

Ternary Intermetallics with High Zinc Content: TT'_2Zn_{20} ($T = \text{Zr, Hf, Nb}$; $T' = \text{Mn, Fe, Ru, Co, Rh, Ni}$) with $\text{CeCr}_2\text{Al}_{20}$ -Type Structure

Nicole Gross, Tono Nasch, and Wolfgang Jeitschko

Anorganisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm Klemm-Strasse 8, D-48149 Münster, Germany

Received May 14, 2001; in revised form July 5, 2001; accepted July 12, 2001

Fourteen new compounds TT'_2Zn_{20} were prepared by reaction of the elemental components. They crystallize with the cubic $\text{CeCr}_2\text{Al}_{20}$ -type structure (space group $Fd\bar{3}m$, $Z = 8$), which was refined from single-crystal X-ray data of $\text{HfRu}_2\text{Zn}_{20}$ ($a = 1406.9(1)$ pm) and $\text{NbFe}_2\text{Zn}_{20}$ ($a = 1387.9(1)$ pm) to conventional residuals of $R = 0.018$ and $R = 0.022$ for 268 and 144 structure factors, respectively, and 17 variable parameters each. The structure of the compound $\text{NbCo}_2\text{Zn}_{20}$ ($a = 1382.2(1)$ pm) was refined from X-ray powder data to $R_F = 0.031$. The occupancy parameters have practically the ideal values for all five atomic sites of the three structures. The largest voids in this structure are octahedral with a size similar to those in the structure of elemental zinc. © 2001 Academic Press

INTRODUCTION

Only a few elements form compounds where they dominate the composition. Borides (e.g., LiB_7 , LaB_6 , WB_4 , MnB_4 , UB_{12}), aluminides (e.g., BaAl_4 , VAl_{10} , WAl_{12} , FeAl_6 , Co_2Al_9), and phosphides (e.g., LiP_7 , RbP_{11} , BaP_{10} , ThP_7 , Ag_3P_{11} , MnP_4) are examples with main group elements. The neighboring elements beryllium (e.g., with CaBe_{13} , ScBe_5 , $\text{Ti}_2\text{Be}_{17}$, FeBe_{12} , $\text{Ru}_3\text{Be}_{17}$), magnesium (e.g., $\text{Eu}_2\text{Mg}_{17}$, $\text{Ce}_5\text{Mg}_{41}$), cadmium (e.g., YCd_6 , EuCd_{11} , $\text{Th}_6\text{Cd}_{23}$), and mercury (e.g., the many compounds with BaHg_{11} -type structure) also form such compounds as well as the light late transition elements where there are many representatives with $\text{Th}_6\text{Mn}_{23}$, Er_2Co_7 , Ce_2Ni_7 , $\text{Th}_2\text{Ni}_{17}$, and CaCu_5 -type structure (1). Zinc is situated in the middle of these elements and it makes no exception. We have in recent years characterized several binary compounds of transition metals with a high content of zinc, e.g., $\text{Ti}_3\text{Zn}_{22}$ and TiZn_{16} (2), $\text{Zr}_5\text{Zn}_{39}$ and ZrZn_{22} (3), NbZn_3 , NbZn_{16} , and $\text{MoZn}_{20.44}$ (4), $\text{Rh}_2\text{Zn}_{11}$ and RhZn_{13} (5). We have also started to synthesize ternary compounds with a high zinc content, and we have already reported on the rare earth (R) transition metal series RT_2Zn_{20} with $T = \text{Fe}$,

Ru , Co , Rh , and Ni which crystallize with $\text{CeCr}_2\text{Al}_{20}$ -type structure (6). Here we report on new compounds with this structure type where early transition metals take the place of the rare earth elements. Such compounds may occur in small amounts in zinc alloys as undesired impurity phases or they could possibly have a desirable influence on their mechanical properties, as it has been discussed for the corresponding aluminum phases $\text{RTi}_2\text{Al}_{20}$ (7,8). Some of the results of the work reported here have already been communicated at a conference (9).

