forms two hydrogen-bonds (Table 4) which range in length from 2.72 to 2.86 A. The ammonium ion is also hydrogen-bonded to the oxygen atoms of the sulfate groups, but one bond (to $O(3)$ and $O(4)$ of the same sulfate ion) is 'bifurcated'. In addition, there is a fairly close approach of the water octahedra along the c axis, the $O(9)$ – $O(9')$ distance being 3.009 Å.

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References

BERGHUIS, J., HAANAPPEL, **IJ. M., POTTERS, J.,** LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* 8, 478.

- BOND, W. L. (1959). *Acta Cryst.* 12, 375.
- JAMES, R.W. (1948). *The Optical Principles of the Diffraction of X-rays,* Appendix III. London: Bell.
- MCWEENY, R. (1951). *Acta Cryst.* 4, 513.
- MONTGOMERY, H. & LINGAFELTER, E. C. (1964a). *Acta Cryst.* 17, 1295.
- MONTGOMERY, H. & LINGAFELTER, E. C. (1964b). *Acta Cryst.* 17, 1478.
- MONTGOMERY, H. & LINGAFELTER, E. C. (1966a). *Acta Cryst.* 20, 659.
- MONTGOMERY, H. & LINGAFELTER, E. C. (1966b). *Acta Cryst.* 20, 728.
- STEWART, J.M. (Editor) (1964). *Crystal Structure Calculations, System X-ray-63,* University of Maryland TR-64-6.
- THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* 26, 293.
- VIERVOLL, H. & ØGRIM, O. (1949). *Acta Cryst.* 2, 277.
- ZALKIN, A., FORRESTER, J. D. & TEMPLETON, D. H. (1964). *Inorg. Chem.* 3, 529.

Acta Cryst. (1966). 20, 733

Crystallographic Data for Cerium-Zinc Compounds*

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Nine compounds were identified in the cerium-zinc system. The X-ray data obtained for CeZn and CeZn₁₁ are consistent with previously reported structures. The compound CeZn₅ is shown to be isostructural with CaCu₅ as previously reported but the lattice constants $a = 5.4163$ to 5.4069 Å and $c=4.2647$ to 4.2757 Å, which correspond to the composition range CeZn₅.₃₆ to CeZn₅.₁₀ respectively, are significantly different. The unit cells and diffraction symmetries for all the remaining compounds except CeZn₇ were determined. Orthorhombic CeZn₂, $a=4.63$, $b=7.54$, $c=7.50$ Å, is isostructural with CeCu₂. CeZn₃ and Ce₃Zn₁₁ are also found to be orthorhombic with $a=4.62$, $b=10.43$, $c=6.64$ Å for CeZn₃ and $a=4.5215$, $b=8.8855$, $c=13.463$ Å for Ce₃Zn₁₁. CeZn_{4.5} is hexagonal with $a=14.60$, $c= 14.11$ Å. Ce₂Zn₁₇ is shown to be isostructural with U₂Zn₁₇, space group *R*3*m*. Only X-ray data on powdered specimens of $CeZn₇$ were obtained.

Introduction

In a study of the cerium-zinc alloy system, X-ray diffraction data along with thermal, metallographic and vapor pressure data were employed to establish the phase diagram. The purpose of this paper is to summarize the X-ray diffraction data obtained; the other data have been reported elsewhere (Chiotti & Mason, 1965).

There are nine compounds in this system; six, $CeZn₃$, CeZn₃.67, CeZn₄.5, CeZn_{5.25}, CeZn₇ and CeZn₁₁ decompose peritectically at 820, 840, 870, 885, 960 and 795 $\mathrm{^{\circ}C}$ respectively, and three, CeZn, CeZn₂ and $CeZn_{8.5}$ melt congruently at 825, 875 and 980 $°C$ respectively.

X-ray work on three of the nine compounds has been reported by earlier investigators. Iandelli & Botti (1937) showed that the compound CeZn has the CsC1 structure, space group *Pm3m*, with $a = 3.704$ Å. Sanderson & Baenziger (1953) determined the structure of $BaCd_{11}$ from single crystal data. They compared powder diffraction data of this compound with powder diffraction data for CeZn₁₁, LaZn₁₁, PrZn₁₁ and SrCd₁₁ and found that all of them give patterns with similar line spacings and relative intensities and suggest they are isostructural with $BaCd₁₁$. The lattice constants for

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the body centered tetragonal cell with four units of CeZn₁₁ are reported to be $a=10.66$, $c=6.86$ Å. The structure of $CeZn_s$ has been reported to have the $CaCu_s$ structure, space group $P6/mmm$, with $a=5.42$, $c=$ 4.17 A by Gladyshevskii, Kripyakevich, Teslyuk, Zarechnyuk & Kuz'ma (1961).

