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MASTER

The Synthesis and Characterization of Some Binary and Ternary Zirconium Iodides

by

Dennis Hugh Guthrie

Ph.D. Thesis submitted to Iowa State University

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

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
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The synthesis and characterization of
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zirconium iodides¹

Dennis Hugh Guthrie

Under the Supervision of John D. Corbett
From the Department of Chemistry
Iowa State University

An investigation into the binary ZrI_4 -Zr and ternary CsI -Zr- ZrI_4 systems has produced several new compounds which were synthesized via high temperature techniques and characterized by x-ray diffraction. The new binary compounds include two polymorphs of ZrI_2 (α and β) as well as a new understanding of a phase described earlier as " $\text{ZrI}_{1.8}$ ". α - ZrI_2 forms as black lath-like crystals by vapor phase transport reactions between Zr and ZrI_4 from 700 to 825°C. Its structure was refined in the monoclinic space group $\text{P2}_1/\text{m}$ with $a = 6.821(2)$, $b = 3.741(1)$, $c = 14.937(3)$ Å and $\beta = 95.66(3)^\circ$, $Z = 4$ ($R = 0.064$). This phase is iso-electronic and isostructural with β - MoTe_2 , a distorted CdI_2 -type structure in which the zirconium atoms are displaced 0.440 Å from the centers of the octahedra along a to form zig-zag metal chains ($d_{\text{Zr-Zr}} = 3.182(3)$ Å) parallel to b . β - ZrI_2 is similarly formed as black gem-like crystals

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between 800-975°C, crystallizing in the trigonal space group $\bar{R}3$ with hexagonal axes $\underline{a} = 14.502(2)$ and $\underline{c} = 9.996(2)$ Å, $z = 18$ ($R = 0.109$). This phase contains a Zr_6I_{12} cluster as $\text{Zr}_6\text{I}_6^i \text{I}_{6 \cdot 2/3}^{1-a} \text{I}_{6 \cdot 1/3}^{a-1}$ ($d_{\text{Zr-Zr}} = 3.20$ Å) and is isostructural with $\text{Sc}_7\text{Cl}_{12} = \text{Sc}^{3+} \text{Sc}_6\text{Cl}_{12}^{3-}$ save for the isolated cation. Guinier x-ray powder diffraction data previously reported for " $\text{ZrI}_{1.8}$ " has now been found to arise from $\alpha\text{-ZrI}_2$ intergrown with an orthorhombic ZrI_2 phase (perhaps isostructural with WTe_2) plus an unknown phase.

The ternary compounds include Cs_2ZrI_6 , $\text{Cs}_3\text{Zr}_2\text{I}_9$ and $\text{CsZr}_6\text{I}_{14}$. The first is isostructural with K_2PtCl_6 . $\text{Cs}_3\text{Zr}_2\text{I}_9$ is formed from the reaction of CsI , ZrI_4 and Zr between 700-900°C as black gem-like crystals which crystallize in the space group $\text{P6}_3/\text{mmc}$ with $\underline{a} = 8.269(1)$ and $\underline{c} = 19.908(3)$ Å, $z = 2$. This phase was found to have a $\text{Cs}_3\text{Cr}_2\text{Cl}_9$ -type structure, $d_{\text{Zr-Zr}} = 3.134(4)$ Å ($R = 0.087$). $\text{CsZr}_6\text{I}_{14}$ forms both rod and gem crystals by the same reaction with more metal between 900-950°C. It crystallizes in the orthorhombic space group Ccmb with $\underline{a} = 14.275(4)$, $\underline{b} = 15.880(4)$ and $\underline{c} = 12.953(4)$ Å ($R = 0.062$). This phase also contains a Zr_6I_{12} cluster as $\text{Zr}_6\text{I}_{10}^i \text{I}_{2 \cdot 2/3}^{1-a} \text{I}_{2 \cdot 1/3}^{a-1} \text{I}_{4 \cdot 1/2}^{a-a}$ (avg. $d_{\text{Zr-Zr}} = 3.31$ Å) and is isostructural with $\text{Nb}_6\text{Cl}_{14}$ and Ta_6I_{14} except that an additional cesium occupies a hole in the binary structure.

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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-ZrI_4 and ternary CsI-Zr-ZrI_4 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 UO_2 . 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-ZrI_4 and ternary CsI-Zr-ZrI_4 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, ZrI_4 and ZrI_3 . The first is an orange-red material obtained at $\sim 350^\circ\text{C}$ from the reaction of I_2 with Zr. Though its structure is similar to those of $\alpha\text{-NbI}_4$ (5), ZrCl_4 (6) and $\beta\text{-ReCl}_4$ (7), it is unique in that the infinite chains of ZrI_6 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) $2.83(5) \leq \text{I:Zr} \leq 3.43(5)$ (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 $360/390^\circ\text{C}$ gradient in a sealed Pyrex tube. However, the powder pattern reported was found to agree well with that of the lower limit triiodide $\text{ZrI}_{2.8}$ (9). In addition to the known compounds ZrI_4 and ZrI_3 , Daake (11) prepared a phase assigned the composition " $\text{ZrI}_{1.8}$ ". This was obtained from the reaction of ZrI_3 or ZrI_4 with a large excess of zirconium at $\sim 750^\circ\text{C}$ 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 " $\text{ZrI}_{1.8}$ " 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 ($\sim 420^\circ\text{C}$) (12). In addition, other more reduced phases such as $\text{ZrI}_{1.7}$, $\text{ZrI}_{1.0}$ and $\text{ZrI}_{0.16}$ (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 ~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 ($T > 900^\circ\text{C}$).

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, $\leq 50^\circ\text{C}$ and 100-200°C, respectively, while below 900°C most gradients were $> 50^\circ\text{C}$. 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 ~ 870 - 950°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 $\beta\text{-ZrI}_2$ gem crystals, while the entire length of the metal strips was coated with a layer of $\beta\text{-ZrI}_2$. Blade-like crystals (5%) were found in the hot end of the tube both on the layer of $\beta\text{-ZrI}_2$ 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 $\alpha\text{-ZrI}_2$ (see $\text{ZrI}_{1.8}$ 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 $\text{ZrI}_2(\alpha)$ 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 $\text{Zr}_6\text{Cl}_{15}$ (20) and Zr_6X_{12} (21), ZrCl_2 (3R-MoS₂-type) (22,23), and the double-metal-layered ZrCl (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 $\text{ZrI}_{2.83}$ (775°C) to $\text{ZrI}_{3.43}$ (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 $\text{ZrI}_{2.8}$ (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 $\alpha\text{-ZrI}_2$.

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. HNO_3 , 45% H_2O , 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 ~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 2 θ 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, $3.74 \text{ \AA}$, 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 $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.107$ 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 $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ 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 $\underline{c}$, 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 $0.440 \text{ \AA}$ from the centers of the octahedral sites toward shared edges of the polyhedra to form zig-zag chains parallel to $\underline{b}$. 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 ($0.016 \text{ \AA}$) 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 $4.47 \text{ \AA}$ except for the shared edge $\text{I2}^b - \text{I2}$ which is $4.89 \text{ \AA}$. 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, $P2_1/m$ (no. 11), $Z = 4$ Lattice parameters: $a = 6.821(2)$ Å, $b = 3.741(1)$ Å, $c = 14.937(3)$ Å,
 $\beta = 95.66(3)$ 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)

$$a_y = 0.25.$$

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

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

Table II. Important distances ($\text{\AA}$) and angles (deg.) in the two independent units.

$a_{1-x, 1-y, 1-z}, b_{1-x, 1-y, -z}, c_{1-x, -y, 1-z}, d_{1-x, -y, -z},$ $e_{1+x, y, z-1}, f_{x, y, z-1}, g_{-x, 1-y, 1-z}, h_{x-1, y, z},$ $i_{2-x, 1-y, 1-z}, j_{-x, -y, 1-z}$			
<u>Distance</u>			
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)
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 α -ZrI₂ 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 $\alpha\text{-ZrI}_2$ are closely comparable to those in the cluster Zr_6I_{12} ($\beta\text{-ZrI}_2$) despite the lower number of metal neighbors in the former. The two Zr-Zr bonds per d^2 metal in $\alpha\text{-ZrI}_2$ 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 $\beta\text{-ZrI}_2$ each zirconium has pairs of metal neighbors in the Zr_6 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 $\alpha\text{-ZrI}_2$. 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 $\alpha\text{-ZrI}_2$ vs. 2.860(2) - 2.947(2) Å for the closer four in $\beta\text{-ZrI}_2$, and 2.863 Å for the average in ZrI_4 (8). The transformation from α - to $\beta\text{-ZrI}_2$ 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 Zr_6 cluster corresponds to a missing iodine atom in a close-packed layer).

The metal-metal interactions in the $\alpha\text{-ZrI}_2$ 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 ($\text{P2}_1/\text{m}$) to an undistorted CdI_2 -type ($\text{P}\bar{3}\text{m1}$) 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 Pnm2_1 structure of WTe_2 . This has been observed for (metastable) $\beta\text{-MoTe}_2$ where the β angle varies discontinuously from 93.92° ($\text{P2}_1/\text{m}$) to 90° (Pnm2_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 $\text{H}\bar{\text{K}}\text{L}$, ($2\theta \leq 50^\circ$) yielded 1119 observed ($I > 3\sigma(I)$) reflections which, when reduced and averaged in Laue symmetry $\bar{3}$, 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 (2θ) 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 $\leq 1 \text{ e/\AA}^3$, even at the center of the cluster.

DESCRIPTION OF THE STRUCTURE

Final positional and thermal parameters for $\beta\text{-ZrI}_2$ 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 (Zr_6I_{12}) 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 interlayer 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 $\alpha\text{-Zr}$ 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 Zr_6I_{12} . 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, $2\theta \leq 50^\circ$)

	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)	38
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)	

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

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 $\text{Zr}_6\text{I}_6^{\text{i i-a}}\text{I}_{6.2/3}^{\text{a-i}}\text{I}_{6.1/3}^{\text{a-i}}$. The Zr-I distances agree with this bonding scheme: the Zr-I^{i} distances of 2.860 - 2.873 Å are shorter than the $\text{Zr-I}^{\text{i-a}}$ distances, 2.917 - 2.946 Å, which are shorter than the $\text{Zr-I}^{\text{a-i}}$ 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 $\text{Sc}^{3+}\text{ScCl}_{12}^{3-}$ ($\text{Sc}_7\text{Cl}_{12}$) 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 $\text{Sc}_7\text{Cl}_{12}$, both have properties which are similar to those of $\text{Zr}_6\text{Cl}_{15}$. 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 $\text{Sc}_7\text{Cl}_{12}$, this whisker is assumed to have the composition $\text{ScCl}_{1.45}$ and an explanation is given by Poeppelmeier (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} , $\text{Zr}_6\text{Cl}_{15}$ and $\text{Sc}_7\text{Cl}_{12}$ 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/ $\text{\AA}^3$ at the center of the $\text{Zr}_6\text{Cl}_{15}$ and

Figure 4. A (11 $\bar{2}$ 0) section of the Zr₆I₁₂ structure which shows only the Zr-I¹ bonds. The dots just above and below the clusters are special positions with $\bar{3}$ symmetry which contain a Sc³⁺ cation in Sc₇Cl₁₂.