SAMPLE PREPARATION AND LATTICE CONSTANTS

Starting materials for the preparation of the compounds TT'_2Zn_{20} were the elemental metals, mostly in the form of powders, and all with nominal purities $> 99.9\%$. Hafnium was in the form of turnings, zinc was in the form of granules. The compounds were prepared by reaction of cold-pressed pellets of the elements usually in the atomic ratio $T:T':\text{Zn} = 1:1:18$ in sealed silica tubes, which were annealed for 120 h at 850°C . It must be mentioned that unreacted zinc accumulates at the cooler parts of the sample tubes. Due to this fact the ampoules were shaken several times during the annealing to enhance the homogeneity of the samples. After this treatment the ampoules were slowly cooled ($5^\circ\text{C}/\text{h}$) to 500°C and annealed further for 120 h, followed by quenching in ice water.

The excess zinc could be separated from the samples mechanically. Nevertheless, the crushed ingots were treated in diluted hydrochloric acid to remove any remaining zinc. The ternary compounds were attacked by the acid at a slower rate. They are stable on air for long periods of time and show metallic luster. Energy-dispersive X-ray fluorescence analyses in a scanning electron microscope did not reveal any impurity elements heavier than sodium.

Guinier powder patterns of the compounds were recorded with $\text{CuK}\alpha_1$ radiation using α -quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. The lattice

TABLE 1
Lattice Constants of the Cubic Compounds TT'_2Zn_{20}
with $CeCr_2Al_{20}$ -Type Structure^a

Compound	<i>a</i> (pm)	<i>V</i> (nm ³)
ZrMn ₂ Zn ₂₀	1403.9(1)	2.7674(3)
ZrFe ₂ Zn ₂₀	1395.5(2)	2.7176(4)
ZrRu ₂ Zn ₂₀	1408.2(2)	2.7925(3)
ZrCo ₂ Zn ₂₀	1390.8(1)	2.6900(3)
ZrRh ₂ Zn ₂₀	1404.8(2)	2.7723(4)
ZrNi ₂ Zn ₂₀	1389.1(1)	2.6809(3)
HfFe ₂ Zn ₂₀	1393.4(2)	2.7054(2)
HfRu ₂ Zn ₂₀	1406.9(1)	2.7851(2)
HfCo ₂ Zn ₂₀	1389.2(1)	2.6811(1)
HfRh ₂ Zn ₂₀	1403.8(1)	2.7663(2)
HfNi ₂ Zn ₂₀	1386.3(1)	2.6645(2)
NbFe ₂ Zn ₂₀	1387.9(1)	2.6735(2)
NbCo ₂ Zn ₂₀	1382.2(1)	2.6407(3)
NbNi ₂ Zn ₂₀	1380.9(1)	2.6337(3)

^aStandard deviations in the place values of the last listed digits are given in parentheses throughout the paper.

constants (Table 1) were refined by least-squares fits. The cell volumes of these compounds are plotted in Fig. 1.

STRUCTURE REFINEMENTS

Single crystals of HfRu₂Zn₂₀ and NbFe₂Zn₂₀ were isolated from the annealed samples and selected for the X-ray data collections on the basis of *Laue* patterns. The intensity data were recorded on a four-circle diffractometer (Enraf-Nonius, CAD4) with graphite-monochromated MoK α radiation and a scintillation counter with pulse-height discrimination. The scans were along the *Laue* streaks ($\theta/2\theta$) with background counts at both ends of each scan. Empirical absorption corrections were made on the basis of psi scans. Further details concerning the data collections are listed in Table 2.

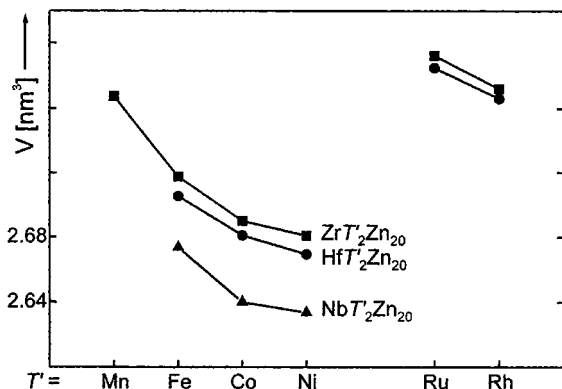


FIG. 1. Cell volumes of the compounds TT'_2Zn_{20} with $CeCr_2Al_{20}$ -type structure.