Experimental procedure

The metals used were Bunker Hill slab zinc $99.99 + \%$ pure, and United Mineral and Chemical Corporation cerium, 99.6% pure. The purity of the cerium was improved somewhat by arc-melting and electron-beam melting. Spectroscopic and vacuum fusion analyses gave the following impurities in ppm: Ca 50, Cu 50, Mg 400, Fe 300, Si 300, O 200, N 5, and H 5. The metals in the desired proportions were sealed in tantalum crucibles, equilibrated in the liquid state and where necessary were heat treated in the solid state to obtain the desired alloy or compound. The tantalum crucibles were closed by heliarc welding under an argon atmosphere and were then enclosed in stainless steel jackets to protect the tantalum from oxidation during heat treatment. The alloys which undergo a peritectic reaction were annealed at temperatures just below the peritectic temperatures for periods of 50 to 94 hours in order to bring about complete reaction, or to eliminate extraneous phases.

X-ray diffraction patterns of powder specimens of 36 different alloys were obtained with a Debye-Scherrer camera or an X-ray diffractometer. The relative intensities of the reflections of several of the compounds were evaluated by measuring the area under the recorded diffractometer peaks. Single crystals of the compounds were isolated, usually from the shrinkage cavities of alloy ingots, and Weissenberg patterns and in some cases precession patterns were taken in order to establish the unit cells and diffraction symmetries for the compounds. Copper K_{α} radiation was used throughout this investigation and the wavelength for a_1 was taken to be $1.54051~\text{\AA}.$

Powder specimens were prepared by crushing the massive alloys under liquid nitrogen in order to minimize residual strains in the powder. Single crystals were also broken from shrinkage cavities with the alloy at liquid nitrogen temperatures. This technique was employed instead of the usual high temperature stress **anneal because on heating under high vacuum the** samples lost zinc by vaporization and under an argon or helium atmosphere the alloy powder or crystals became discolored indicating the formation of cerium oxide.

An IBM 7074 computer was used to help reduce the raw data to the most useful form. Two programs *Determination of Lattice Parameters with the Aid of a Computer* by Mueller, Heaton & Miller (1960) and Mueller & Heaton (1961) and *Crystallographic d-Space Computer Program,* by Mueller, Meyer & Simonsen (1962) were found to be quite useful.

Results and discussion

A summary of the lattice constants and possible space groups for eight of the compounds is given in Table 1. The data for CeZn and CeZn₁₁ were taken from the literature, although data from powder specimens were also obtained for these compounds in the present investigation. The results were found to be consistent with the data cited.

CeZn2, 48.27 wt. % *zinc*

Crystals of $CeZn_2$ were observed to be tetragonal prisms. Weissenberg *Okl* data and precession photographs of *hOl* through *h31* layers were taken and the reflections observed satisfied the conditions, $h + k + l =$ 2n for hkl reflections and $h = 2n$ for hk0 reflections. The unit cell is body-centered orthorhombic with $a=4.63$, $b=7.54$, $c=7.50$ Å, and the possible space groups are *Imma* and *I2ma* or *Im2a.* The *Okl* Weissenberg photograph showed reflection intensities with the same general trend of the corresponding *Okl* reflection intensities for CeCu₂ reported by Larson & Cromer (1961) . Debye-Scherrer powder patterns of the two compounds were also compared visually and found to be similar in line spacing and relative intensities. These observations show that $CeZn₂$ is isostructural with $CeCu₂$ (Larson & Cromer, 1961).

CeZn3, 58.33 *wt.% zinc*

A crystal of $CeZn_3$ was isolated from crushed fragments of a 57.5% zinc alloy and Weissenberg photographs of the *Okl, lkl, 2kl,* and *3kl* layers were made. Precession photographs were also made of the *hkO, hkl, hk2, hk3* and *hOl* layers. All films showed 2m layer symmetry and the observed reflections obeyed the conditions $h + k = 2n$ for *hkl* data and $l = 2n$ for *hOl* data. The lattice constants of the C-centered orthorhombic cell are $a=4.62$, $b=10.43$, $c=6.64~\text{\AA}$; and the three possible space groups are *Cmcm, C2cm* and *Cmc2.*

A diffractometer pattern of the powdered alloy gave d-spacings which, down to 1.20 Å, were in good agreement with those computed from the single-crystal data.

