755	940
12	4	1505	1502	11	56	15	4	736	794	21	90	26	8	2662	2681	6	86	12	25	5	3036	2595	22	23	13	1217	1171
12	6	1612	1566	11	58	15	5	1937	2478	21	92	27	9	8563	8236	6	88	12	26	6	2563	3497	22	24	13	2131	2436
12	8	1250	1240	11	60	15	6	1937	2478	21	94	28	10	5853	5362	6	90	12	27	7	1204	1387	22	25	13	2469	2423

CsZr₆I₁₄ (Crystal I) F_oF_c × 10

18	3	1300	1223	0	2	470	476	0	8	4224	3650	8	11	5778	5722	1	10	489	538	11	11	1169	1266	4	10	9720	8079
18	6	404	619	9	3	337	435	0	9	7200	6527	8	12	3998	3720	1	11	970	1033	11	12	1025	1109	4	11	3461	3121
18	7	1391	1451	9	4	486	486	0	10	5656	4950	8	13	3362	3145	1	13	2338	2396	13	3	2078	2000	4	13	2757	2616
18	8	1115	1121	9	5	773	847	0	11	7236	6865	8	14	3729	3746	1	16	2200	2424	13	4	390	467	4	14	5527	5513
20	0	6346	6203	9	6	1000	1053	0	12	5369	4630	8	15	2952	3164	3	1	462	615	13	5	1088	1748	6	0	861	904
20	2	471	679	9	7	1153	1304	0	13	4147	3687	10	0	3404	3178	3	2	983	1047	13	6	742	820	6	1	363	394
20	3	1932	2003	9	8	724	712	0	14	5348	5014	10	1	801	730	3	3	2760	2790	13	7	1427	1465	6	2	1624	1809
20	4	5853	6215	9	9	3071	2850	0	15	3570	3592	10	2	805	899	3	4	687	742	13	9	910	931	6	3	1068	951
20	5	1200	1194	9	10	1420	1467	0	16	1778	1688	10	3	873	756	3	5	2108	2274	13	10	376	356	6	4	765	1018
				9	12	491	528	2	0	1759	1497	10	4	716	852	3	6	856	786	13	11	976	1122	6	5	1010	946
				9	14	1244	1394	2	1	758	937	10	6	317	438	3	7	2084	2171	13	12	523	505	6	6	1476	1600
				11	1	1260	827	2	2	420	405	10	7	1331	1187	3	8	552	359	15	1	1908	1827	6	7	390	162
				11	2	472	592	2	3	877	1142	10	8	2689	2670	3	9	618	422	15	8	712	844	6	14	1697	1690
				11	3	1052	914	2	4	2732	2758	18	10	1214	1260	3	10	883	852	15	9	1946	2004	6	11	852	879
				11	4	1170	1046	2	6	1306	1353	10	12	463	694	3	11	1705	1471	17	1	392	451	6	12	562	549
				11	6	371	333	2	7	1230	1162	10	13	676	800	3	12	752	862	17	2	1113	1201	6	14	1390	1504
				11	7	973	907	2	8	2176	2085	12	0	1648	1266	3	13	949	583	17	5	469	600	6	0	3630	3200
				11	8	548	601	2	9	351	89	12	1	297	152	3	14	1503	1629	17	6	602	727	6	1	421	420
				11	11	1485	1462	2	12	1099	1147	12	2	1384	1422	3	15	1586	1694	17	7	652	838	8	2	904	1295
				11	12	1597	1612	2	13	971	928	12	4	1539	1463	5	1	413	320	17	8	1837	1644	8	3	3279	2090
				13	1	1881	1640	2	14	431	732	12	6	2349	2374	5	3	3146	3348	19	1	991	1039	8	5	1628	1465
				13	3	1067	1073	2	15	705	841	12	7	743	800	5	4	397	512	19	2	1205	1319	8	7	1228	1076
				13	4	608	693	2	16	1377	1556	12	13	561	645	5	5	3138	3284	19	4	510	540	8	8	1610	1045
				13	5	3772	3507	4	0	3712	5674	14	0	1439	1271	5	6	1495	1366	19	5	536	552	8	9	1450	1320