TABLE 2
Crystal Data for HfRu₂Zn₂₀ and NbFe₂Zn₂₀

Compound	HfRu ₂ Zn ₂₀	NbFe ₂ Zn ₂₀
Space group	$Fd\bar{3}m$ (No. 227)	$Fd\bar{3}m$ (No. 227)
Formula units/cell, <i>Z</i>	8	8
Pearson symbol	cF184	cF184
Formula mass	1688.23	1512.20
Lattice constants from		
Guinier powder		
[<i>single-crystal</i>] data		
<i>a</i> (pm)	1406.9(1) [1408.1(2)]	1387.9(1) [1388.7(2)]
<i>V</i> (nm ³)	2.7851(2) [2.7917(6)]	2.6735(2) [2.6780(7)]
Calculated density		
(g/cm ³)	8.05	7.51
Crystal size (μm)	75 × 50 × 25	60 × 60 × 20
$\theta/2\theta$ scans up to 2θ	70°	60°
Range in <i>h, k, l</i>	± 22, ± 22, 0–22	± 20, ± 20, 0–20
Ratio highest/lowest transmission	1.21	2.15
Total number of reflections	6304	3696
Internal residual, <i>R_i</i> (<i>I</i>)	0.079	0.103
Unique reflections	355	220
Reflections with <i>I_o</i> > 2σ(<i>I_o</i>)	268	144
Number of variables	17	17
Highest/lowest residual electron density (e/Å ³)	1.3/–2.0	1.9/–1.4
Conventional residual, <i>R</i> (<i>F</i> > 2σ)	0.018	0.022
Weighted residual, <i>R_w</i> (all <i>F</i> ² values)	0.043	0.045

The single-crystal data of HfRu₂Zn₂₀ and NbFe₂Zn₂₀ were evaluated using the program system MOLEN (10) and for the final structure refinements the program package SHELX-97 (11) was used. The structures were recognized to be isotypic with CeCr₂Al₂₀ (12) on the basis of their Guinier powder patterns. This was confirmed during the full-matrix least-squares refinements with atomic scattering factors, corrected for anomalous dispersion. The weighting schemes included a term which accounted for the counting statistics and a parameter correcting for isotropic secondary extinction was optimized as a least-squares variable.

To check for deviations from the ideal compositions, occupancy parameters were refined together with variable anisotropic displacement parameters in separate series of least-squares cycles. These parameters varied between 97.7(2) % for the Hf and 101.1(2)% for the Zn1 positions of HfRu₂Zn₂₀. For NbFe₂Zn₂₀ they varied between 98.5(6)% for the Fe and 102.6(5)% for the Nb positions. Hence, for both compounds no great deviations from the ideal compositions were found, and in the final refinement cycles with anisotropic displacement parameters we assumed the ideal occupancy values for both compounds. The final difference

Fourier analyses showed no significant electron densities at sites suitable for additional atomic positions. The final residuals, atomic parameters, and the interatomic distances are given in Tables 2–4. The crystallographic data have been deposited.¹

The structure of NbCo₂Zn₂₀ was refined from X-ray powder diffractometer data which confirmed the CeCr₂Al₂₀-type structure. The intensity data were recorded from a fine powder placed between acetate foils. A rotating sample holder was used on a focussing powder diffractometer (STOE Stadi P) with monochromated CuK α ₁ radiation and a linear position-sensitive detector in transmission geometry. A total of 3251 intensity data were collected in the 2-theta range of 10–75° with a step width of 0.02°.