Ce₃Zn₁₁, 63.12 *wt.*% zinc

Two single crystals of this compound were studied. One was aligned about its ' a ' axis and the other about **its 'b' axis and numerous precession and Weissenberg** photographs were obtained from each crystal. The data from both crystals showed that the compound is bodycentered orthorhombic. No systematic absences other than those due to body-centering were observed and the four possible space groups are *Immm, Imm2* (or $I2mm$, $Im2m$), $I222$ and $I2₁2₁2₁$. Back-reflection Weissenberg data gave $a=4.5215$, $b=8.8855$, $c=$ 13.463 Å.

The diffractometer pattern of a powder specimen of a 63.1% zinc alloy was obtained and the line positions and their intensities were measured. These data are

Table 1. *Summary of crystallographic data for cerium-zinc compounds*

* Formula units per unit cell.

† Data from Iandelli & Botti (1937).

 \ddagger Composition ranges from 70.4 to 71.1 wt % Zn, and the lattice constants, a_0 =5.4163 to 5.4069 A and c_0 =4.2647 to 4.2757 A.

§ Data from Sanderson & Baenziger (1953).

Table 2. *X-ray powder data for* $Ce₃Zn₁₁$

* Values from diffractometer pattern of 63.08 % Zn alloy. t Relative intensities measured from diffractometer charts with a planimeter and scaled to *1/lo=* 100 for strongest peak. n.o. = not observed.

 $\hat{\theta}$

listed in Table 2. The d-spacings were also calculated from the single-crystal data and found to be in good agreement with the corresponding values in Table 2.

CeZn4.5, 67-74 *wt. % zinc*

Rotation and Laue patterns of two crystals which were isolated from a 65.2% zinc alloy were taken and found to be identical. The observed Laue symmetry was D_{6h} . One of these crystals was employed in taking Weissenberg photographs of the *hkO* through *hk5* layers and precession photographs of the *hOl, hkl, h2l* and *hhl* layers. Only those *hhl* reflections with *l=2n* were observed. No other systematic extinctions were found and the possible space groups are $P\bar{6}2c$, $P6_3mc$ and $P6₃$ *mmc*.

The lattice constants as determined from Weissenberg and rotation films are $a = 14.60$, $c = 14.11$ Å. The *c/a* ratio is 0.966 and the volume of the unit cell is 2605 Å³. All the possible space groups require an even number of atoms of each kind in the unit cell. The cell formula $Ce_{26}Zn_{114}$ yields a volume contraction of 0.84% which is consistent with the trend in the calculated volume change for the other compounds and the resulting stoichiometry, CeZn_{4.4}, agrees with the results of Valeckis & Van Deventer (1963) and Valeckis, Rosen & Feder (1961). A more precise stoichiometry probably cannot be established without a detailed structure analysis.

The diffractometer pattern of a powder specimen of a 67.5% zinc alloy was compared with the *d*-spacings calculated from single-crystal results. Since there are over 1100 possible lines, only the front reflections for the region up to 50 $^{\circ}$ 2 θ were compared. All the 46 observed lines were accounted for. There were 99 calculated lines in the investigated region; twenty-five were not observed and because of the close proximity of some of the calculated lines their resolution was not expected and the remaining 74 lines could be accounted for by the 46 observed lines.

CeZn5, 70.00 *wt.% zinc*

Gladyshevskii *et al.* (1961) have previously reported that $CeZn₅$ is isostructural with $CaCu₅$. However, their lattice constants, $a=5.42$, $c=4.17 \text{ Å}$, differ significantly from the constants found in this investigation, and although it was found that the compound exists over a composition range, the variation in lattice constants **was not sufficient to account for the discrepancy.**

There exists a fairly large group of $AB₅$ compounds having the CaCu₅ structure, type $D2_a$, space group *P6/mmm* with A in (a): 0, 0, 0, 2B_I in (c): $\pm (\frac{1}{2}, \frac{2}{3}, 0)$, and $3B_{II}$ in (g): $\frac{1}{2}$, 0, $\frac{1}{2}$, 0, $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ (Dwight, 1961; Wernick & Geller, 1959). Dwight has shown that the known AB_5 compounds have the above structure if $1.26 \le R_A/R_B \le 1.61$. The radius ratio R_{Ce}/R_{Zn} is 1.33.