				13	7	785	674	4	1	281	204	14	4	3692	3570	5	7	2130	2169					8	10	1850	1745
				13	8	1075	1056	4	2	1610	1405	14	6	1911	1991	5	9	1685	1457					8	11	1806	1856
				13	11	1704	1601	4	4	3764	4038	14	9	448	170	5	10	446	465					10	0	3040	2922
				13	12	913	1091	4	5	302	225	14	10	1306	1286	5	11	1385	1295					10	1	2350	2082
				13	13	2216	2380	4	6	4518	4459	14	12	1003	1228	5	13	1132	1974					10	2	1624	1688
				15	1	985	998	4	7	663	691	16	0	4868	4211	5	14	1461	1690					10	3	1441	1530
				15	2	507	324	4	8	1943	1836	16	1	4844	4443	5	15	2029	2221					10	4	749	502
				15	3	1370	1285	4	10	1167	938	16	2	5128	4569	7	1	1152	1023					10	7	2645	2459
				15	5	2952	2907	4	11	610	616	16	3	5481	5230	7	2	1450	1339					10	8	1492	1486
				15	6	546	681	4	12	613	540	16	4	2565	2320	7	3	454	367					10	10	2313	2300
				15	10	573	629	4	13	834	898	16	5	4403	4276	7	5	1408	1267					10	11	962	1000
				15	11	426	882	4	14	2843	2863	16	6	3311	3056	7	6	1059	1012					10	13	900	1013
				15	12	375	318	4	15	530	678	16	7	3726	3683	7	8	2205	2129					12	0	920	906
				17	1	762	841	6	0	1290	1299	16	8	2854	2725	7	9	1733	1543					12	1	3643	3029
				17	3	365	493	6	3	626	612	16	9	3418	3422	7	13	1506	1540					12	2	2100	2172
				17	5	1059	1139	6	4	4272	4515	16	10	3643	3705	7	15	462	520					12	3	2751	2444
				17	6	929	1016	6	6	2460	2429	18	0	1930	1954	9	1	1574	1402					12	5	3382	3093
				17	7	559	709	6	7	749	650	18	2	423	646	9	2	2444	2518					12	6	9125	8470
				17	9	1064	1070	6	16	1584	1348	18	3	465	475	9	3	511	460					12	7	2527	2264
				17	10	932	1092	6	12	1463	1464	18	4	526	687	9	5	2385	2246					12	9	1996	2005
				19	1	369	294	6	13	509	775	18	6	520	496	9	6	1885	1717					12	10	5801	5046
				19	3	878	1078	6	14	1679	1801	18	7	754	787	9	7	1187	1110					12	11	1498	1614
				19	4	583	689	6	15	563	519	18	8	1704	1785	9	8	3436	3122					14	2	1277	1320
				19	7	461	578	6	16	1092	1396	20	2	554	895	9	9	551	604					14	3	1157	1073
				8	0	5562	5263	8	0	5562	5263	20	3	394	408	9	10	576	717					14	4	971	1046
				8	1	8267	7511	8	1	8267	7511	9	11	963	1138	9	11	963	1138					14	5	776	799
				8	2	8019	7465	8	2	8019	7465	9	13	1956	2018	4	1	3361	3462					14	6	1368	1451
				0	0	5591	4710	8	3	9803	9147	11	1	1490	1543	4	2	13011	13820					14	10	964	1160
				0	1	9196	8981	8	4	6609	6183	1	1	874	1395	11	2	1884	1681					14	11	649	900
				0	2	9371	9374	8	5	8044	7330	1	2	2637	3313	11	3	1007	1020					14	0	1303	1372
				0	3	16239	12230	8	6	7170	6509	11	4	989	851	11	4	750	816					16	3	897	908
				0	4	9325	9320	8	7	6083	5910	1	5	3310	2801	11	7	1437	1413					16	4	356	663
				0	5	9098	9093	8	8	4126	3462	1	6	2045	2007	11	8	946	913					16	5	471	610