The atomic scattering factors, corrected for anomalous dispersion, were provided by the Rietveld least-squares program FULLPROF (14). In the final refinement cycles a total of 15 parameters were optimized, including 3 positional parameters, 5 isotropic displacement parameters, the zero point, the scale factor, the lattice constant, and 4 parameters to fit the peak profile with a pseudo-Voigt function. The number of reflections resulting from this compound was 87. The lattice constant of the sample, obtained from the powder diffractometer data, was 1387.0(1) pm, in reasonable agreement with the lattice constant of 1382.2(1) pm from the Guinier powder data. As a check for the composition we refined occupancy parameters for all five atomic positions with an overall constant displacement parameter and a fixed scale factor. The resulting occupancy parameters varied between 98(4)% for the Nb and the Zn3 positions and 101(4)% for the Zn1 position. Thus, only insignificant deviations from the ideal composition were observed, and in the final refinement cycles we resumed to the ideal occupancies. The corresponding X-ray density is 7.64 g cm⁻³. The goodness of fit (χ^2) was 6.98, while the residuals amounted to $R_{\text{Bragg}} = 0.017$ and $R_F = 0.031$. The atomic parameters and the interatomic distances are listed in Tables 3 and 4.

DISCUSSION

With the presently reported 14 zinc compounds $TT'_2\text{Zn}_{20}$ the number of CeCr₂Al₂₀-type phases has increased to 133. These include 70 aluminum compounds (7, 8, 12, 15–23) with valence electron counts between 70 for CaTi₂Al₂₀ and 75 for $RT'_2\text{Al}_{20}$ ($T' = \text{Cr, Mo, W}$) and 49 zinc compounds $RT'_2\text{Zn}_{20}$ (6) and UFe₂Zn₂₀ (24) with valence electron counts between 59 for the series RFe₂Zn₂₀ and 63 for the

¹Data may be obtained from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, by quoting the registry numbers CSD-411975 (HfRu₂Zn₂₀) and CSD-411976 (NbFe₂Zn₂₀). E-mail: crysdata@fiz-karlsruhe.de.

TABLE 3
Atomic Parameters of HfRu₂Zn₂₀, NbFe₂Zn₂₀, and NbCo₂Zn₂₀^a

Atom	$Fd\bar{3}m$	x	y	z	B	CN
HfRu ₂ Zn ₂₀						
Hf	8a	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	0.51(1)	16
Ru	16d	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.31(1)	12
Zn1	96g	0.06000(2)	0.06000	0.32316(2)	0.88(1)	12
Zn2	48f	0.48811(4)	$\frac{1}{8}$	$\frac{1}{8}$	0.65(1)	12
Zn3	16c	0	0	0	1.07(2)	14
NbFe ₂ Zn ₂₀						
Nb	8a	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	0.72(2)	16
Fe	16d	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.72(3)	12
Zn1	96g	0.06073(3)	0.06073	0.32130(4)	1.19(1)	12
Zn2	48f	0.48770(6)	$\frac{1}{8}$	$\frac{1}{8}$	0.93(1)	12
Zn3	16c	0	0	0	1.15(3)	14
NbCo ₂ Zn ₂₀						
Nb	8a	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	0.4(1)	16
Co	16d	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.9(1)	12
Zn1	96g	0.0601(1)	0.0601	0.3225(1)	0.5(1)	12
Zn2	48f	0.4885(3)	$\frac{1}{8}$	$\frac{1}{8}$	0.7(1)	12
Zn3	16c	0	0	0	1.0(1)	14

^aThe positional parameters correspond to the second setting of space group $Fd\bar{3}m$ with the origin at the center. They were standardized with the program STRUCTURE TIDY (13). The next to last column contains the isotropic displacement parameters B ($\times 10^4$ pm²) of NbCo₂Zn₂₀ and the equivalent isotropic displacement parameters of the corresponding anisotropic parameters of HfRu₂Zn₂₀ and NbFe₂Zn₂₀. The coordination numbers CN are listed in the last column.

series RNi₂Zn₂₀. Thus, the valence electron counts of the aluminum and zinc compounds do not overlap. An intermediate valence electron count exists with between 68 and 74 for the magnesium containing aluminides with the somewhat different compositions Mg₃T'₂Al₁₈ ($T' = \text{Ti, V, Ta, Cr, W, Mn}$) (25–29). The presently reported CeCr₂Al₂₀-type compounds are the first compounds known to contain an early transition metal for the cerium site of CeCr₂Al₂₀.