X-ray diffractometer patterns of four different alloy compositions were taken in order to establish the composition range for the compound. The extrapolated least-squares lattice constants are given in Table 3

Table 3. *Variation with composition of the lattice constants of CeZn₅ compound*

Alloy			
wt. $\%$ Zn	а	с	cla
$70.00*$	5.4163 Å	4.2647 Å	0.7874
70.50	5.4152	4.2669	0.7879
70.99	5.4081	4.2736	0.7902
$71.97*$	5.4069	4.2757	0.7908

* These alloys contained detectable traces of their neighboring phase.

along with the *c/a* ratios. The statistical uncertainty in the extrapolated lattice constants was calculated to be $+0.00005$ Å or less; however, the accuracy and relative precision of the lattice constants for the different alloys is estimated to be within ± 0.0005 Å. It is also to be noted that the volume per unit cell calculated from the lattice constants varies only slightly, 108.4 to 108.3 \AA ³, over the composition range observed. The 70.0% zinc alloy showed the presence of CeZn_{4.5} and the 71.97% zinc alloy showed the presence of $CeZn₇$. In the two phase regions the lattice constants, and consequently the *c/a* ratio, do not vary with the over-all composition. A composition range of 70.4 to 71.1% zinc for the compound was obtained by plotting *c/a versus* composition and assuming linear variation of *c/a* within the single phase region. This result is in excellent agreement with the work of Valeckis & Van Deventer (1963) who reported the stoichiometry as $CeZn_s$.

The reflection intensities were calculated for CeZn5 based on the $CaCu₅$ structure. The atomic scattering factors and dispersion data for cerium and zinc were obtained from the compilation in *International Tables for X-ray Crystallography* (1962, p. 210 and p. 213 respectively). The observed intensities measured from a diffractometer scan of a powder specimen of a 70.0% zinc alloy were scaled so that the intensity of the strongest peak was 100 arbitrary intensity units. No temperature factor correction was applied to the observed data. However, other corrections were made with particular attention given to dispersion corrections. The dispersion correction for cerium is about 20% when copper $K\alpha$ radiation is used. The calculated intensities were scaled to the observed intensities by making $\sum I_e = \sum I_o$. The intensity data are compared in Table 4. Although the observed and calculated intensities do not match perfectly, there can be little doubt that $CeZn₅$ has the $CaCu₅$ structure. The poorest agreement **was found in the back reflection region which is the** most sensitive to temperature factor correction.

On the basis of the proposed structure the interatomic distances were calculated from the lattice constants for the 70.0% Zn sample. The interatomic distances (in accord with the type D_{2d} structure described previously) are

* Relative intensities for 70.00 wt. % zinc powder specimen measured to I_0 (max.) = 100. from diffractometer charts with a planimeter and scaled

 I/I_0

 $\ddot{\textbf{r}}$ Calculated intensities for CeZn₅ based on CaCu₅ structure with *I_c* scaled to *I_o* so that $\sum l_c = \sum l_o$. n.o. =not observed.

The fact that the composition range for this compound lies completely on the high zinc side may be due to vacant cerium sites, zinc in interstitial positions or zinc in cerium lattice sites. The observation that the unit cell volume remains nearly constant over the composition range observed and a consideration of the structure of the compound suggests that zinc atoms or pairs of zinc atoms occupy some of the cerium lattice sites.

CeZn₇, 76.56 *wt.*% zinc

All the crystals obtained for this compound were square based pyramids with well developed faces; how-

* Values from diffractometer measurements of 76.53 wt. $\%$ zinc alloy powder specimens.

t Relative intensities measured from diffractometer charts with a planimeter and scaled to $I/I_0 = 100$ for strongest peak.

ever, X-ray oscillation photographs showed that they were multiple crystals. Several small chips of these crystals and fragments of the bulk alloy were also examined but with no better results. Consequently only diffractometer data were obtained for this compound.

The d-spacing data given in Table 5 are averaged results obtained from several diffractometer scans of 76.5% zinc alloy powder specimens. Intensity data are given only up to 80° 2 θ (d = 1.20 Å). Attempts to index the pattern on the basis of a hexagonal, tetragonal or orthorhombic unit cell failed, either because the cell has less than orthorhombic symmetry or because of the complexity of the diffraction pattern.