				0	6	8535	8737	8	9	5748	5470	1	7	828	951	11	9	638	806					16	9	408	764
				0	7	7145	7077	8	10	5499	4712	1	8	3376	3004	11	10	1114	1073					14	2	1624	1834

CsZr₆L₁₄ (Crystal I) F_oF_c x 10

18 1 1188 1256	11 7 1167 1119	4 12 944 1250	1 8 822 936	H = 14	16 4 440 481	4 5 1424 1458	M = 18
18 2 727 946	11 10 1069 1117	4 13 924 1054	1 11 1777 1725	K L FO FC		4 7 374 249	K L FO FC
18 3 834 917	11 12 462 676	4 14 927 958	1 12 582 726		H = 15	4 8 1373 1301	0 3 1508 1558
	13 1 480 496	6 0 1543 1599	1 13 1165 1338		K L FO FC	4 9 1189 1203	0 4 1610 1645
H = 11	13 2 1774 1849	6 1 1742 1824	3 1 1840 2243			4 10 1226 1450	0 5 642 716
K L FO FC	13 3 599 88	6 2 1906 2029	3 2 1604 1518			6 0 1636 1749	0 6 667 384
1 1 3170 3160	13 5 964 898	6 3 1657 1499	3 3 935 999			6 1 1251 1835	0 7 616 705
1 2 1065 2028	13 8 927 998	6 4 504 908	3 4 805 620			6 2 1398 1627	0 8 944 1274
1 3 969 1252	13 10 2130 2281	6 7 2521 2323	3 5 1415 1419			6 3 1048 1226	2 1 470 347
1 4 1708 1663	13 11 461 678	6 8 846 1001	3 6 1899 1715			6 4 814 1046	2 2 1367 1578
1 6 1573 1593	15 1 1158 1159	6 10 1517 1712	3 7 803 835			6 5 1651 1498	2 3 537 473
1 7 1323 1181	15 2 1146 1073	6 11 742 769	3 8 1650 1547			6 6 1108 1099	2 4 407 409
1 9 2361 2261	15 3 596 647	6 13 1293 1456	3 9 2134 2002			6 7 987 973	4 0 4550 3904
1 11 1715 1828	15 6 680 778	6 15 1059 9589	3 12 503 656			6 8 423 607	4 1 1852 1965
1 12 2843 2624	15 8 1177 1320	6 16 4097 3994	3 13 1003 1061			6 9 1468 1225	4 2 1161 1273
3 2 1840 1837	15 9 489 742	6 17 2950 2810	5 1 2531 2458			6 10 991 1168	4 3 5520 5520
3 3 1232 1091	17 1 1081 1289	6 18 4941 9166	5 2 2263 2318			6 11 978 1062	4 4 5261 2625
3 5 2026 1699	17 2 431 575	6 19 3222 3077	5 3 476 549			6 12 1976 1851	4 5 934 823
3 6 563 469	17 3 406 485	6 20 735 90	5 4 1841 981			6 13 1362 1265	4 6 808 724
3 7 859 840	17 4 493 703	6 21 3104 2956	5 5 578 774			6 14 398 401	4 7 3102 3283
3 8 1422 960	17 6 406 558	6 22 8681 7619	5 6 2626 2430			6 15 1690 1578	6 0 691 1030
3 10 2508 2525		6 23 3371 3495	5 7 641 864			6 16 570 605	6 2 1289 1525
3 12 438 373	H = 12	6 24 1135 1126	5 8 2158 2260			6 17 1333 1567	4 3 1086 1030
3 13 550 444	K L FO FC	6 25 4897 5227	5 9 2385 2460			6 18 736 857	4 4 718 629
3 14 1297 1484	0 0 11937 11810	6 26 1905 2011	5 12 1157 1251			6 19 1761 743	6 5 476 561
3 15 817 844	0 1 6218 5400	6 27 1575 1645	5 13 447 664			6 20 427 548	6 6 1566 1719
5 1 319 235	0 3 2942 2570	6 28 464 624	7 1 1365 1191			6 21 2279 2162	0 3 934 1007
5 2 3347 3190	0 4 11843 10912	6 29 1949 984	7 2 839 939			6 22 2715 2744	10 1 537 645