The atomic positions of the CeCr₂Al₂₀-type compounds correspond to those found for ZrZn₂₂ (3, 30) and Mg₃Cr₂Al₁₈ (25). In these compounds, the large atoms Ce, Zr, and one of the Mg atoms of Mg₃Cr₂Al₁₈ occupy analogous sites with the coordination number CN 16 (Fig. 2). The other sites have lower CNs with CN 14 for one Al and one Zn site in CeCr₂Al₂₀ and ZrZn₂₂ and the second Mg site in Mg₃Cr₂Al₁₈. All other atoms have CN 12 in the three structures. The scattering power of aluminum and magnesium differs by only one electron. Thus, it seems possible that one or the other compound reported with the compositions Mg₃T'₂Al₁₈ ($T' = \text{Ti, V, Ta, Cr, W, Mn}$) has a composition and an atom distribution corresponding to that of CeCr₂Al₂₀.

A look at Table 3 reveals that the thermal parameters of the Zn3 positions with the relatively large CN of 14 are rather high when compared to the thermal parameters of the other zinc positions which have CN 12. This indicates

TABLE 4
**Interatomic Distances in the Structures of HfRu₂Zn₂₀,
 NbFe₂Zn₂₀, and NbCo₂Zn₂₀^a**

	HfRu ₂ Zn ₂₀	NbFe ₂ Zn ₂₀	NbCo ₂ Zn ₂₀	
<i>T</i> :	12Zn1	307.3	300.2	302.0
	4Zn3	304.6	300.5	300.3
<i>T'</i> :	6Zn2	249.3	245.9	245.7
	6Zn1	276.0	275.2	273.0
Zn1:	1Zn1	258.7	252.3	254.6
	2Zn1	264.9	259.1	260.1
	1Zn2	265.7	263.2	263.1
	1 <i>T'</i>	276.0	275.2	273.0
	2Zn2	278.6	276.6	275.3
	2Zn1	287.3	286.4	284.3
	2Zn3	298.6	293.1	294.0
	1 <i>T</i>	307.3	300.2	302.0
Zn2:	2 <i>T'</i>	249.3	245.9	245.7
	2Zn1	265.7	263.2	263.1
	4Zn2	272.4	269.5	267.8
	4Zn1	278.7	276.6	275.3
Zn3:	12Zn1	298.6	293.1	294.0
	2 <i>T</i>	304.6	300.5	300.3

^a The distances in these compounds $TT'Zn_{20}$ were calculated with the lattice constants of Table 1. All distances shorter than 380 pm are listed. The standard deviations are all equal to or less than 0.1 pm (HfRu₂Zn₂₀), 0.2 pm (NbFe₂Zn₂₀), and 0.4 pm (NbCo₂Zn₂₀), respectively.

that the zinc atoms of this position with the higher coordination number are less tightly bonded to their environments. On the other hand, the hafnium and niobium atoms have small thermal parameters in spite of their high CN of 16. This reflects their relatively high atomic mass.

The interatomic distances of NbFe₂Zn₂₀ and NbCo₂Zn₂₀ are similar (Table 4), as could be expected because of the similar lattice constants of the two compounds. HfRu₂Zn₂₀ has a larger lattice constant and the interatomic distances in this compound are *all* larger than the corresponding distances in NbFe₂Zn₂₀ and NbCo₂Zn₂₀. From atomic size considerations this would not be necessary for the Zn–Zn distances. Apparently, the relatively large hafnium and ruthenium atoms do not only expand their coordination polyhedra. The space requirements of these large atoms result in an expansion of the whole structure, thus weakening the Zn–Zn bonds.

In previous publications on compounds with a high content of zinc we have emphasized the fact that these compounds contain relatively large voids (2–5). The structure of MoZn₆ even contains voids which are occupied by gold atoms in the Cu₃Au-type subcell of this compound (31). A typical characteristic of intermetallics is the dense packing. Therefore, the formation of voids is remarkable. We have argued that these voids, formed by the zinc atoms, contain nonbonding electrons, occupying orbitals of the zinc atoms. This is to some extent already suggested by the structure of elemental zinc, which is classified as hexagonal

close packed. However, it has a large *c/a* ratio, resulting in unequal Zn–Zn distances, where each zinc atom has six zinc neighbors at 264.4 pm and six zinc atoms further away at 291.2 pm. The homologous element cadmium has an even higher *c/a* ratio with corresponding Cd–Cd distances of 297.9 and 329.3 pm (32). Finally, in the homologous element mercury, the nonbonding character of many electrons is immediately apparent, since it is a liquid at room temperature. Another most convincing example in this respect is the structure of Zr₅Zn₃₉, which achieves a similar electron count as the very closely related structure of Ce₅Mg₄₁ (where cerium is trivalent) by leaving certain Mg positions of Ce₅Mg₄₁ unoccupied (3).