$\text{Sc}_7\text{Cl}_{12}$, 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" $\text{ZrI}_{1.8}$

INTRODUCTION

A phase identified as $\text{ZrI}_{1.8}$ 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 $\sim 750^\circ\text{C}$ for two weeks. The initial thrust of this research was to obtain single crystals of " $\text{ZrI}_{1.8}$ "; 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 $a = 3.738(1)$, $b = 6.817(2)$ and $c = 14.860(4)$ 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_2^1). 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 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 $\pm 2e/\text{\AA}^3$ at all points except the atom positions which had 4-6 $e/\text{\AA}^3$ (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 $\underline{a} = 3.75$, $\underline{b} = 6.85$ and $\underline{c} = 15.0 \text{ \AA}$ 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 $\underline{a} = 3.74$, $\underline{b} = 6.93$ and $\underline{c} = 14.85 \times n \text{ \AA}$, 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 $\alpha\text{-ZrI}_2$ (calc.) $\text{ZrI}_{1.8}$ (obs.) and an orthorhombic ZrI_2 (calc. using WTe_2 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 the $\text{ZrI}_{1.8}$ graph differ from the patterns above and below because of preferred orientation problems. The three extra lines dotted in the $\text{ZrI}_{1.8}$ 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 $\sim 150^\circ\text{C}$ gradients, e.g. $600\text{--}750^\circ\text{C}$ or $750\text{--}900^\circ\text{C}$. 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 $600\text{--}975^\circ\text{C}$ has been explored. Above 800°C , temperatures were explored by both small and large gradients, $\leq 50^\circ\text{C}$ and $100\text{--}200^\circ\text{C}$, respectively, while below 800°C most gradients were $> 50^\circ\text{C}$. 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 ($\sim 600\text{--}700^\circ\text{C}$), Cs₃Zr₂I₉ ($\sim 700\text{--}900^\circ\text{C}$), CsZr₆I₁₄ ($\sim 900\text{--}950^\circ\text{C}$) and "Q" ($\sim 950\text{--}1000^\circ\text{C}$).

Cs₂ZrI₆ (see Appendix C) was obtained in $\sim 600\text{--}700^\circ\text{C}$ 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 ~ 900 – 980°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 – 925°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 $(\underline{chc})_2$ 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 $P3lc$ 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 $\text{P6}_3/\text{mmc}$ 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 2θ 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, $(\underline{\text{c}}\underline{\text{h}}\underline{\text{c}})_2$. 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

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

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

Table VI. Bond Distances ($\text{\AA}$) 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: $\square \text{AcBcA} \square \text{CaBaC} \square \dots$ (a, c: M; A, B, C: CsI_3 -layers).

Figure 7. Perspective views of the $\text{Y}_2\text{I}_9^{3-}$ (left) and $\text{Zr}_2\text{I}_9^{3-}$ (right) groups in their $\text{Cs}_3\text{M}_2\text{I}_9$ 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 $d_{z^2}^1$ 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 $0.2 \text{ \AA}$ 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 $\text{Zn}_2\text{Mo}_3\text{O}_8$ (49), $\text{CsNb}_4\text{X}_{11}$ ($\text{X} = \text{Cl}, \text{Br}$) (62), $\text{K}_4\text{Nb}_6\text{Cl}_{18}$ (63), and $\text{Mg}_3\text{Nb}_6\text{O}_{11}$ (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 $\text{M}'\text{Mo}_6\text{X}_8$ ($\text{X} = \text{S}, \text{Se}, \text{Te}$) formula. In addition to the Chervel phases other ternary clusters have recently been synthesized such as NaMo_4O_6 (66), $\text{CsNb}_6\text{I}_{11}$ (67) and now $\text{CsZr}_6\text{I}_{14}$.

In the CsI-Zr-ZrI_4 ternary system no other cluster compounds are known to date and no other $\text{M}'\text{M}_6\text{X}_{14}$ phases have been reported. However, the analogous binary clusters $\text{Nb}_6\text{Cl}_{14}$ (68) and Ta_6I_{14} (69) are known. The structural aspects of $\text{CsZr}_6\text{I}_{14}$ as well as its supposed hydride, $\text{CsZr}_6\text{I}_{14}\text{H}_x$, will be discussed. In addition, a comparison of these ternary $\text{M}'\text{M}_6\text{X}_{14}$ 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 $a = 4.086(2)$, $b = 3.973(2)$, $c = 12.962(3)$ Å and $\gamma = 119.1(4)^\circ$. The space group $P2_1/m$ was originally chosen (c unique) since the extinction 00ℓ ($\ell \neq 2n$) was observed and a centric cell was predicted by an HPR plot. Because of the shortness of the a and 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 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 b axial photo which would increase 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 $a = 14.275(4)$, $b = 15.880(4)$ and $c = 12.953(4)$ 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 $0kl$ ($l \neq 2n$) 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>a_0^*</u>	<u>b_0^*</u>	<u>c_0^*</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 $\text{Zr}_6\text{I}_{10}^{\text{i i-a}} \text{I}_{2 \cdot 2/3}^{\text{a-i}} \text{I}_{2 \cdot 1/3}^{\text{a-a}} \text{I}_{4 \cdot 1/2}$. 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.

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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

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

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	
	$\text{CsZr}_6\text{I}_{14}\text{H}_x$ (Crystal 1)	$\text{CsZr}_6\text{I}_{14}$ (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	
	$\text{CsZr}_6\text{I}_{14}\text{H}_x$ (Crystal 1)	$\text{CsZr}_6\text{I}_{14}$ (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 $\text{Zr}_6\text{I}_{14}^-$ 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} ($12\text{ e}/\text{Zr}_6$) to $\text{Zr}_6\text{I}_{14}^-$ ($11\text{ e}/\text{M}_6$) since there are fewer electrons for metal-metal bonding. However, the observed increase from $3.194 - 3.204\text{ \AA}$ in Zr_6I_{12} to $3.368 - 3.430\text{ \AA}$ in $\text{Zr}_6\text{I}_{14}^-$, crystal 1, was much larger than expected. This is especially evident when compared with a somewhat analogous transition from $\text{CsNb}_6\text{I}_{11}$ ($20\text{ e}/\text{M}_6$) (67) to Nb_6I_{11} ($19\text{ e}/\text{M}_6$) (71) where the average Nb-Nb distance increases a mere $0.025\text{ \AA}$ from $2.825(2)$ to $2.850(3)\text{ \AA}$. 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 $\sim 0.08\text{ \AA}$ longer in crystal 1 than in 2, $3.368 - 3.430$ and $3.286 - 3.350\text{ \AA}$, respectively. The longer metal distances in crystal 1 are presumed to be indirect evidence for the presence of hydrogen in crystal 1 ($\text{CsZr}_6\text{I}_{14}\text{H}_x$) relative to crystal 2 ($\text{CsZr}_6\text{I}_{14}$). 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, $\sim\text{ZrH}_{1.4}$, made at $\sim 450^\circ\text{C}$ 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°C ; the H:Zr atomic ratio should be <0.01 (72).

In $\text{Nb}_6\text{I}_{11}\text{D}$ the deuterium is known, via a neutron study (73), to lie in the middle of the niobium cluster. Therefore, in the similar clusters $\text{CsNb}_6\text{I}_{11}\text{H}$ (74) and now $\text{CsZr}_6\text{I}_{14}\text{H}_x$ the hydrogen is presumed to occupy a

similar position. The three systems $\text{Nb}_6\text{I}_{11}-\text{Nb}_6\text{I}_{11}\text{H}$, $\text{CsNb}_6\text{I}_{11}-\text{CsNb}_6\text{I}_{11}\text{H}$ 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 $\text{Zr}_6\text{I}_{14}^-$ cluster is not the only M_6X_{14} cluster known, there are two binary analogs, $\text{Nb}_6\text{Cl}_{14}$ (68) and Ta_6I_{14} (69). All three crystallize in the same space group Cmca (No. 64). However, $\text{Zr}_6\text{I}_{14}^-$ 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 $\text{CsZr}_6\text{I}_{14}$ 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 $\text{Nb}_6\text{Cl}_{14}$ 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 $\text{CsZr}_6\text{I}_{14}$ 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, $\text{ZrI}_{2.4}$, in a 425-140°C gradient (76). A product analyzed as $\text{ZrI}_{1.2+0.1}$ 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 $\alpha\text{-ZrI}_2$ 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 $\alpha\text{-ZrI}_2$ 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°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 ($750\text{--}815^\circ\text{C}$) 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 $700\text{--}850^\circ\text{C}$ 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., $M^+Zr_6I_{12}^-$. 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 $\text{ZrI}_4\text{:CsI:Zr}$ 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 $\text{CsZr}_6\text{I}_{14}\text{H}_x$.

REFERENCES

1. J. H. Schemel, "ASTM Manual on Zirconium and Hafnium", ASTM Special Technical Publication 639, American Society for Testing and Materials, Philadelphia, PA, 1977, p. 57.
2. B. Cox and J. C. Wood, in "Corrosion Problems in Energy Conservation and Generation", C. S. Tedmon, Jr., Ed., The Electrochem. Soc. Softbound Proceedings Series, NY, 1974, p. 275.
3. D. Cubicciotti, S. M. Howard and R. L. Jones, J. Nucl. Mat. **78**, 2 (1978).
4. H. S. Rosenbaum, Electrochem. Tech. **4**, 153 (1966).
5. L. F. Dahl and D. L. Wampler, Acta Cryst. **15**, 903 (1962).
6. F. Meller and I. Fankuchen, Acta Cryst. **8**, 343 (1955).
7. M. J. Bennett, F. A. Cotton, B. M. Foxman, P. F. Stoluby, J. Am. Chem. Soc. **89**, 2759 (1967).
8. B. Krebs, G. Henkel and M. Dartmann, Acta Cryst. **B35**, 274 (1979).
9. R. L. Daake and J. D. Corbett, Inorg. Chem. **17**, 1192 (1978).
10. F. R. Sale and R. A. Shelton, J. Less-Common Met. **9**, 60 (1965).
11. R. L. Daake, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1976.
12. D. Cubicciotti and K. H. Lau, J. Electrochem. Soc. **126**, 771 (1979).
13. D. Cubicciotti, D. L. Hildenbrand, K. H. Lau and P. D. Kleinschmidt, in "Proceedings of the Symposium on High Temperature Metal Halide Chemistry", Vol. 78-1, D. L. Hildenbrand and D. Cubicciotti, Eds., The Electrochem. Soc. Inc., Princeton, NJ, 1978, p. 217.
14. G. Engel, Z. Krist. **90**, 341 (1935).
15. A. Broll, H. G. von Schnering and H. Schäfer, J. Less-Common Metals **22**, 243 (1970).
16. J. D. Corbett, Inorg. Synthesis **22** (accepted).
17. D. G. Adolphson and J. D. Corbett, Inorg. Chem. **15**, 1820 (1976).

18. P. D. Kleinschmidt, D. Cubicciotti and D. L. Hildenbrand, J. Electrochem. Soc. 125, 1543 (1978).
19. D. H. Guthrie, Iowa State University, Ames Lab., Quarterly reports, (1977-80).
20. J. D. Corbett, R. L. Daake, K. R. Poeppelmeier and D. H. Guthrie, J. Am. Chem. Soc. 100, 652 (1978).
21. H. Imoto, J. D. Corbett and A. Cisar, Inorg. Chem. 20, 145 (1981).
22. S. I. Troyanov and V. I. Tsirel'nikov, Russ. J. Phys. Chem. (Engl. Transl.) 48, 1174 (1974).
23. A. Cisar, J. D. Corbett and R. L. Daake, Inorg. Chem. 18, 836 (1979).
24. A. W. Struss and J. D. Corbett, Inorg. Chem. 9, 1373 (1970).
25. S. I. Troyanov, Vestn. Mosk. Univ., Khim. 28, 369 (1973).
26. R. L. Daake and J. D. Corbett, Inorg. Chem. 16, 2029 (1977).
27. K. R. Poeppelmeier and J. D. Corbett, J. Am. Chem. Soc. 100, 5039 (1978).
28. W. L. Rohrbaugh and R. A. Jacobson, Inorg. Chem. 13, 2535 (1974).
29. P. Main, M. M. Woolfson and F. Germain, "MULTAN, a Computer Program for the Automatic Solution of Crystal Structures", University of York Printing Unit, U.K. (1971).
30. J. D. Scott, Queens University, Kingston, Ontario, private communication (1971).
31. "International Tables for X-ray Crystallography", Vol. III, 2nd Ed., Kynoch Press, Birmingham, England, 1962.
32. B. E. Brown, Acta Cryst. 20, 268 (1966).
33. J. A. Wilson and A. D. Yoffe, Adv. Phys. 18, 193 (1969).
34. H. F. Franzen and J. Graham, Z. Kristallogr. 123, 133 (1966).
35. J. D. Corbett, Adv. Chem. Ser. 186, 389 (1980).
36. E. Warkentin and H. Bärnighausen, Z. Anorg. Allg. Chem. 459, 187 (1979).
37. L. J. Guggenberger and R. A. Jacobson, Inorg. Chem. 7, 2257 (1968).