5 4 588 624	0 5 5327 3479	6 30 880 1045	7 3 1373 1245			6 23 1087 1193	
5 5 1263 1302	0 6 1351 104	6 31 473 509	7 4 1125 999			6 24 2085 2050	
5 6 354 382	0 7 4660 4289	6 32 934 1230	7 5 690 201			6 25 796 883	
5 8 2015 1681	0 8 810362 9180	6 33 1099 1230	7 6 1802 1720			6 26 3703 771	
5 10 3342 3133	0 9 3934 3511	6 34 1281 1863	7 7 1420 1539			6 27 1481 1441	
5 12 1051 1090	0 11 774 756	6 35 1415 1214	7 8 1281 1063			6 28 948 861	
5 13 447 664	0 12 5977 5792	6 36 473 344	9 1 1415 1214			6 29 1866 1920	
5 14 1303 1476	0 13 2774 2633	6 37 1434 1523	9 2 473 344			6 30 788 1002	
7 1 2446 2329	2 0 1310 1335	6 38 1104 1024	9 3 1434 1523			6 31 2172 1940	
7 3 1034 1154	2 1 884 839	6 39 1423 1399	9 4 1104 1024			6 32 1486 1518	
7 4 643 716	2 2 2203 2090	6 40 1223 1298	9 5 1423 1399			6 33 1549 1468	
7 5 333 271	2 3 664 745	6 41 1528 1470	9 6 1223 1298			6 34 2435 2523	
7 7 783 1009	2 4 1140 1084	6 42 1251 1363	9 7 1528 1470			6 35 498 718	
7 8 1267 1140	2 5 919 928	6 43 1161 1055	9 8 1251 1363			6 36 1110 1042	
7 9 1548 1570	2 6 615 439	6 44 497 440	11 3 1161 1055			6 37 474 475	
7 11 1375 1491	2 7 425 405	6 45 843 522	11 4 497 440			6 38 3177 3078	
7 12 965 1187	2 8 1566 1629	6 46 402 814	11 5 843 522			6 39 1162 1419	
9 1 2630 2491	2 9 496 496	6 47 1495 1981	11 6 402 814			6 40 943 1013	
9 2 2097 2000	2 10 1566 1629	6 48 5669 5588	11 7 1495 1981			6 41 4372 4081	
9 3 814 870	2 11 496 496	6 49 1989 1778	11 8 5669 5588			6 42 456 4291	
9 4 1633 1527	2 12 802 1027	6 50 601 358	6 50 1989 1778			6 43 2596 2378	
9 6 1576 1620	4 1 1070 1022	6 51 2475 2640	6 51 601 358			6 44 3722 3685	
9 7 603 757	4 2 445 599	6 52 5607 5788	6 52 2475 2640			6 45 3731 3567	
9 9 1850 1933	4 3 3039 3592	6 53 715 896	6 53 5607 5788			6 46 3445 3493	
9 10 627 772	4 4 715 896	6 54 1389 1314	6 54 715 896			6 47 1831 1769	
9 11 1306 1421	4 5 1389 1314	6 55 747 629	6 55 1389 1314			6 48 3893 4019	
9 12 2298 2529	4 6 747 629	6 56 2009 1825	6 56 747 629			6 49 2819 2895	
11 3 1511 1364	4 7 2009 1825	6 57 914 564	6 57 2009 1825			6 50 1860 1908	
11 4 567 482	4 8 914 564	6 58 551 569	6 58 914 564			6 51 587 709	
11 5 2219 2011	4 9 654 658	6 59 2219 2011	6 59 551 569			6 52 456 607	
11 6 1469 1401	4 10 551 569	6 60 2129 1844	6 60 2219 2011				
	4 11 2219 2011						

CsZr₆I₁₄ (Crystal 2) F_oF_c x 10

M = -16	-3 6 399 511	6 14 865 927	3 8 1639 1843	13 9 2094 2056	6 0 4548 4357	16 2 1145 1162
K L FO FC	-1 13 267 306	6 12 418 472	3 9 2107 2182	13 10 2120 2054	6 1 2796 2728	16 3 1654 1698