Consequently, we have now also searched for voids in the CeCr₂Al₂₀-type structure of HfRu₂Zn₂₀. In Table 5 we list the positions and the atomic environments of four different voids V1–V4. Their positions are shown in Fig. 2. These voids are large enough to accommodate interstitial atoms like carbon or oxygen, although the difference Fourier syntheses of HfRu₂Zn₂₀ and NbFe₂Zn₂₀ did not reveal any remarkable electron densities at these locations. The six nearest atomic positions of the voids V1, V2, and V4 form distorted octahedra, while the void V3 is situated in a distorted tetrahedron formed by a Hf and three Zn1 atoms (Table 5). However, in contrast to the previous examples cited above, we have not found any voids in the CeCr₂Al₂₀-type structure which are larger than octahedral. Any close packed structure made up of metal atoms of the same size will contain octahedral voids. Thus, the presence of octahedral voids in HfRu₂Zn₂₀ is not surprising. On the other hand, the weighted average V–Zn distance of 197.9 pm for the three voids V1 (on position 96g), V2 (32e), and V4 (8b) in HfRu₂Zn₂₀ is similar to the V–Zn distance of 197.1 pm for the octahedral voids calculated by us for a hexagonal close packed structure of zinc atoms with an atomic radius of 139.4 pm. However, this atomic radius already takes account for the fact that the structure of elemental zinc is not really close packed, as was pointed out above.

TABLE 5
Vacancies in the Structure of HfRu₂Zn₂₀

<i>Fd</i> $\bar{3}m$	<i>x</i>	<i>y</i>	<i>z</i>		
V1	96g	0.310	0.310	0.121	
V2	32e	0.283	0.283	0.283	
V3	32e	0.200	0.200	0.200	
V4	8b	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	
V1:	2Zn1	194.9	V3:	3Zn1	174.4
	2Zn1	195.6		1Hf	182.8
	1Zn3	207.9		3Zn3	298.5
	1Zn2	209.5	V4:	6Zn2	192.6
V2:	3Zn1	193.5			
	3Zn2	193.6			