38. L. D. Landau and E. M. Lifshitz, "Statistical Physics", Chap. 14, Pergamon Press, London, 1962.
39. H. F. Franzen, C. Haas and F. Jellinek, Phys. Rev. **B10**, 1248 (1974).
40. R. Clarke, E. Marseglia and H. P. Hughes, Phil. Mag. **B38**, 121 (1978).
41. Kh. S. Lopis, S. I. Troyanov and V. I. Tsirel'nikov, Russ. J. Inorg. Chem. (Engl Transl.) **24**, 1306 (1979).
42. H. Schäfer and H. G. Schnering, Angew. Chem. **76**, 833 (1964).
43. A. Simon, Angew. Chem. **93**, 23 (1981).
44. K. R. Poeppelmeier, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1978.
45. G. H. Stout and L. H. Jensen, "X-ray Structure Determination", Collier-Macmillan Ltd., London, 1968, p. 408-10.
46. P. Coppens and W. C. Hamilton, Acta Crystallogr. **A26**, 71 (1971).
47. L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, NY, 1960, p. 410.
48. D. J. Robbins and A. J. Thomson, J. Chem. Soc., Dalton Trans. 2350 (1972).
49. W. H. McCarroll, L. Katz and R. Ward, J. Am. Chem. Soc. **79**, 5410 (1957).
50. K. R. Poeppelmeier, J. D. Corbett, T. P. McMullen, D. R. Torgeson and R. G. Barnes, Inorg. Chem. **19**, 129 (1980).
51. G. Meyer and A. Schönmund, Mat. Res. Bull. **15**, 89 (1980).
52. O. Lindqvist, Acta Chem. Scand. **22**, 2943 (1968).
53. B. Chabot and E. Parthé, Acta Crystallogr. **B34**, 645 (1978).
54. D. Ho, W. C. Riley and R. A. Jacobson, Cryst. Struct. Commun. **7**, 111 (1978).
55. G. J. Wessel and D. J. W. IJdo, Acta Crystallogr. **10**, 466 (1957).
56. F. A. Cotton and D. A. Ucko, Inorg. Chim. Acta **6**, 161 (1972).

57. R. Saillant, R. B. Jackson, W. E. Streib, K. Folting and R. A. D. Wentworth, Inorg. Chem. 10, 1453 (1971).
58. C. Brosset, Arkiv Kemi 12A, 1 (1935).
59. R. D. Burbank and H. T. Evans, Acta Crystallogr. 1, 330 (1948).
60. J. R. Chang, G. L. McPherson and J. L. Atwood, Inorg. Chem. 14, 3079 (1975).
61. D. H. Guthrie, G. Meyer and J. D. Corbett, Inorg. Chem. 20, 1192 (1981).
62. A. Broll, A. Simon, H. G. von Schnering and H. Schäfer, Z. Anorg. Allg. Chem. 367, 1 (1969).
63. A. Simon, H. G. von Schnering and H. Schäfer, Z. Anorg. Allg. Chem. 361, 235 (1968).
64. B. O. Marinder, Chem. Scripta 11, 97 (1977).
65. R. Chevrel, M. Sergent and J. Prigent, J. Solid State Chem. 3, 515 (1971).
66. C. C. Torardi and R. E. McCarley, J. Am. Chem. Soc. 101, 3963 (1976).
67. H. Imoto and J. D. Corbett, Inorg. Chem. 19, 1241 (1980).
68. A. Simon, H. G. von Schnering, H. Wöhrle and H. Schäfer, Z. Anorg. Allg. Chem. 339, 155 (1965).
69. D. Bauer, H. G. von Schnering and H. Schäfer, J. Less-Common Metals 8, 388 (1965).
70. B. A. Karcher, Iowa State University, Ames, Iowa, private communication (1980).
71. L. R. Bateman, J. F. Blount and L. F. Dahl, J. Am. Chem. Soc. 88, 1082 (1966).
72. A. Simon, A. Anorg. Allg. Chem. 355, 311 (1967).
73. R. Speiser in "Metal Hydrides", W. M. Mueller, J. P. Blackledge and G. G. Libowitz, Eds., Academic Press, New York, NY, 1968, p. 72.
74. H. Imoto, Max-Planck-Institute, Stuttgart, West Germany, private communication (1981).

75. B. Cox, Chalk River Nuclear Lab., Chalk River, Ontario, Canada, private communication (1979).
76. D. Cubicciotti and K. H. Lau, J. Electrochem. Soc. 128, 196 (1981).
77. R. E. Araujo, M. S. Thesis, Iowa State University, Ames, Iowa, 1981.
78. H. F. Franzen and D. H. Guthrie, Iowa State University, Ames, Iowa, unpublished research.
79. H. J. Mattausch, J. B. Hendricks, R. Eger, J. D. Corbett and A. Simon, Inorg. Chem. 19, 2128 (1980).
80. K. R. Poeppelmeier and J. D. Corbett, Inorg. Chem. 16, 1107 (1977).
81. A. Simon and H. G. von Schnering, J. Less-Common Met. 11, 31 (1966).
82. C. C. Torardi and R. E. McCarley, J. Solid State Chem. (1981).
83. V. J. Minkiewicz, D. E. Cox and G. Shirane, Solid State Comm. 8, 1001 (1970).
84. A. Zalkin, K. Lee and D. H. Templeton, J. Chem. Phys. 37, 697 (1962).
85. G. Meyer, Institute fuer Anorganische Chemie I, Giessen, West-Germany, private communication (1980).

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HALLELUJAH

APPENDIX A.

OBSERVED AND CALCULATED STRUCTURE FACTOR

AMPLITUDES (X10) FOR α -ZrI₂

K = 0															
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	180	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	K = 1			
-5	6	45	44	-1	1	27	31	3	1	96	97	H	L	FO	FC
-5	7	39	39	-1	2	9	11	3	2	45	49	-7	1	103	99
-5	8	65	62	-1	3	30	33	3	3	80	89	-7	2	57	52
-5	9	74	68	-1	4	61	64	3	4	110	120	-7	3	74	64
-5	10	52	46	-1	5	146	148	3	5	67	102	-7	4	122	116
-5	11	175	163	-1	6	5	5	3	6	99	100	-7	6	51	49
-5	12	79	74	-1	7	163	169	3	7	73	79	-7	7	39	35
-5	13	21	19	-1	8	109	120	3	8	143	140	-7	8	83	77
-5	14	46	44	-1	9	95	94	3	9	77	77	-7	9	71	69
-5	15	56	56	-1	10	9	11	3	10	140	132	-6	2	51	53
-4	1	27	25	-1	11	88	92	3	11	55	54	-6	4	48	47
-4	2	68	61	-1	12	74	80	3	12	133	127	-6	5	70	71
-4	3	233	215	-1	13	142	149	3	13	35	35	-6	6	26	29
-4	4	86	84	-1	14	24	23	3	14	110	99	-6	8	27	28
-4	5	47	43	-1	15	92	97	3	15	37	37	-6	9	119	121
-4	6	48	42	-1	16	76	78	4	0	86	81	-6	10	45	47
-4	7	173	155	-1	17	65	71	4	1	222	225	-6	12	39	41
-4	8	56	53	0	2	132	123	4	2	78	73	-5	1	150	151
-4	9	11	13	0	4	214	198	4	4	64	63	-5	2	118	117
-4	11	44	40	0	6	153	139	4	5	175	173	-5	3	31	30
-4	12	19	20	0	7	14	1	4	6	52	49	-5	4	117	112
-4	13	16	16	0	8	281	273	4	7	4	6	-5	5	85	79
-4	16	6	7	0	9	6	1	4	8	22	23	-5	6	98	90
-3	1	97	99	0	10	60	61	4	9	53	57	-5	7	24	23
-3	2	18	20	0	12	37	34	4	10	22	25	-5	8	58	53
-3	3	90	94	0	14	60	52	4	11	13	16	-5	9	88	76
-3	4	98	106	1	0	3	4	4	13	6	7	-5	10	66	60
-3	5	74	95	1	1	8	10	5	1	98	110	-5	11	16	18
-3	6	65	64	1	3	10	13	5	2	36	41	-5	12	30	27
-3	7	66	94	1	4	60	66	5	3	52	59	-5	14	5	5
-3	8	164	166	1	5	173	185	5	4	32	36	-4	2	58	69
-3	9	73	76	1	6	38	39	5	5	33	36	-4	4	37	43
				1	7	123	120	5	6	65	69	-4	5	47	45
				1	8	121	118	5	7	75	84	-4	6	179	177

-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	35
-4	13	56	58	1	1	16	16	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	108
-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	53	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	166	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	-6	2	37	40	1	6	134	128	0	0	270	235
2	1	198	206	-5	1	118	113	1	8	25	28	0	2	54	47
2	2	116	130	-5	2	92	88	1	9	36	35	0	4	108	99
2	3	82	77	-5	3	18	22	1	10	42	44	0	6	77	65
2	4	164	169	-5	4	86	84	1	11	63	62	1	3	6	7
2	5	158	150	-5	5	62	61	1	12	9	11	1	4	35	33
2	6	14	14	-5	6	69	68	2	0	49	50	1	5	95	91
2	7	23	25	-5	7	17	16	2	1	5	5	1	6	20	19
2	9	87	82	-5	8	40	41	2	2	98	93	1	7	64	61
2	10	63	59	-4	2	38	30	2	3	41	38	2	0	47	47
2	11	13	12	-4	4	24	25	2	4	11	10	2	1	126	130
2	12	46	45	-4	5	34	33	2	6	55	56	2	2	75	70
2	14	34	37	-4	6	130	129	2	7	83	79	2	3	55	50
3	0	9	12	-4	7	5	9	2	8	102	98	2	4	106	105
3	1	81	79	-4	8	101	99	2	9	39	25	2	5	99	98
3	2	39	40	-4	9	47	48	2	10	143	139	2	6	5	7
3	3	70	68	-4	10	53	56	2	11	68	67	3	0	6	5
3	4	102	98	-3	1	221	218	3	0	52	8	3	1	48	48
3	5	59	56	-3	2	11	11	3	1	68	73	3	2	24	26
3	6	87	85	-3	3	34	35	3	2	12	13	3	3	40	41
3	7	63	61	-3	5	132	127	3	3	158	148				
3	8	124	120	-3	7	68	72	3	7	128	129				
3	9	69	65	-3	9	93	96	3	8	6	9				
3	10	120	114	-3	10	12	10	3	9	21	24				
3	11	47	46	-3	12	7	11	3	10	10	12				
3	12	114	111	-2	1	7	7	4	0	49	46				
3	13	32	31	-2	2	76	80	4	2	23	23				
4	0	74	69	-2	4	62	64	4	3	30	30				
4	1	197	189	-2	5	39	43	4	4	123	115				
4	2	64	60	-2	6	50	54	4	6	124	120				
4	4	53	53	-2	7	44	46	4	7	52	50				
4	5	141	147	-2	9	65	69	4	8	40	41				
4	6	43	42	-2	10	144	157	5	0	97	98				
4	7	5	5	-2	11	42	42	5	1	8	9				
4	8	18	20	-2	12	40	41	5	2	74	76				
4	9	50	49	-1	1	18	20	5	3	64	63				
4	10	20	22	-1	2	192	190	5	4	76	79				
4	11	13	14	-1	3	130	129	5	5	24	26				
5	1	87	93	-1	4	14	13	5	6	34	36				
5	2	32	35	-1	5	124	125	6	0	38	40				
5	3	50	49	-1	6	134	140								
5	4	31	31	-1	7	10	10								
5	5	31	32	-1	9	19	20								
5	6	57	60	-1	10	50	54								
5	7	72	72	-1	11	60	62								
5	9	33	34	-1	13	39	41								
5	9	145	148	0	1	20	16								

APPENDIX B.