-2 2 275 493		6 14 343 344	3 10 2314 2221	15 1 768 770	6 2 2185 2094	16 6 302 592
-2 5 797 776		8 0 2666425845	3 11 537 472	15 2 1723 1692	6 3 3706 3380	16 7 1455 1420
	M = -4	8 0 41664414638	3 12 1285 1226	15 3 733 736	6 6 254 55	18 2 367 538
	K L FO FC	8 6 3907 3866	3 13 535 706	15 5 846 803	6 7 3521 3671	18 4 1679 1633
	M = -15	8 8 81673716006	3 14 2357 2306	15 6 754 840	6 8 2508 2476	
K L FO FC	-14 4 487 291	8 10 1578 1479	5 1 4139 4339	15 8 2415 2364	6 9 786 776	
-7 4 228 91	-8 12 568 398	8 12 10442 9985	5 2 4396 4224	15 9 943 1002		M = 3
-1 6 378 481	-6 4 323 768	10 0 3388 4357	5 4 1637 1494	17 2 336 497	6 11 1128 1068	K L FO FC
	-6 5 462 585	10 2 327 185	5 6 1220 1472	17 3 847 936	6 12 812 909	1 1 2683 2951
		10 4 5825 5785	5 8 2265 2224	17 5 2343 2307	6 13 2104 2096	1 2 1859 1711
		10 6 4239 4238	5 9 3769 3741		8 0 335 425	1 3 2893 3182
		10 10 2211 2082	5 10 2787 2748		8 1 304 67	1 6 3038 3044
		10 12 1683 1694	5 12 1574 1527		8 2 1522 1426	1 7 2169 2114
		12 0 227 111	5 13 257 162		8 3 517 666	1 8 1981 1848
		12 2 774 782	5 14 2556 2587		8 4 2163 2475	1 11 2973 2951
		12 4 1891 1450	7 1 469 37		8 5 458 511	1 14 1791 1742
		12 6 1741 1774	7 2 1679 1542		8 6 2088 2124	1 15 1353 1329
		12 8 956 1052	7 3 568 792		8 7 393 352	3 1 2384 2733
		12 10 588 559	7 4 296 90		8 8 429 110	3 2 3812 2799
		14 0 2190 2179	7 5 2852 2428		8 9 454 443	3 3 278 678
		14 2 1279 1320	7 6 598 712		8 10 277 482	3 4 724 648
		14 4 327 297	7 8 3169 3056		8 11 893 866	3 5 3041 2586
		14 6 520 574	7 11 812 807		8 12 995 995	3 6 2610 2969
		14 8 1974 2064	7 12 1238 1199		8 13 327 215	3 7 1822 1885
		14 10 1137 1234	7 13 548 610		10 0 567 655	3 8 3168 3171
		16 0 1258412053	7 14 458 562		10 1 545 565	3 10 479 536
		16 2 834 898	9 1 2327 3291		10 2 584 588	3 11 2598 2573
		16 4 1105210667	9 3 2667 3136		10 3 431 401	3 13 1531 1496
		16 6 1223 1380	9 4 916 929		10 4 3172 3110	3 14 410 524
		16 8 9114 8592	9 5 5688 5812		10 5 688 652	5 1 3934 3685
		18 0 1441 1238	9 6 247 312		10 6 1915 1965	5 2 5127 4828
		18 2 279 599	9 7 359 513		10 7 321 427	5 3 397 611
		18 4 3393 3505	9 8 2169 2134		10 8 305 254	5 4 1371 1284
			9 9 1243 1074		10 9 325 311	5 5 3215 3632
			9 10 589 574		10 10 584 531	5 6 3955 5051
			9 11 1636 1626		10 11 1186 1159	5 7 1503 1547
			9 12 2071 2033		10 12 1079 1095	5 8 4645 4537
			9 13 2745 2797		12 0 3788 3430	5 9 1825 1865
			11 1 1464 1312		12 1 7684 6781	5 10 381 382
			11 2 1004 934		12 2 21093010298	5 11 3828 3857
			11 3 1148 1281		12 3 9828 9173	5 12 1124 1054
			11 4 471 489		12 4 4244 3843	5 13 1700 1652
			11 5 3265 3328		12 5 7201 6833	7 1 2781 2881