Ce₂Zn₁₇, 79.86 wt.% zinc

The powder pattern of a 79.8% zinc alloy was compared with a powder pattern of $U_2 Zn_{17}$. The patterns appear to be nearly identical in position and intensity of the observed lines. A single crystal was picked from this alloy and Weissenberg *hOl, hll, h2l* and *h3l* data were obtained and precession photographs of the *hkO* through *hk6,* and several *hhl* layers were taken. The *hOl* layer Weissenberg photograph of $Ce₂Zn₁₇$ was compared visually with a corresponding Weissenberg pattern of $U_2 Z n_{17}$ and found to be very similar. Therefore, it may be concluded that $Ce₂Zn₁₇$ is isostructural with the rhombohedral modification of U_2Zn_{17} (Vold & Peterson 1961) and (Markarov & Vinogradov 1956). The lattice constants for the corresponding hexagonal unit cell for $Ce₂Zn₁₇$ were determined from back reflection Weissenberg data to be $a=9.0708 \pm 1.005$ 0.0005 Å and $c=13.2844 + 0.0005$ Å.

In an alloy system such as the cerium-zinc system in which a large number of compounds are formed, it is very difficult to establish definitely the true stoichiometry of the compounds on the basis of the usual thermal and metallographic data. Similarly it is not always possible to infer correctly the stoichiometry of a compound from X-ray data alone; for example, the $AB₅$ compound listed in Table 1 has a stoichiometry corresponding closely to $CeZn_{5.25}$. Microstructures indicate the compound designated as $CeZn₇$ is also actually richer in zinc than the formula indicates. In view of the X-ray data presented here and the thermal and metallographic data presented elsewhere (Chiotti & Mason, 1965) there can be little doubt that all the cerium-zinc compounds which are stable over the temperature **range investigated have been identified. Compounds** which might form very slowly at near room temperatures are excluded.

The phase diagram for the yttrium-zinc system (Chiotti, Mason & Gill, 1963) shows a similar series of compounds; the compounds $YZn₇$ and $YZn_{4.5}$ were not indicated on the phase diagram. The crystal structures of the yttrium-zinc compounds have been investigated by Earle Ryba and coworkers at The Pennsylvania State University. Data obtained by Sree Harsha (1964), when compared with the data on the ceriumzinc compounds, indicate that the compound designated as YZn_4 on the phase diagram is actually Y_3Zn_{11} and the compound YZn_5 is very probably $YZn_{4.5}$. The metallography of the alloys in this region of the yttriumzinc system should be reexamined. It is also interesting to note that they find the space group for $YZn₃$ is *Pnma* with $a = 6.690$, $b = 4.405$ and $c = 10.111$ whereas the data in Table 1 for $CeZn_3$ do not include this space group but do show very similar lattice constants indicating the two structures are closely related.

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References

- CHIOTTI, P., MASON, J. T. & GILL, K. J. (1963). *Trans. Met. Soc. AIME,* 227, 910.
- CHIOTTI, P. & MASON, J. T. (1965). *Trans. Met. Soc. AIME*, 233, 786.
- DWmHT, A. E. (1961). *Trans ASM,* 53, 479.
- GLADYSHEVSKII, E. I., KRIPYAKEVICH, P. I., TESLYUK, M. YU., ZARECHNYUK, O. S. & KUZ'MA, YU, B. (1961). *Soviet Physics Crystallography,* 6, 207.
- IANDELLI, A. & BOTTI, E. (1937). *Gazz. chim. Ital.* 67, 638.
- *International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- LARSON, A. C. & CROMER, D. T. (1961). *Acta Cryst.* 14, 73.
- MARKAROV, E. S. & VINOGRADOV, S. I. (1956). *Kristallografiya,* 1, 634.
- MUELLER, M. H., HEATON, L. & MILLER, K. T. (1960). *Acta Cryst.* 13, 828.
- MUELLER, M. H. & HEATON, L. (1961). *Determination of Lattice Parameters with the Aid of a Computer. U. S.* Atomic Energy Commission Report ANL-6176.
- MUELLER, M. H., MEYER, E. F. H. & SIMONSEN, S. H. (1962). *Crystallographic d-Space Computer Program. U. S.* Atomic Energy Commission Report ANL-6519.
- SANDERSON, M. J. & BAENZIGER, N. C. (1953). *Acta Cryst.* 6, 627.
- SREE HARSHA, K. S. (1964). Thesis, *The Crystal Structure of Intermetallic Compounds in the Yttrium-Zinc System.* The Pennsylvania State University, University Park, Penn.
- VALECI<IS, E., ROSEN, C. L. & FEDER, H. M. (1961). *J. Phys. Chem.* 65, 2127.
- VALECKIS, E. & VAN DEVENTER, E. (1963). U. S. Atomic Energy Report ANL-6648, 120.
- VOLD, C. & PETERSON, D. T. (1961). *The Structure of* U_2Zn_{17} . U. S. Atomic Energy Commission Report IS-246.
- WERNICK,J.H. & GELLER, S. (1959). *Acta Cryst.* 12, 662.