OBSERVED AND CALCULATED STRUCTURE FACTOR

AMPLITUDES (X10) FOR β -ZrI₂

L = 0				4 0 78 106	0 13 562 430	13-10 135 108
H K FO FC				4 6 115 118	1 8 6 3	13 -7 251 207
1 1 121 144				4 9 40 41	1 11 312 274	13 -4 97 100
1 4 219 266				5 -2 263 334	2 0 68 83	13 -1 128 161
1 7 168 188				5 1 38 45	2 6 207 194	13 2 66 68
1 10 206 208				5 4 120 125	2 9 228 220	14 -9 142 107
1 13 160 173				5 7 35 40	2 12 189 168	14 -6 230 231
2 2 217 277				5 10 62 57	3 -2 335 262	14 -3 65 71
2 5 1067 1466				6 -4 483 481	3 1 1319 1873	14 0 84 90
2 8 91 96				6 -1 63 92	3 4 65 75	
2 11 147 141				6 2 767 935	3 7 61 65	L = 3
3 0 182 246				6 5 183 193	3 10 105 112	H K FO FC
3 3 211 235				6 8 34 34	4 -1 38 62	0 0 1174 1146
3 6 257 295				7 -6 280 233	4 2 256 262	0 6 168 155
3 9 108 124				7 -3 81 106	4 5 159 163	1 7 263 247
4 1 345 428				7 0 34 44	4 8 29 26	1 10 199 183
4 4 46 42				7 3 342 366	4 11 114 125	1 13 70 67
4 7 74 79				7 6 50 50	5 -3 440 446	2 -1 442 355
4 10 517 538				7 9 8 14	5 0 162 201	2 2 283 251
5 2 168 203				8 -5 73 75	5 3 21 22	2 5 972 952
5 8 166 181				8 -2 103 119	5 6 794 878	2 8 303 281
5 11 70 85				8 1 258 273	5 9 47 44	2 11 53 54
6 0 87 104				8 4 100 106	6 -5 535 392	3 0 165 149
6 3 188 220				8 7 565 579	6 -2 155 189	3 3 116 112
6 6 205 228				9 -7 108 89	6 4 250 262	3 6 310 314
6 9 81 88				9 -4 75 74	6 7 160 171	3 9 88 92
7 1 187 220				9 -1 44 42	6 10 17 17	3 12 78 85
7 4 191 188				9 2 214 238	7 -4 292 265	4 -2 204 178
7 7 100 109				9 5 11 14	7 -1 57 69	4 1 313 322
8 2 236 261				9 8 113 119	7 2 348 371	4 4 153 165
8 5 66 68				10 -6 31 19	7 5 32 38	4 7 10 19
8 8 128 141				10 -3 97 107	7 8 164 171	4 10 592 586
9 0 23 10				10 0 92 95	8 -6 1309 1179	5 -4 376 282
9 3 653 712				10 3 72 79	8 -3 193 225	5 -1 57 55
9 6 39 38				11 -8 104 77	8 0 163 183	5 2 74 76
10 1 152 158				11 -5 801 837	8 3 255 270	5 5 90 91
10 4 136 132				11 -2 54 59	8 6 102 108	5 8 97 106
10 7 74 76				11 1 29 29	8 9 91 89	5 11 81 86
11 2 52 55				11 4 126 119	9 -8 211 154	6 -3 213 210
11 5 154 160				12-10 90 66	9 -5 46 43	6 3 158 172
12 0 97 108				12 -7 118 110	9 -2 124 139	6 6 17 20
12 3 134 144				12 -4 116 116	9 1 189 190	6 9 80 88
13 1 31 17				12 -1 15 16	9 4 125 126	7 -5 64 48
				12 2 62 67	9 7 95 100	7 -2 901 952
				13-12 70 52	10 -7 266 223	7 1 194 205
L = 1				13 -9 23 6	10 -1 794 880	7 4 67 63
H K FO FC				13 -6 262 266	10 2 165 173	7 7 148 155
0 8 28 18				13 -3 34 33	10 5 35 32	8 -7 53 42
0 14 173 143				13 0 597 578	11 -9 117 83	8 -4 175 171
1 0 186 222				14-11 56 55	11 -6 29 27	8 -1 243 254
1 12 301 267				14 -0 175 160	11 -3 48 52	8 2 157 159
2 1 34 22				14 -5 200 201	11 0 83 94	8 8 19 18
2 4 26 9				14 1 76 80	11 3 97 91	9 -6 184 160
2 7 124 118					12-11 207 136	9 -3 324 319
2 10 238 227				L = 2	12 -8 93 79	9 3 614 625
2 13 88 93				H K FO FC	12 -5 175 226	9 6 86 92
3 -1 142 177				0 1 303 253	12 -2 124 144	10 -8 249 187
3 5 65 67				0 7 116 106	12 1 123 118	10 -5 156 129
3 11 103 113				0 10 52 47	12 4 428 427	10 -2 134 147
4 -3 1124 1119						

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	FD	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	FD	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	FD	FC
				2	5	759	667	0	1	286	324
				2	8	84	88	0	4	58	70
				3	0	148	141	1	2	9	20
				3	3	54	48	1	5	135	149
				3	6	73	75	2	0	119	141
				4	-2	335	306	2	3	34	41
				4	1	161	159	3	-2	52	57
				4	4	8	13	3	1	615	667
				4	7	122	129	4	-1	34	39
				5	-4	443	435	4	2	117	124
				5	-1	26	21	5	-3	87	78
				5	2	95	93	5	0	58	69
				5	5	58	61	6	-2	116	140
				6	-3	238	251				
				6	3	252	270				
				7	-2	719	667				
				7	1	237	238				
				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 2 θ 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 $\text{\AA}$) in $\text{Cs}_3\text{Zr}_2\text{I}_9$ (2.895 $\text{\AA}$). Using $a = 11.659 \text{ \AA}$ and $x = 0.246$, the powder on the following page was calculated. The observed powder agrees quite well in both intensity and 2 θ verifying that Cs_2ZrI_6 is isotypic with K_2PtCl_6 as well as Cs_2ZrCl_6 .

Calculated and observed Guinier powder patterns for Cs_2ZrI_6

hkl	¹		²	
	$2\theta_{\text{obs.}}$	$2\theta_{\text{calc.}}$	$I_{\text{obs.}}$	$I_{\text{calc.}}$
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 $I_{\text{calc.}} \geq 0.3/10$ 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

M	L	FO	FC
0	2	555	-045
0	4	979	-682
0	6	6509	-8816
0	8	223	-76
0	10	215	-111
0	12	6623	7162
0	14	1874	-1764
0	16	220	-93
0	18	2694	-2538
0	20	896	786
0	24	1659	1559
0	26	1331	-1306
M	L	FO	FC
0	2	609	-755
0	4	1151	1105
0	6	165	67
0	8	186	-95
0	10	1778	-1496
0	12	694	-608
0	14	719	-59
0	16	1098	994
0	18	544	-562
0	20	758	829
0	22	584	319
0	24	210	-370
0	26	2011	1947
0	28	339	-271
0	30	248	237
0	32	689	-655
0	34	1057	-1007
0	36	495	-431
0	38	549	-582
0	40	614	574
0	42	732	-672
0	44	438	426
0	46	238	251
0	48	87	-9
0	50	874	856
0	52	98	-18
0	54	119	108
0	56	1517	1271
0	58	435	-322
0	60	464	321
0	62	1142	1234
0	64	1667	-1678
0	66	69	-8
0	68	1687	-1676
0	70	120	0
0	72	424	663
0	74	374	391
0	76	77	0
0	78	1412	1276
0	80	1802	961
0	82	1130	-1035
0	84	913	-829

0	8582	8660
2	428	-573
2	3	154
2	4	881
2	5	261
2	6	5624
2	7	291
2	8	194
2	9	634
2	10	91
2	11	198
2	12	5821
2	14	1335
2	15	122
2	16	171
2	18	1748
2	19	4
2	20	568
2	22	179
2	24	1234
2	26	1046
M	L	FO
0	8	1394
0	1	292
0	2	387
0	3	68
0	4	385
0	5	341
0	6	833
0	7	294
0	8	1436
0	10	1369
0	11	331
0	12	480
0	13	117
0	14	224
0	16	1042
0	17	262
0	18	823
0	19	85
0	20	883
0	22	699
0	23	148
0	24	86
0	25	95
0	1	397
0	1	842
0	2	76
0	3	185
0	5	1181
0	6	561
0	8	752
0	9	935
0	10	644
0	11	387
0	12	178
0	13	1486

Cs₃Zr₂I₉

1	14	221
1	15	219
1	16	512
1	17	880
1	18	355
1	19	484
1	20	446
1	21	582
1	22	385
1	23	161
1	25	683
2	0	511
2	1	542
2	2	135
2	3	282
2	4	119
2	5	1053
2	6	341
2	7	226
2	8	828
2	9	556
2	10	389
2	11	265
2	12	288
2	13	1866
2	14	297
2	15	276
2	16	324
2	17	655
2	18	169
2	19	132
2	20	491
2	21	597
2	22	289
2	23	124
2	24	186
2	25	533
3	0	464
3	2	341
3	4	233
3	6	895
3	8	938
3	10	928
3	12	111
3	13	194
3	14	168
3	16	759
3	18	662
3	20	693
3	22	581
M	L	FO
0	8	696
0	1	1450
0	2	2919
0	3	3833
0	4	3179
0	5	2115

0	6	328
0	7	2589
0	8	2882
0	9	2604
0	10	2461
0	11	419
0	12	81
0	13	848
0	14	1327
0	15	1669
0	16	1693
0	17	368
0	18	562
0	19	1121
0	20	894
0	21	388
0	22	1824
0	23	278
0	24	221
0	25	236
1	0	886
1	1	225
1	2	344
1	4	238
1	5	271
1	6	794
1	7	154
1	8	1818
1	10	1073
1	11	274
1	12	284
1	13	115
1	14	154
1	16	817
1	17	194
1	18	629
1	19	126
1	20	683
1	21	86
1	22	510
1	23	110
1	24	97
2	0	513
2	1	949
2	2	2163
2	3	2957
2	4	2349
2	5	1518
2	6	278
2	7	1841
2	8	1918
2	9	1924
2	10	1814
2	11	279
2	13	615
2	14	986
2	15	1284
2	16	1382
2	17	271

2	18	427
2	19	889
2	20	646
2	21	288
2	22	780
2	23	216
3	0	77
3	1	712
3	2	93
3	3	319
3	5	473
3	6	491
3	7	88
3	8	266
3	9	86
3	12	277
3	11	89
3	12	86
3	13	924
3	14	86
3	15	135
3	16	232
3	17	386
3	18	378
3	19	175
3	20	118
3	21	125
3	22	159
4	0	3665
4	1	288
4	2	253
4	4	352
4	6	2679
4	8	99
4	10	97
4	12	2454
4	14	658
4	16	112
4	18	748
4	20	236
M	L	FO
0	8	109
0	1	786
0	2	73
0	3	526
0	4	92
0	5	668
0	6	588
0	7	94
0	8	423
0	9	112
0	10	281
0	13	1168
0	14	89
0	15	238
0	16	263
0	17	481

0	18	583
0	19	243
0	21	137
0	22	198
0	24	144
1	0	94
1	1	764
1	2	177
1	3	83
1	4	115
1	5	629
1	6	478
1	7	175
1	8	334
1	9	268
1	10	468
1	11	83
1	13	1149
1	16	388
1	17	587
1	18	345
1	19	313
1	20	192
1	21	259
1	23	96
2	0	888
2	1	362
2	2	271
2	5	363
2	6	362
2	7	218
2	8	594
2	9	178
2	10	599
2	11	374
2	12	389
2	13	189
2	14	78
2	16	449
2	17	288
2	18	488
2	19	97
2	20	398
2	21	132
2	22	264
3	0	182
3	1	544
3	2	152
3	3	284
3	4	94
3	5	468
3	6	285
3	8	218
3	9	392
3	10	393
3	12	185
3	13	785
3	14	89
3	15	185

2/2

3 16 288 -382
3 17 394 379
3 18 147 -198
3 19 122 189
3 20 142 223
4 0 255 -235
4 1 107 154
4 4 114 115
4 5 584 -492
4 6 98 -134
4 7 383 274
4 8 353 389
4 9 298 -298
4 11 124 64
4 12 131 -182
4 13 350 365
4 14 147 -151
4 15 180 141
4 17 239 -288
5 2 151 -192
5 4 174 192
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 2 368 -594
0 4 461 -591
0 6 2418 -2938
0 7 755 31
0 8 99 -69
0 9 252 -3
0 10 96 82
0 12 2774 2881
0 14 839 -819
0 16 150 -178
0 18 1024 -1826
0 20 322 308
0 22 184 147
1 0 257 -256
1 1 488 -371
1 3 320 -314
1 4 88 -34
1 5 614 600
1 6 289 -239
1 7 99 -124
1 8 419 402
1 9 462 470
1 10 323 318
1 11 96 -115
1 12 155 -174
1 13 713 -716
1 14 87 -125
1 15 211 -230
1 16 270 -256
1 17 423 426