			11 6 970 973		12 6 9721 9040	7 2 1774 1850
			11 8 309 413		12 7 5192 4893	7 3 1322 1413
			11 9 681 689		12 8 2845 2563	7 4 1191 1303
			11 10 1046 1037		12 9 6173 5929	7 5 1216 1363
			11 11 1444 1446		12 10 6757 6285	7 6 541 384
			11 12 334 410		12 11 5284 5135	7 7 1469 1534
			13 1 1953 1986		14 0 3649 3581	7 8 386 507
			13 2 2407 2314		14 1 2132 2032	7 9 698 752
			13 3 457 489		14 2 1742 1806	7 10 1158 1196
			13 4 862 788		14 3 2715 2646	7 11 2506 2527
			13 5 554 694		14 4 2862 2822	7 12 1155 1169
			13 6 343 472		14 5 8165 7669	7 13 459 536
			13 7 941 997		14 6 2312 2243	7 14 1492 1683
			13 8 1499 1455		14 7 1299 1247	9 1 1792 2011
					14 8 11692 8303	9 2 1798 2288
					14 9 475 595	
					14 10 2299 2407	
					16 0 1297 1394	
					16 1 824 786	
					16 2 7394 7124	

CsZr₆I₁₄ (Crystal 2) F_oF_c × 10

3	2409	2509	2	6	482	77	12	5	525	569	5	8	1357	1322	M = 6	8	8	2706	2722	3	4	1357	1430
5	292	454	2	7	1085	1356	12	6	348	346	5	9	919	1063	K L FO FC	8	1	859	963	3	5	3105	3599
6	2645	2522	2	8	1299	1204	12	7	243	308	5	10	1066	1001	0	0	4899	4639	8	2	1055	1052	
7	1915	2014	2	9	249	302	12	8	1004	1080	5	11	854	952	0	1	1926	1710	8	3	3494	3471	
8	1893	1867	2	10	3139	3143	12	9	320	455	5	12	3190	3115	0	2	1503	1470	8	4	810	763	
9	201	124	2	11	573	019	12	10	1515	1590	5	13	1673	1831	0	3	5640	5255	8	5	910	802	
11	2580	2594	2	12	924	1016	12	11	453	555	5	14	697	692	0	4	264	479	8	6	1564	1420	
11	1	373	343	2	13	656	710	14	0	1997	2125	7	1	375	857	0	5	1330	1380	8	7	2044	2098
11	2	803	807	2	14	819	802	14	1	1740	1684	7	2	2024	2427	0	6	636	861	8	8	1252	1200
11	4	478	436	4	0	4619	4319	14	2	1443	1539	7	3	760	646	0	7	2750	2790	8	9	1644	1599
11	5	1526	1420	4	1	1698	1570	14	3	1654	1598	7	4	660	843	0	8	3074	3136	8	10	620	923
11	8	301	405	4	2	1744	1686	14	4	2012	2009	7	5	747	681	0	9	1632	1589	10	0	2551	2545
11	9	769	803	4	3	3664	3399	14	5	443	751	7	6	1064	1000	0	10	1296	1323	10	1	2462	2391
11	10	1375	1330	4	4	525	559	16	1	4754	4711	7	7	884	880	0	11	2623	2458	10	2	1834	1841
11	11	1291	1290	4	5	1699	1802	16	2	9126	8549	7	8	1279	1191	0	12	620	924	10	3	2595	2503
11	12	1064	1013	4	6	470	1004	16	3	3873	3600	7	9	515	503	0	13	1674	1701	10	4	509	501
13	1	2184	2122	4	7	2129	2333	16	4	1715	1517	7	10	1789	1759	0	14	1643	1572	10	5	233	193
13	2	2492	2375	4	8	1288	1360	16	5	3966	3869	7	12	405	513	2	0	1377	1359	10	6	343	476
13	3	647	738	4	9	1048	1153	16	6	8738	8524	9	1	2361	2583	2	1	2317	2194	10	7	2950	2960
13	4	360	422	4	10	2428	2105	16	7	3985	3861	9	2	4946	4960	2	2	1877	1856	10	8	1851	1883