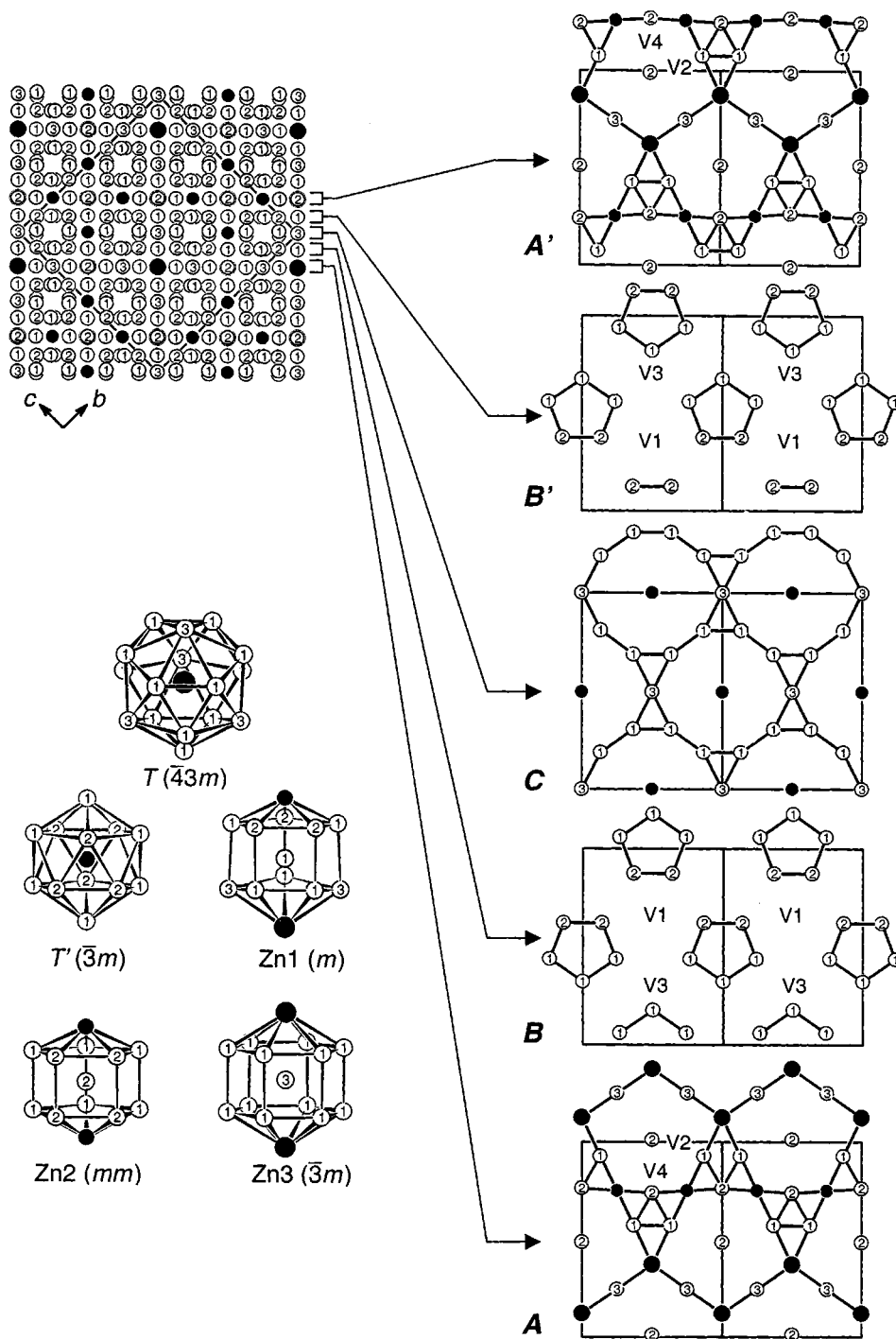


FIG. 2. The $CeCr_2Al_{20}$ -type structure of the compounds TT'_2Zn_{20} . In the upper left-hand corner this cubic structure is projected along the a axis. A sequence of atomic layers is outlined and these layers are shown on the right-hand side. The atomic layers of the type A (and A') are situated on mirror planes. Thus, the layers of the type A are positioned between two layers of the type B , and the layers A' are in between two layers B' . In the lower left-hand corner the five different coordination polyhedra occurring in this structure are outlined. The site symmetries of the central atoms are given in parentheses. It should be emphasized that the structure is shown here as consisting of atomic layers in order to facilitate its visualization. Chemical bonding within and between the atomic layers is of comparable strength as can be concluded from the coordination polyhedra of all atoms and from the fact that all translation periods are the same in this cubic structure.

ACKNOWLEDGMENTS

We thank Dipl.-Ing. U. Ch. Rodewald for the competent collection of the four-circle diffractometer data. We also acknowledge K. Wagner and H.-J. Göcke for the work at the scanning electron microscope. We are further indebted to G. Höfer (Heraeus Quarzschmelze) and W. Gerhartz (Degussa AG) for generous gifts of silica tubes and platinum metals, respectively. This work was also supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the International Centre for Diffraction Data.