1 18 185 -135
1 19 99 187
1 20 268 319
1 21 361 486
2 0 358 -316
2 1 538 -588
2 2 1286 -1182
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 1802 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 16 785 788
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 3 249 228
3 4 405 481
3 5 184 -138
3 6 383 -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 0 184 -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 10 587 -682
4 11 287 -16
4 12 91 -86
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 0 348 -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 13 409 411
0 14 139 -214
0 15 135 143
0 17 312 -346
0 20 249 346
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 1 431 394
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 5 186 -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 15 668 661
0 16 589 684
1 1 481 438
1 2 185 141
1 3 148 -193
1 4 322 -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 = 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 -53
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)

$$\text{CeZr}_6\text{I}_{14} \text{ (Crystal 1)} F_o/F_c \times 10$$

12	14	384	386	5	2	2381	2225	15	9	707	740	4	14	8613	7962	12	12	2378	2836	3	4	3474	3171
4	L	FO	FC	14	2	2470	1853	5	9	3040	3445	15	14	476	388	4	11	474	4670	12	13	2946	2703
2	2	349	78	14	2	1332	1281	5	10	1373	2209	15	13	462	400	4	11	3714	3711	12	14	4494	4686
0	4	15351	15663	10	6	592	751	5	12	1547	1394	17	1	352	294	4	13	1916	3294	12	15	2539	2596
0	4	5193	5111	10	6	1778	1881	5	13	407	272	17	2	381	348	4	14	8468	7356	10	9	1633	3312
0	4	1579022017		14	12	430	1012	5	14	2561	2493	17	3	1813	1813	4	15	3899	2923	14	1	1956	1931
0	14	2449	2761	16	4	1300	1812	5	14	1939	1104	17	5	2404	2462	4	16	1675	1652	14	2	1673	1713
0	12	27741	1224	16	2	473	492	5	17	1564	1635	17	7	381	102	4	17	4894	4189	14	3	2351	2356
0	14	3697	3656	16	4	9922	9591	7	1	718	178	17	4	1551	1522	6	4	4938	4151	14	5	334	274
0	16	7346	6037	16	4	1424	1493	7	2	1349	1401	19	1	1333	1399	6	1	2627	2624	14	6	344	496
0	18	1172	1184	16	4	4570	4594	7	3	513	974	19	3	423	524	6	2	2837	2477	14	7	2847	2693
2	0	1763	1928	14	12	5494	6152	7	4	348	194	19	5	1837	1788	6	3	3284	3491	14	8	2457	2223
2	2	935	876	18	0	1420	1127	7	5	2239	2405	19	6	492	559	6	4	321	125	14	11	2223	2283
2	4	4594	4685	18	2	494	619	7	6	404	754	19	9	977	1261	6	6	639	267	14	11	1127	1128
2	6	3381	3352	18	4	3524	3359	7	8	3112	2847	21	2	921	962	6	7	3422	3614	14	12	465	412
2	8	791	585	18	6	2241	2289	7	11	1135	861	21	3	471	526	6	8	2725	2466	14	13	1275	1517
2	12	1269	1139	18	10	844	823	7	12	1141	1143	21	5	749	972	6	9	364	344	16	2	1119	1113
2	12	1814	1801	20	0	1092	1002	7	13	1141	1092					6	10	2479	2559	16	1	591	547
2	14	1662	1645	20	4	1504	1496	7	14	594	597					6	11	1221	1042	16	2	1017	1061
2	16	2199	2293	20	6	1341	1471	7	16	1873	1944					6	12	748	837	16	3	1302	1263
2	18	533	450	22	2	452	715	9	1	2497	3482					6	13	2896	1947	16	6	573	612
4	0	3948	3655					9	2	634	72					6	15	1332	1338	16	7	1129	1844
4	2	1774	1793					9	3	2519	3249					6	16	412	440	16	8	432	544
4	4	349	212					9	4	404	497					6	18	262	381	16	2	354	527
4	6	655	657					9	5	5755	5497					6	1	286	229	16	4	1632	1676
4	6	3662	3693					9	6	2745	2124					6	2	1485	1453	20	2	2112	2118
4	10	799	924					9	7	1401	1044					6	4	2949	3474	20	1	3561	3591
4	14	1259	1176					9	11	1404	1349					6	5	834	484	22	2	4966	4929
4	16	2057	1922					9	12	2784	1495					6	6	2025	2614	22	3	3924	3931
6	0	1435	1792					9	13	3422	3157					6	8	376	173	20	4	1214	1152
6	2	1431	1473					9	15	439	645					6	10	424	569	20	5	3114	3312
6	4	984	914					9	16	1294	1430					6	12	478	687	20	6	4153	4082
6	6	1523	1493					11	1	1205	947					6	14	2347	2179	20	7	2732	2953
6	8	2445	2218					11	2	1297	1153					6	13	1262	1442	20	8	1515	1414
6	10	523	741					11	3	474	1043					6	16	434	249	22	10	1467	1552
6	12	439	743					11	4	424	429					14	1	1936	1105	22	1	671	734
6	14	1635	1456					11	5	2549	2732					14	2	1449	1491	22	2	848	981
6	16	2554	2568					11	6	894	449					14	3	1347	1467	22	3	794	964
8	2	554	494					11	10	1551	1348					16	4	2145	2169	16	4	2925	2808
8	4	14151	13471					11	11	1244	1134					16	5	519	534	16	5	1747	1746
8	6	3581	3694					11	12	373	426					16	7	1863	1452	16	7	324	223
8	8	1714014046						11	13	1255	1304					16	9	332	253	16	9	332	253
8	10	1741	1424					11	14	1516	1614					16	11	953	936	1	3	2315	2493
8	12	9724	9509					11	15	407	434					16	12	1126	1135	1	5	775	120
8	14	2364	2409					13	1	2042	1953					16	13	662	697	1	4	2833	2974
8	16	5934	5094					13	2	2224	2373					16	14	1248	1270	1	6	2194	2273
10	0	3241	3922					13	4	793	632					16	15	432	544	1	8	409	394
10	2	568	554					13	7	1068	1244					16	16	471	415	1	8	2405	1974
10	4	5746	5583					13	8	1724	1435					16	17	479	746	1	11	3072	2964
10	6	3951	3726					13	9	2293	1935					16	18	3036	3225	1	14	2405	1721
10	8	2024	1794					13	10	2237	2351					16	19	4567	9332	1	15	1297	1274
10	12	2436	2224					13	12	509	757					16	20	21503716855		1	16	1914	1911
10	14	2248	2054					13	14	1759	1945					16	21	458167649		1	17	829	898
10	16	1918	2116					15	1	336	476					16	22	48482	8322	1	18	1841	2534
12	0	334	383					15	2	1564	1473					16	23	5161911319		1	19	5284	4066
12	2	643	475					15	3	442	556					16	24	41392015456		1	20	2622	2157
12	4	1505	1525					15	5	342	467					16	25	4905	3758	1	21	6325	5524
12	6	1612	1566					15	6	738	794					16	26	8668	4182	1	22	6668	4182
12	8	1259	1244					15	8	1937	2474					16	27	5851	5305	1	23	1244	1567

CoZr₆I₁₄ (Crystal I) F₀F_c x 10

13 5 1757 1574	2 2 2613 3624	10 2 3158 3968	H P S	9 3 317 215	0 3 4846 4711	0 14 1294 1588
13 6 2268 2027	2 1 469 720	10 1 1459 1800	K L FO FC	9 4 1417 1421	0 4 301 466	0 6 2653 2791
13 7 1391 1412	2 2 2911 2024	10 2 2502 2050	1 1 2082 2731	9 5 1491 1210	0 5 1266 1017	0 1 857 1466
13 8 3056 2739	2 3 1599 1722	10 3 2461 2812	1 2 5334 5651	9 6 933 807	0 7 2742 2750	0 2 1130 1147
13 9 596 640	2 4 344 360	10 4 317 134	1 3 878 493	9 7 351 543	0 8 3323 3291	0 3 3126 3159
13 10 596 591	2 5 280 439	10 5 864 780	1 4 1765 1714	9 8 3027 2825	0 9 1225 1219	0 4 565 668
13 11 2359 2130	2 6 771 269	10 6 471 866	1 5 1486 1830	9 9 1440 1409	0 10 1113 1149	0 5 1402 951
13 12 1219 1272	2 7 1332 1557	10 7 2671 2496	1 6 1096 2048	9 10 3569 3495	0 11 2714 2382	0 6 365 405
13 13 453 428	2 8 1632 1477	10 8 1374 1456	1 7 3484 3171	9 11 743 804	0 12 494 492	0 7 1821 1543
15 1 1553 1463	2 10 3446 3234	12 12 3443 2891	1 9 1854 1923	9 12 1865 1847	0 13 1342 1342	0 8 2231 2249
15 2 2361 2122	2 11 554 586	12 11 1627 1613	1 10 4171 3784	9 14 2138 2225	0 14 1574 1376	0 9 964 982
15 3 369 124	2 12 631 799	12 12 540 757	1 12 2090 2015	9 16 1557 1779	0 15 619 650	0 10 523 529
15 4 1425 1014	2 13 476 492	12 13 1221 1186	1 13 570 574	11 1 1742 1837	0 16 1221 1544	0 11 1845 1610
15 5 1658 1427	2 14 716 930	12 14 788 924	1 14 2453 2515	11 2 2130 2179	0 17 933 1480	0 12 421 741
15 6 794 775	2 15 674 675	12 15 1190 1207	1 15 664 783	11 3 469 574	0 18 1466 1157	0 13 1827 416
15 7 419 611	2 16 447 247	12 16 2549 2737	1 16 1704 1752	11 6 1297 1172	0 19 2100 1986	0 14 413 730
15 8 1076 1042	4 0 3423 4022	12 2 1173 1121	3 1 1590 2211	11 7 384 491	0 20 1666 1743	0 15 1471 1370
15 9 571 625	4 1 1516 1633	12 3 453 493	3 3 1713 2293	11 8 3039 2633	0 21 1536 1546	0 16 2100 2241
15 10 1326 1217	4 2 1729 1695	12 4 414 436	3 4 923 868	11 9 1244 1372	0 22 1572 1517	0 17 1211 2462
15 11 1251 1373	4 3 3244 3160	12 5 311 115	3 5 1714 2491	11 10 479 467	0 23 447 416	0 18 1724 1734
15 12 1437 1494	4 4 543 683	12 6 1212 1133	3 6 554 418	11 11 613 806	0 24 1731 1740	0 19 5130 2132
15 13 941 919	4 5 1692 1000	12 7 335 233	3 7 563 786	13 1 936 1014	0 25 2473 2347	0 20 421 736
17 1 1122 1211	4 6 2063 2221	12 8 1066 1553	3 8 2628 2462	13 3 1371 1335	0 26 1396 1495	0 21 2664 2510
17 2 930 1060	4 7 1441 1410	12 9 693 742	3 9 1168 1365	13 4 861 854	0 27 516 767	0 22 1030 1044
17 3 426 450	4 8 747 704	12 10 434 610	3 10 837 952	13 5 1799 1799	0 28 445 371	0 23 1368 1404
17 4 360 353	4 9 2076 2091	12 11 655 749	3 12 1059 1834	13 6 1029 736	0 29 1146 1246	0 24 1164 1426
17 5 624 777	4 10 2452 2525	12 12 1010 1900	3 13 1443 1426	13 7 1721 1446	0 30 1674 1516	0 25 1422 1547
17 6 1169 1147	4 11 302 322	14 1 1424 1471	3 14 455 636	13 8 559 573	0 31 561 640	0 26 636 894
17 7 515 651	4 12 440 580	14 2 1296 1364	3 16 1496 1500	13 11 398 404	0 32 1273 1462	0 27 1432414384
17 8 1650 1775	4 13 494 656	14 3 1355 1241	5 1 1079 1543	13 12 1777 1098	0 33 2204224289	0 28 1440 1526
19 1 451 402	4 14 1292 1472	14 4 1422 1465	5 2 1411 1480	13 13 1440 1547	0 34 3867 3881	0 29 459 764
19 2 401 367	6 0 3244 2089	14 5 445 823	5 3 2117 2584	13 14 629 403	0 35 366 396	0 30 3000 2783
19 3 793 963	6 1 1539 1494	14 6 1672 1492	5 4 1491 1462	15 1 719 610	0 36 3102 2809	0 31 1185411445
19 4 572 692	6 2 2196 2241	14 7 1204 1235	5 5 2670 3337	15 2 447 440	0 37 1510214261	0 32 2290 1997
21 1 721 834	6 3 1170 1367	14 8 426 612	5 6 1677 1731	15 3 652 446	0 38 2494 2523	0 33 1395 1360
21 2 467 463	6 4 325 474	16 1 4472 4227	5 7 492 652	15 4 1330 1225	0 39 3017 2821	0 34 1143 435
21 3 477 490	6 5 345 324	16 2 7827 7940	5 8 1584 1545	15 5 7 900 882	0 40 2491 2647	0 35 1106610253
21 4 445 251	6 6 1404 1405	16 3 4509 4075	5 9 804 982	15 6 754 714	0 41 1616115906	0 36 2501 2273
	6 7 1367 1144	16 4 1401 1524	5 10 1219 971	15 7 490 503	0 42 3243 3004	0 37 1342 1213
	6 8 2923 2638	16 5 3968 3973	5 11 519 695	17 1 1047 1105	0 43 1269 1137	0 38 7859 6642
	6 9 1254 1134	16 6 8733 7924	5 12 2060 2418	17 2 2135 1939	0 44 824 614	0 39 745 740
	6 10 533 767	16 7 3515 3334	5 13 2890 2282	17 3 412 344	0 45 9315 6962	0 40 472 901
	6 11 564 765	16 8 3147 3104	5 14 710 940	17 4 1336 1268	0 46 1607 1459	0 41 1130 635
	6 12 4423 5203	16 9 5057 8043	7 1 358 494	17 5 659 815	0 47 2141 2454	0 42 755 470
	6 13 151614693	16 10 2467 2507	7 2 2394 2453	17 6 1895 2045	0 48 1593 1435	0 43 410 557
	6 14 920614331	16 11 2403 1455	7 3 740 597	19 1 870 945	0 49 6422 6448	0 44 3323 3496
	6 15 3426 3439	16 12 1041 958	7 4 659 793	19 2 1759 1807	0 50 935 1100	0 45 771 740
	6 16 8361 7439	16 13 1693 1426	7 5 836 649	19 3 349 384	0 51 1627 1785	0 46 2415 2221
	6 17 3238 1673	16 14 1533 1516	7 6 695 696	19 4 434 604	0 52 724 753	0 47 520 410
	6 18 1004 959	16 15 649 706	7 7 697 553	19 5 1804 1132	0 53 1314 1001	0 48 1556 1761
	6 19 7404 6780	16 16 1380 1018	7 8 1537 1363	19 6 1837 1896	0 54 3400 3980	0 49 415 540
	6 20 10104 9461	16 17 963 1476	7 9 489 575	21 1 623 773	0 55 941 929	0 50 1015 1462
	6 21 7445 7506	16 18 1837 1466	7 10 2364 2229	21 2 434 522	0 56 2769 2697	0 51 1304 1326
	6 22 1334 1475	16 19 1487 1573	7 11 367 193		0 57 599 705	0 52 702 693
	6 23 3444 3150	16 20 1409 618	7 12 527 427		0 58 420 381	0 53 474 693
	6 24 8306 8120	16 21 610 714	7 13 612 760		0 59 1774 697	0 54 393 476
	6 25 1446 1459	16 22 7494 6854	9 1 1466 1459		0 60 2452 1913	0 55 1118 1264
	6 26 1378 1245	16 23 1742 1610	9 2 4763 4933		0 61 1466 941	0 56 1832 1676
	6 27 3862 3930	16 24 1030 1017			0 62 1642 1645	0 57 943 1142