13	5	1790	1587	4	11	2533	2491	18	0	2050	2063	9	4	1781	1710	2	3	1816	1703	10	9	446	512
13	6	1977	1923	4	12	897	965	18	1	991	923	9	5	1425	1300	2	4	1107	1269	10	10	1630	1740
13	7	1231	1264	6	0	3374	3058	18	2	1654	1783	9	6	852	715	2	5	857	670	10	11	1006	1078
13	8	2085	2902	6	1	1952	1810					9	8	3054	3014	2	6	1556	1546	12	0	14834	1497
13	9	456	609	6	2	2460	2377					9	9	1775	1823	2	7	2508	2509	12	1	2133	1999
15	1	1753	1724	6	3	1560	1866					9	10	3086	3050	2	8	1463	1482	12	2	424	666
15	2	2816	2724	6	4	1999	1940					9	11	1046	1014	2	9	907	980	12	3	3566	3352
15	4	1283	1260	6	5	948	962					9	12	1979	1973	2	10	260	300	12	4	412451	1668
15	5	1577	1544	6	6	2623	2634					11	1	2179	2252	2	11	905	990	12	5	1064	1148
15	6	931	956	6	7	1365	1299					11	2	2579	2563	2	12	1667	1694	12	6	1257	930
15	7	439	534	6	8	823	887					11	3	651	677	2	13	247	402	12	7	810635	9990
15	8	1525	1570	6	9	533	711					11	4	350	435	4	0	246592	3667	12	8	2770	2643
17	1	1401	1422	8	1	6611	5542					11	5	1416	1350	4	1	4576	4321	14	0	1049	071
17	3	1226	1219	8	2	15850	14961					11	6	527	662	4	2	255	178	14	1	935	1001
17	6	576	607	8	3	9956	9847					11	7	3200	3165	4	3	3435	3168	14	2	603	706
				8	4	3722	3148					11	8	1465	1502	4	4	416590	14677	14	3	2946	2498
				8	5	7544	7263					11	9	379	454	4	5	3158	2833	14	4	840	886
				8	6	14968	14430					11	10	1109	1229	4	6	2681	2685	14	5	2321	2434
				8	7	3447	3669					11	11	1417	1414	4	7	3069	2942	14	6	1124	1070
				8	8	946	876					13	3	1408	1420	4	8	815797	15285	16	4	1446	1563
				8	9	6111	5592					13	4	943	923	4	9	3667	3339	16	5	841	949
				8	10	4706	8226					13	5	1597	1635	4	10	1180	1154				
				8	11	5422	5112					13	6	705	753	4	11	836	787				
				8	13	2944	2803					13	7	371	536	4	12	9296	9003				
				10	0	3283	3063					13	8	1410	1429	4	13	1687	1680				
				10	1	1824	1848					13	9	1026	1061	4	14	1822	1665				
				10	2	2590	2546					13	10	360	531	6	0	1122	1030				
				10	3	3230	3133					15	1	713	706	6	1	762	686				
				10	4	835	770					15	2	370	416	6	2	1302	1003				
				10	5	450	705					15	3	464	544	6	3	362	361				
				10	6	2593	2586					15	4	1548	1592	6	4	3319	3705				
				10	7	145	1242					15	5	1004	1081	6	5	1153	1139				
				10	8	383	509					17	1	1127	1127	6	6	2840	2402				
				10	9	2000	2850					17	2	1747	1771	6	7	532	580				
				10	10	1601	1763					17	3	236	257	6	8	255	438				
				10	12	935	1013					17	4	329	525	6	9	347	351				
				12	0	2946	2947					17	5	2731	3007	6	10	925	926				
				12	1	1162	1114					17	6	1871	1946	6	11	1464	1506				
				12	2	332	331					17	7	921	1039	6	12	1464	1506				
				12	3	332	331					17	8	878	941	6	13	878	941				