REFERENCES

- P. Villars, "Pearson's Handbook, Desk Edition." Materials Information Society, Materials Park, OH, 1997.
- X.-A. Chen, W. Jeitschko, M. E. Danebrock, Ch. B. H. Evers, and K. Wagner, *J. Solid State Chem.* **118**, 219 (1995).
- X.-A. Chen and W. Jeitschko, *J. Solid State Chem.* **121**, 95 (1996).
- T. Nasch and W. Jeitschko, *J. Solid State Chem.* **143**, 95 (1999).
- N. Gross, G. Kotzyba, B. Künnen, and W. Jeitschko, *Z. Anorg. Allg. Chem.* **627**, 155 (2001).
- T. Nasch, W. Jeitschko, and U. Ch. Rodewald, *Z. Naturforsch.* **52b**, 1023 (1997).
- P. Li, Sh. Dai, and Ch. Li, *Mater. Sci. Eng. A* **280**, 128 (2000).
- A. G. Jackson, Y. R. Mahajan, and S. D. Kirchoff, *Ser. Metall.* **20**, 1247 (1986).
- N. Gross, T. Nasch, and W. Jeitschko, *Z. Kristallogr. Suppl.* **17**, 138 (2000).
- B. A. Frenz and Associates, Inc. and Enraf-Nonius, "SDP Program Package." College Station, TX; Delft, Holland, 1985.
- G. M. Sheldrick, "SHELX-97, a Program Package for the Solution and Refinement of Crystal Structures." Universität Göttingen, Germany, 1997.
- P. I. Krypyakevich and O. S. Zarechnyuk, *Dopov. Akad. Nauk Ukr. RSR. Ser. A* 364 (1968).
- L. M. Gelato and E. Parthé, *J. Appl. Crystallogr.* **20**, 139 (1987).
- J. Rodriguez-Carvajal, "FULLPROF, a Program for Rietveld Refinement and Pattern Matching Analysis," Version 3.1c, Jan. 1996, LLB (Saclay, France), based on the code provided by D. B. Wiles and A. Sakthivel, *J. Appl. Crystallogr.* **14**, 149 (1981).
- R. M. Rykhal', O. S. Zarechnyuk, and O. P. Mats'kiv, *Vestn. L'vovsk. Univ. Khim.* **21**, 46 (1979).
- O. S. Zarechnyuk, T. I. Yanson, O. I. Ostrovskaya, and P. L. Shevchuk, *Vestn. L'vovsk. Univ. Khim.* **29**, 44 (1988).
- K. Okuda, S. Noguchi, Y. Nakazawa, and M. Ishikawa, *J. Phys. Soc. Jpn.* **58**, 4296 (1989).
- N. B. Manyako, T. I. Yanson, and O. S. Zarechnyuk, *Izv. Akad. Nauk SSSR, Met.* **2**, 202 (1990).
- S. Niemann and W. Jeitschko, *J. Solid State Chem.* **114**, 337 (1995).
- V. M. T. Thiede, W. Jeitschko, S. Niemann, and Th. Ebel, *J. Alloys Compd.* **267**, 23 (1998).
- Z. Huaiying, Y. Jialin, T. Sui, Z. Yinghong, and Z. Jianmin, *J. Alloys Compd.* **299**, 232 (2000).
- H. Jinli, L. Jianlie, Z. Huaiying, Z. Yinghong, and Y. Jialin, *J. Alloys Compd.* **307**, 199 (2000).
- I. Halevy, E. Sterer, M. Aizenshtein, G. Kimmel, D. Regev, E. Yahel, L. C. J. Pereira, and A. P. Gonçalves, *J. Alloys Compd.* **319**, 19 (2001).
- A. P. Gonçalves, J. C. Waerenborgh, A. Amaro, M. Godinho, and M. Almeida, *J. Alloys Compd.* **271-273**, 456 (1998).
- S. Samson, *Acta Crystallogr.* **11**, 851 (1958).
- K. M. Kerimov, S. F. Dunaev, and E. M. Sljusarenko, *J. Less-Common Met.* **133**, 297 (1987).
- K. M. Kerimov and S. F. Dunaev, *J. Less-Common Met.* **153**, 267 (1989).
- F. W. Gayle, F. S. Biancianiello, R. J. Schaefer, and R. D. Jiggets, *Powder Diffraction* **7**, 223 (1992).
- H.-K. Fun, H.-Ch. Lin, T.-J. Lee, and B.-Ch. Yip, *Acta Crystallogr. Sect. C* **50**, 661 (1994).
- S. Samson, *Acta Crystallogr.* **14**, 1229 (1961).
- R. Lux, V. Kuntze, and H. Hillebrecht, *Z. Kristallogr. Suppl.* **18**, 107 (2001).
- J. Donohue, "The Structures of the Elements." Wiley, New York, 1974.