CoZr₆I₁₄ (Crystal I) F_oF_c x 10

10	3	1302	1223	9	2	477	476	0	0	4224	3650	8	11	5778	5722	1	10	449	538	11	11	1169	1266	4	13	9788	8479	
10	6	464	419	9	3	337	435	0	0	7209	4527	8	12	3998	3720	1	11	970	1033	11	12	1025	1109	4	11	3461	3121	
10	7	1391	1451	9	4	486	486	0	10	5658	4950	8	13	3382	3145	1	13	2338	2344	13	3	2776	2442	4	13	2757	2616	
10	8	1115	1121	9	5	773	847	0	11	7234	6665	8	14	3729	3744	1	14	2240	2424	13	4	394	461	4	14	5527	5513	
20	0	6346	6283	9	6	1040	1053	0	12	5369	4431	8	15	2952	3164	3	1	462	615	13	5	1484	1744	6	4	841	994	
20	2	471	479	9	7	1153	1364	0	13	4142	3487	10	0	3404	3178	3	2	983	1047	13	6	742	824	6	1	363	394	
20	3	1932	2403	9	8	724	712	0	14	5348	5414	10	1	591	738	3	3	2760	2794	13	7	1427	1465	6	2	1624	1489	
20	4	5853	6215	9	9	3171	2450	0	15	5579	3592	10	2	405	499	3	4	447	742	13	8	914	931	4	3	1468	951	
20	5	1240	1194	9	10	1424	1467	0	16	1778	1444	10	3	873	756	3	5	2144	2274	13	9	376	356	6	4	765	1414	
				9	12	491	528	2	0	1759	1497	10	4	716	852	3	6	856	784	13	11	976	1122	6	5	1016	946	
				9	14	1244	1394	2	1	754	937	10	6	317	434	3	7	2284	2171	13	12	523	565	6	6	1476	1649	
				11	1	1464	827	2	2	420	445	12	7	1331	1147	3	8	552	359	15	1	1996	1827	6	7	399	182	
				11	2	972	592	2	3	477	1142	12	8	2689	2670	3	9	618	422	15	2	712	844	6	14	1697	1699	
				11	3	1452	914	2	4	2732	2754	13	10	1214	1264	3	10	883	852	15	3	1446	2484	6	11	852	679	
				11	4	1174	1046	2	6	1376	1353	14	12	463	494	3	11	1745	1471	17	1	392	451	6	12	562	549	
				11	6	371	333	2	7	1234	1162	14	13	676	806	3	12	752	842	17	2	1113	1241	6	14	1394	1564	
				11	7	973	947	2	8	2176	2405	12	0	1048	1244	3	13	549	583	17	5	469	604	8	1	3436	3299	
				11	8	544	441	2	9	351	89	12	1	297	152	3	14	1583	1629	17	6	642	721	4	1	421	429	
				11	11	1485	1462	2	12	1099	1147	12	2	1364	1422	3	15	1586	1694	17	7	652	834	6	2	994	1495	
				11	12	1597	1612	2	13	971	924	12	4	1539	1463	5	1	413	320	17	8	1837	1644	8	3	3279	2694	
				13	1	1441	1444	2	14	431	732	12	6	2349	2374	5	3	3146	3348	19	1	941	1439	4	5	1620	1465	
				13	3	1447	1473	2	15	725	841	12	7	743	820	4	4	397	512	19	2	1205	1319	4	7	1228	1476	
				13	4	446	443	2	16	1377	1544	12	13	561	645	5	5	3138	3244	19	4	514	546	4	4	1619	1645	
				13	5	4772	3447	4	0	3712	5674	14	0	1439	1271	5	6	1445	1366	19	5	536	552	4	4	1454	1324	
				13	7	745	674	4	1	241	244	14	4	3692	3576	5	7	2136	2169					4	10	1850	1785	
				13	8	1224	1456	4	2	1414	1405	14	6	1911	1991	5	9	1685	1457					6	11	1886	1856	
				13	11	1744	1641	4	0	3764	4234	14	9	444	174	5	10	446	465					6	10	3248	2922	
				13	12	913	1491	4	5	322	225	14	10	1384	1246	5	11	1385	1295					6	0	4727	4634	
				13	13	2214	2384	4	6	4514	4459	14	12	1093	1220	5	13	1132	1474					6	1	1254	1457	
				15	1	945	944	4	7	463	691	16	4	4808	4211	5	14	1461	1694					6	2	1531	1492	
				15	2	547	324	4	8	1943	1836	16	1	4844	4043	5	15	2029	2221					6	3	4216	4304	
				15	3	1374	1285	4	10	1167	934	16	2	5124	4569	7	1	1152	1423					6	7	2645	2459	
				15	5	2952	2947	4	11	414	418	16	3	5481	5230	7	2	1454	1339					6	6	876	578	
				15	6	504	481	4	12	613	540	16	4	2565	2324	7	3	454	347					6	7	2464	1956	
				15	10	573	424	4	13	434	498	16	5	4443	4276	7	4	1448	1267					6	8	2336	2224	
				15	11	426	442	4	14	2843	2863	16	6	3311	3454	7	6	1059	1412					6	9	1835	1645	
				15	12	375	314	4	15	534	474	16	7	3726	3483	7	8	2245	2129					6	10	2534	2513	
				17	1	742	441	6	0	1240	1249	16	8	2854	2725	7	9	1733	1543					6	11	2877	2714	
				17	3	345	493	6	3	624	612	16	9	3418	3422	7	13	1546	1548					6	14	485	478	
				17	5	1459	1139	6	4	4272	4515	16	10	3643	3725	7	15	462	528					6	0	2677	2524	
				17	6	929	1416	6	6	2463	2429	18	0	1930	1954	9	1	1574	1462					6	1	1777	1711	
				17	7	559	709	6	7	749	450	18	2	423	646	9	2	2440	2518					6	2	1964	2454	
				17	9	1444	1474	6	11	1544	1348	18	3	465	475	9	3	511	460					6	3	697	665	
				17	10	932	1492	6	12	1463	1464	18	4	526	487	9	5	2345	2244					6	5	457	546	
				19	1	349	294	6	13	509	775	18	6	420	446	9	6	1845	1717					6	6	627	801	
				19	3	474	1474	6	14	1679	1441	18	7	754	787	9	7	1187	1110					6	7	1824	1823	
				19	4	543	609	6	15	563	519	18	8	1744	1745	9	8	3436	3122					6	8	1187	1205	
				19	7	441	578	6	16	1492	1396	20	2	554	895	9	9	551	604					6	10	2415	2402	
								6	0	5562	5263	20	3	394	488	9	10	976	717					6	13	869	652	
								6	1	8267	7511					9	11	963	1130					6	14	597	649	
								6	2	8919	7465					9	13	1956	2410					6	1	3341	3462	
								6	3	9403	9147					11	1	1490	1543					6	2	13011	13824	
								6	4	4629	6183					11	2	1884	1681					6	3	4887	4855	
								6	5	8444	7134					11	3	1047	1424					6	4	765	896	
								6	6	7170	6529					11	4	754	814					6	5	5227	4814	
								6	7	6083	5914					11	7	1437	1413					6	6	61203	11587	
								6	8	4124	3462					11	8	944	913					6	7	2143	1453	
								6	9	5748	5474					11	9	634	426					6	8	391	101	
								6	10	5499	4712					11	10	1114	1473					6	9	3281	2944	
																								6	10	4	1624	1634

CoZr₆L₁₄ (Crystal I) F₀F_c × 10

10 1 114A 1256	11 7 1147 1119	4 12 98A 125A	1 8 822 936	M = 14	16 M 444 481	4 5 1414 1454	M = 18
10 2 727 944	11 12 1269 1117	4 13 98A 1050	1 11 1777 1725	M L F ₀ F _c	M L F ₀ F _c	4 7 374 249	M L F ₀ F _c
10 3 830 917	11 12 442 676	4 14 927 956	1 12 582 726	0 0 3224 2902	M = 15	4 4 1373 1341	0 0 1679 1723
M = 11	13 1 444 496	6 1 1742 1820	1 13 1165 1336	0 1 720 842	M L F ₀ F _c	4 4 1149 1203	0 4 1619 1645
4 L F ₀ F _c	13 2 1774 1849	6 1 1742 1820	3 1 1849 2143	0 2 1619 1473	1 1 545 544	4 1 1226 1458	0 5 642 716
1 1 1179 316A	13 3 599 88	6 2 1946 2029	3 2 1804 1518	0 3 2665 2287	1 2 575 659	4 1 1636 1749	0 6 667 384
1 2 1565 242A	13 5 964 898	6 3 1637 1499	3 3 935 999	0 5 549 148	1 3 2671 2495	4 1 1251 1235	0 7 616 785
1 3 949 1252	13 8 927 994	6 4 504 994	3 4 645 624	0 6 3546 3282	1 5 3485 3152	4 7 1398 1427	0 8 944 1274
1 4 1748 1663	13 10 2134 2281	6 7 2521 2323	3 5 1415 1419	0 7 1267 1242	1 7 1651 1494	4 1 1488 1226	2 1 476 347
1 6 1573 1591	13 11 461 676	6 8 446 1401	3 6 1899 1715	0 8 1926 1578	1 9 1653 1446	4 1 966 1292	2 2 1367 1579
1 7 1323 1101	15 1 1158 1159	6 10 1517 1712	3 7 883 635	0 9 430 535	1 10 947 973	4 1 1147 1299	2 6 537 473
1 9 2361 2241	15 2 1146 1073	6 11 742 769	3 8 1654 1547	0 14 512 423	1 11 1859 1144	4 2 7237 7269	2 7 437 699
1 11 1715 1424	15 3 546 647	6 13 1293 1456	3 9 2134 2042	2 1 451 466	3 3 947 973	4 3 445 536	4 4 4558 3044
1 12 2843 2624	15 4 624 774	6 15 1055 9589	3 12 583 656	2 4 3233 2811	3 4 423 467	4 4 1452 1965	4 1 3852 3916
3 2 1844 1837	15 8 1177 1320	6 16 997 3994	3 13 1043 1461	2 6 871 1474	3 5 1444 1383	4 5 1161 1273	4 3 1529 1566
3 3 1239 1691	15 9 449 742	6 3 2958 2819	5 1 2531 2458	2 8 918 1109	3 6 1468 1225	4 6 5613 5524	4 4 5548 5556
3 5 2826 1699	17 1 1081 1289	6 4 9491 9166	5 2 2263 2318	2 12 1145 1493	3 9 991 1168	4 7 532 492	4 5 2619 2625
3 6 563 469	17 2 631 575	6 5 3222 3277	5 3 474 599	4 2 4085 4621	5 3 978 1062	4 8 534 424	4 6 966 981
3 7 859 844	17 3 406 485	6 6 735 94	5 4 1041 941	4 1 6912 6427	5 5 1974 1851	4 9 816 723	4 7 3182 3283
3 8 1422 949	17 4 493 723	6 7 3104 2956	5 5 578 774	4 2 3788 3152	5 6 1362 1265	4 1 719 727	6 4 671 1439
3 19 2544 2525	17 6 446 558	6 8 8481 7619	5 6 2626 2418	4 3 4927 4464	7 2 394 471	4 3 552 427	6 5 1249 1525
3 12 438 373	M = 17	6 9 3371 3445	5 7 641 844	4 4 4242 4912	7 3 1494 1578	4 4 1574 1617	6 6 1096 1034
3 13 558 544	M L F ₀ F _c	6 11 1135 1126	5 8 2158 2048	4 5 5169 4693	7 4 1676 1667	4 5 574 665	6 7 718 629
3 14 1297 1654	0 0 11937 11814	6 12 4497 5227	5 9 2387 2468	4 6 3487 3463	7 5 1333 1367	4 6 1439 1654	6 8 426 537
3 15 817 444	0 1 6718 5424	6 13 1985 2311	5 12 1157 1251	4 7 4626 4193	7 12 736 857	4 7 632 789	6 9 476 541
5 1 319 235	0 2 2942 2974	6 14 1575 1645	5 13 447 644	4 8 3679 3333	9 1 741 743	4 8 615 794	6 10 1546 1719
5 2 5347 3194	0 3 11843 14912	6 15 1392 1292	7 1 1365 1191	4 9 3644 3247	9 2 427 544	4 9 368 393	6 11 930 1087
5 4 544 424	0 4 11843 14912	6 16 464 424	7 2 839 939	4 10 2722 1844	9 3 2219 2162	4 10 538 518	6 12 1077 1196
5 5 1263 1382	0 5 3327 3879	6 17 1409 984	7 3 1373 1245	4 11 3994 3259	9 4 2715 2764	4 12 1029 1424	10 1 537 645
5 6 354 382	0 6 1351 124	6 18 889 1045	7 4 1125 999	4 12 3363 3558	9 5 1447 1193		
5 8 2015 1681	0 7 4661 4249	6 19 473 549	7 5 692 241	6 2 2985 2954	9 6 1224 1241		
5 10 3342 3133	0 8 11367 9181	6 20 434 1234	7 6 1882 1729	6 3 743 771	11 1 2673 2475	M = 17	M = 19
5 12 1251 1094	0 9 3939 3511	6 21 1409 1234	7 7 1142 1539	6 4 1481 1441	11 2 419 372	M L F ₀ F _c	M L F ₀ F _c
5 13 447 664	0 10 774 746	6 22 779 1133	7 8 1281 1463	6 5 948 961	11 3 403 448	1 1 1368 1452	1 1 1368 1452
5 14 1383 1474	0 11 5977 5792	6 23 2177 2184	9 1 1415 1214	6 6 1066 1924	11 4 633 434	1 2 1251 1262	1 2 1251 1262
7 1 2444 2329	0 12 2774 2633	6 24 354 464	9 2 473 344	6 7 1047 1042	11 5 399 539	1 3 437 429	1 3 437 429
7 3 1034 1154	2 1 1314 1335	6 25 1696 1649	9 3 1434 1523	6 8 1184 1424	11 6 633 434	1 4 399 539	1 4 399 539
7 4 643 710	2 2 2253 2098	6 26 1266 1471	9 4 1223 1399	6 9 1423 1399	11 7 646 484	1 5 399 539	1 5 399 539
7 5 333 271	2 3 444 745	6 27 1223 1294	9 5 1251 1363	9 6 1144 1424	11 8 1066 1924	1 6 646 484	1 6 646 484
7 7 763 1409	2 4 1144 1404	6 28 1926 1470	11 1 1161 1059	9 7 1423 1399	6 10 1424 1424	1 7 1066 1924	1 7 1066 1924
7 8 1267 1149	2 5 919 924	6 29 1294 1511	11 2 1793 1699	9 8 1144 1424	6 11 1424 1424	1 8 1424 1424	1 8 1424 1424
7 9 1548 1570	2 6 415 439	6 30 1444 1559	11 3 497 448	9 9 1144 1424	6 12 1424 1424	1 9 1424 1424	1 9 1424 1424
7 11 1375 1491	2 7 425 445	6 31 1495 1981	11 4 443 522	9 10 1144 1424	6 13 1424 1424	1 10 1424 1424	1 10 1424 1424
7 12 945 1187	2 8 1566 1629	6 32 842 814	11 5 643 801	9 11 1144 1424	6 14 1424 1424	1 11 1424 1424	1 11 1424 1424
9 1 2634 2491	2 9 496 496	6 33 5669 5548	11 6 439 434	9 12 1144 1424	6 15 1424 1424	1 12 1424 1424	1 12 1424 1424
9 2 2497 2499	2 10 862 1227	6 34 1499 1778	13 1 1499 1533	9 13 1144 1424	6 16 1424 1424	1 13 1424 1424	1 13 1424 1424
9 3 414 479	4 1 3447 3396	6 35 691 358	13 2 1553 1355	9 14 1144 1424	6 17 1424 1424	1 14 1424 1424	1 14 1424 1424
9 4 1479 1427	4 2 1479 1427	6 36 2475 2649	13 3 388 596	9 15 1144 1424	6 18 1424 1424	1 15 1424 1424	1 15 1424 1424
9 6 1576 1420	4 3 445 599	6 37 5687 5788	13 4 469 584	9 16 1144 1424	6 19 1424 1424	1 16 1424 1424	1 16 1424 1424
9 7 643 757	4 4 3489 3592	6 38 2039 2163	13 5 1576 1636	9 17 1144 1424	6 20 1424 1424	1 17 1424 1424	1 17 1424 1424
9 9 1854 1933	4 5 715 896		13 6 1238 1258	9 18 1144 1424	6 21 1424 1424	1 18 1424 1424	1 18 1424 1424
9 10 627 772	4 6 1349 1314	M = 13	13 7 1498 1643	9 19 1144 1424	6 22 1424 1424	1 19 1424 1424	1 19 1424 1424
9 11 1346 1021	4 7 747 429	M L F ₀ F _c	15 1 418 594	9 20 1144 1424	6 23 1424 1424	1 20 1424 1424	1 20 1424 1424
9 12 2298 2529	4 8 2009 1425	1 1 1886 1675	15 2 1367 1366	9 21 1144 1424	6 24 1424 1424	1 21 1424 1424	1 21 1424 1424
11 1 1511 1360	4 9 2167 2257	1 2 914 564	15 3 1264 1334	9 22 1144 1424	6 25 1424 1424	1 22 1424 1424	1 22 1424 1424
11 4 567 492	4 10 654 654	1 3 1219 1157	15 4 744 954	9 23 1144 1424	6 26 1424 1424	1 23 1424 1424	1 23 1424 1424
11 5 2219 2051	4 11 451 549	1 4 984 474	15 5 759 875	9 24 1144 1424	6 27 1424 1424	1 24 1424 1424	1 24 1424 1424
11 6 1469 1491	4 12 2249 2244	1 5 2129 1848		9 25 1144 1424	6 28 1424 1424	1 25 1424 1424	1 25 1424 1424

CaZr₆I₁₄ (Crystal 2) F_o/F_c x 10

H = -16	-3 6 399 511	6 10 465 927	3 8 1630 1843	13 9 2094 2154	6 0 4548 4357	16 2 1145 1162
K L FO FC	-1 13 247 346	6 12 418 472	3 9 2107 2182	13 10 2120 2154	6 1 2796 2728	16 3 1654 1696
-2 2 275 493		6 14 343 344	3 10 2314 2221	15 1 768 774	6 2 2155 2194	16 6 342 382
-2 5 727 776	H = -4	6 12 466 425 645	3 11 537 472	15 2 1723 1692	6 3 3746 3380	16 7 1455 1428
	K L FO FC	6 4166 441 4636	3 12 1285 1226	15 3 733 736	6 6 254 55	16 8 367 536
H = -15	-14 4 447 291	6 4 3967 3466	3 13 535 796	15 5 846 683	6 7 3521 3671	16 9 1679 1633
K L FO FC	-8 12 560 398	6 4147 37 16126	3 14 2357 2368	15 6 754 844	6 8 2574 2476	
-7 4 224 91	-6 4 323 704	6 14 1576 1479	5 1 4139 4339	15 8 2415 2364	6 9 766 774	
-1 6 374 481	-6 5 462 545	6 1217 442 9485	5 2 4396 4224	15 9 943 1442	6 10 2554 2546	
		14 4 3388 4357	5 4 1637 1494	17 2 336 497	6 11 1127 1466	
H = -13	H = -3	14 2 327 185	5 7 1220 1472	17 3 647 936	6 12 812 909	
K L FO FC	K L FO FC	12 4 5825 5785	5 8 2265 2224	17 5 2343 2367	6 13 2194 2496	
-9 4 331 396	-9 14 233 76	14 6 4239 4238	5 9 3769 3741		6 14 335 425	
-7 6 286 414	-5 10 494 382	14 10 2211 2482	5 10 2747 2744	H = 2	6 15 344 67	
-1 2 243 350	-1 5 422 446	14 12 1643 1694	5 12 1574 1527	K L FO FC	6 16 1522 1424	
	-1 9 225 168	12 4 227 111	5 13 257 162	6 0 2358 2138	6 17 517 666	
	-1 10 244 268	12 2 724 782	5 14 2556 2547	6 1 1346 1122	6 18 2163 2475	
H = -12		12 4 1891 1452	7 1 469 57	6 2 1882 1664	6 19 458 511	
K L FO FC		12 4 1741 1774	7 2 1679 1542	6 3 947 791	6 20 2490 2124	
-19 1 292 274		12 4 956 1452	7 3 568 792	6 4 4126 3882	6 21 343 352	
-6 14 247 445		12 14 588 559	7 4 294 98	6 5 1441 924	6 22 429 112	
	H = -11	14 4 2190 2179	7 5 2552 2426	6 6 3456 3353	6 23 456 443	
	K L FO FC	14 2 179 1324	7 6 548 712	6 7 643 1413	6 24 277 482	
-13 1 342 354	-14 15 259 277	14 4 327 297	7 8 3169 3056	6 8 974 1186	6 25 843 866	
		14 6 524 574	7 11 812 847	6 9 341 274	6 26 945 995	
H = -14		14 8 1974 2464	7 12 1238 1199	6 10 327 215	6 27 567 855	
K L FO FC		14 10 1137 1234	7 13 544 614	6 11 1056 1792	6 28 1 545 565	
-12 4 246 247		14 12 586 12453	7 14 456 562	6 12 660 694	6 29 584 586	
	H = -4	16 2 434 494	9 1 2327 3291	6 13 789 751	6 30 431 461	
	K L FO FC	16 411 521 1467	9 3 2667 3136	6 14 2127 2294	6 31 4172 3114	
-7 3 337 395		14 4 1223 1384	9 4 414 429	6 15 1715 1563	6 32 548 652	
-7 7 332 220		16 4 9114 4592	9 5 5688 5812	6 16 1126 1450	6 33 6195 1985	
-5 2 364 581		14 4 1041 1238	9 6 247 312	6 17 1521 1364	6 34 321 427	
-5 4 419 664		14 2 279 599	9 7 359 513	6 18 1491 1428	6 35 345 254	
-3 9 364 334		14 4 3493 3565	9 8 2169 2134	6 19 2454 2363	6 36 325 311	
			9 9 1243 1474	6 20 584 531	6 37 1144 1159	
	H = -8		9 10 589 574	6 21 1419 1555	6 38 1479 1695	
K L FO FC			9 11 1636 1626	6 22 1465 1765	6 39 3768 3436	
-14 7 271 220			9 12 2071 2033	6 23 1072 1041	6 40 7465 6761	
-12 1 254 162			9 13 2745 2797	6 24 486 518	6 41 2109 2024	
-12 6 401 363			11 1 1464 1312	6 25 482 499	6 42 9827 9173	
-6 2 463 379			11 2 1044 934	6 26 1463 1118	6 43 4244 3643	
-6 4 225 146			11 3 1144 1241	6 27 1465 1347	6 44 7201 6633	
			11 4 471 489	6 28 1177 1223	6 45 3721 3444	
	H = -7		11 5 3263 3326	6 29 3655 3529	6 46 5192 4693	
K L FO FC			11 6 974 973	6 30 1149 9574	6 47 2445 2563	
-15 2 310 314			11 7 349 413	6 31 2177 2516 652	6 48 6173 5949	
-7 4 264 154			11 8 641 689	6 32 3176 3168 683	6 49 6757 6285	
			11 9 1046 1437	6 33 4 8986 8356	6 50 5264 5135	
	H = -6		11 10 1444 1446	6 34 5115 431 4935	6 51 3649 3581	
K L FO FC			11 11 334 418	6 35 6154 761 5464	6 52 2132 2332	
-9 14 363 504			11 12 1453 1453	6 36 7 5693 3981	6 53 2 1742 1686	
-2 9 371 327			13 1 1432 2254	6 37 2491 2788	6 54 2715 2644	
			13 2 3499 3402	6 38 4 9101 8442	6 55 2462 2822	
	H = -5		13 3 579 957	6 39 4 8165 7669	6 56 2312 2283	
K L FO FC			13 4 1479 1362	6 40 11 8692 8303	6 57 475 595	
-13 2 292 467			13 5 1747 2042	6 41 12 3217 3452	6 58 2299 2407	
-9 3 298 145			13 6 544 510	6 42 13 3479 2677	6 59 1297 1394	
			13 7 476 1197	6 43 7394 7124	6 60 1 824 786	

$$\text{CeZr}_6\text{I}_{14} \text{ (Crystal 2)} \cdot \text{F}_2\text{O}_2 \cdot x \text{H}_2\text{O}$$

0	3	2469	2509	2	4	462	77	12	9	525	549	5	8	1357	1322	M = 6	8	4	2786	2722	3	4	1357	1436
0	5	252	252	2	7	1285	1356	12	4	368	346	5	9	919	1063	K L FU FC	8	1	859	963	3	5	3105	3590
0	6	2645	2552	2	8	1200	1204	12	7	243	308	5	10	1866	1001	0	8	4899	4639	8	2	1255	1452	
0	7	1915	2014	2	9	249	302	12	4	1004	1004	5	11	154	952	0	1	1926	1710	8	3	3494	3471	
0	8	1013	1067	2	10	3139	3143	12	9	328	455	5	12	3198	3115	0	2	1503	1470	8	4	814	763	
0	9	261	124	2	11	373	619	12	10	1515	1590	5	13	1673	1031	0	3	5640	5255	8	5	918	802	
0	11	2500	2594	2	12	924	1016	12	11	453	555	5	14	697	692	0	4	264	479	8	7	1564	1424	
11	1	373	343	2	13	656	716	14	0	1997	2125	7	1	375	457	0	5	1334	1360	8	8	2644	2496	
11	2	443	867	2	14	819	882	14	1	1744	1684	7	2	2024	2027	0	6	636	861	8	9	1252	1240	
11	4	478	436	4	0	4619	4319	14	2	1443	1530	7	3	760	646	0	7	2758	2798	8	11	1844	1599	
11	5	1526	1422	4	1	1698	1574	14	3	1650	1598	7	4	668	843	0	8	3674	3134	8	12	620	923	
11	8	361	405	4	2	1744	1684	14	7	2122	2009	7	5	747	681	0	9	1632	1569	10	4	2551	2545	
11	9	769	603	4	3	3664	3399	14	8	443	751	7	6	1764	1600	0	10	1296	1323	10	1	2462	2391	
11	10	1375	1334	4	4	525	559	14	9	4754	4711	7	7	884	800	0	11	2623	2458	10	2	1834	1841	
11	11	1291	1294	4	5	1699	1692	14	2	9126	8549	9	8	1279	1191	0	12	420	924	12	3	2595	2523	
11	12	1044	1044	4	6	474	1004	14	3	3673	3604	7	9	514	503	0	13	1674	1701	12	4	549	541	
13	1	2164	2122	4	7	2129	2333	16	4	1715	1517	7	10	1769	1759	0	14	1643	1572	14	5	233	153	
13	2	2492	2375	4	8	1268	1364	16	5	3966	3800	7	12	405	513	2	15	1377	1359	14	6	343	476	
13	3	647	730	4	9	1468	1153	16	6	4734	4524	9	1	2361	2593	2	1	2317	2194	12	7	2954	2964	
13	4	368	422	4	10	2528	2105	16	7	3985	3461	9	2	4946	4964	2	2	1877	1856	12	8	1851	1883	
13	5	1794	1587	4	11	2553	2491	16	8	2559	2463	9	4	1781	1716	2	3	1816	1713	12	9	446	512	
13	6	1972	1923	4	12	407	965	16	1	991	923	9	5	1425	1394	2	4	1107	1069	14	12	1638	1743	
13	7	1233	1264	6	0	3374	3050	14	2	1454	1783	9	6	652	715	2	5	657	670	14	11	1406	1478	
13	8	2005	2002	6	1	1952	1814					9	4	3054	3210	2	6	1556	1544	12	10	1408	13497	
13	9	456	609	6	2	2064	2377	M = 5				9	9	1775	1823	2	7	2500	2529	12	1	2133	1999	
15	1	1753	1724	6	3	1544	1866	K L FU FC				9	10	3066	3454	2	8	1463	1462	12	2	424	666	
15	2	2016	2720	6	4	1999	1904	1	1	2537	2749	9	11	1806	1814	2	10	907	902	12	3	3506	3352	
15	4	1263	1260	6	5	948	962	1	2	6216	5085	9	12	1979	1473	2	11	268	390	12	4	121451	1660	
15	5	1577	1540	6	12	2623	2634	1	3	748	554	11	1	2179	2252	2	12	905	904	12	6	1464	1148	
15	6	931	954	6	11	1315	1290	1	4	2319	2022	11	2	2579	2563	2	13	1667	1494	12	7	1257	939	
15	7	439	530	6	12	873	887	1	5	1404	1999	11	3	651	677	2	14	247	402	12	8	140635	9490	
15	8	1525	1574	6	14	533	711	1	6	941	1064	11	4	350	435	0	12	445923	2667	12	9	2778	2643	
17	1	1401	1422	8	1	6611	5542	1	7	318	319	11	6	1416	1356	4	1	4576	4321	14	2	1949	071	
17	3	1226	1219	8	2	21540	14461	1	8	3402	3297	11	7	527	662	4	2	255	176	14	2	935	1061	
17	4	576	607	8	3	4956	9407	1	9	1466	1947	11	8	3240	3165	4	3	3435	3164	14	3	693	706	
				8	4	3272	3140	1	10	3376	3242	11	9	1465	1502	4	4	416590	4677	14	4	2946	2496	
				8	5	1544	7263	1	11	672	721	11	10	379	454	4	5	3158	2633	14	5	848	886	
				8	6	41468	14434	1	12	2265	2144	11	11	1149	1249	4	6	2681	2685	14	6	2321	2434	
				8	7	1407	3609	1	14	2707	2732	13	1	1417	1414	4	7	3609	2642	16	3	1124	1474	
				8	9	904	476	3	1	2446	2678	13	3	1008	1020	4	8	517971	15285	16	4	1640	1503	
				8	4	6111	5592	3	2	358	275	13	4	983	923	4	9	3667	3339	16	6	841	900	
				8	11	4706	8226	3	3	1995	2211	13	5	1597	1435	4	10	1140	1154					
				8	12	5422	5112	3	4	897	875	13	6	705	753	4	11	830	767	M = 7				
				8	13	2944	2893	3	5	1623	1642	13	7	371	530	4	12	9298	9083	K L FU FC				
				10	4	1243	3063	3	7	493	1115	13	8	1412	1429	4	13	1667	1684	1	1	3370	3515	
				10	1	1624	1684	3	8	2409	2404	13	9	1026	1061	4	14	1822	1805	1	2	1264	1359	
				10	2	2592	2546	3	9	1418	1446	13	10	360	531	4	15	1122	1034	1	3	871	901	
				10	3	1213	3133	3	10	349	421	15	1	713	796	4	1	762	860	1	4	717	1009	
				10	5	835	779	3	11	1260	1315	15	2	378	416	4	2	1302	1003	5	1	1760	1603	
				10	6	450	795	3	12	1961	1975	15	3	464	544	4	3	362	361	6	2	2222	2246	
				10	7	2503	2506	3	13	1226	1198	15	4	1548	1592	4	4	3319	3795	6	3	1530	1564	
				10	8	1145	1242	3	14	635	684	15	5	1004	1081	4	5	1153	1139	1	8	1421	1432	
				10	9	383	549	5	1	1760	1955	17	1	1127	1127	4	6	2040	2402	1	9	3513	3064	
				10	10	2440	2450	5	2	1834	1747	17	2	1747	1771	4	7	532	502	1	10	1310	1352	
				10	11	1801	1763	5	3	2470	2646	17	3	236	257	4	8	255	438	1	12	435	546	
				10	12	935	1013	5	4	1747	1845	17	4	329	525	4	10	307	351	1	13	597	731	
				12	0	2906	2947	5	5	2731	3497					4	11	925	924	1	14	1140	1117	
				12	2	1142	1114	5	6	1871	1946					6	12	1064	1576	3	1	2968	3231	
				12	3	332	331	5	7	921	1039					6	13	876	941	3	2	265	300	

$$\text{CeZr}_6\text{I}_{14} \text{ (Crystal 2)} F_o/F_c \times 10$$
[illegible]