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Niobium and Molybdenum Compounds with High Zinc Content: $NbZn_3$, $NbZn_{16}$, and $MoZn_{20.44}$

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Well-developed crystals of the title compounds were obtained by slow cooling of binary alloys with high zinc content. Their crystal structures have been determined from four-circle X-ray diffractometer data. The Cu_3Au-type structure of $NbZn_3$ was confirmed. $NbZn_{16}$ has $TiZn_{16}$-type structure: *Cmcm*, $a = 769.6(1)$ pm, $b = 1143.6(1)$ pm, $c = 1166.3(1)$ pm, $Z = 4$, $R = 0.021$ for 943 structure factors and 50 variable parameters. $MoZn_{20.44}$ crystallizes with a new structure type and 392 atoms in the cubic face-centered cell: $F\bar{4}3m$, $a = 1846.4(1)$ pm, $R = 0.059$ for 768 F values and 64 variables. The atoms are situated at 17 different crystallographic positions. One molybdenum site has icosahedral zinc coordination. The other molybdenum atoms were found on a position with mixed Mo/Zn occupancy. It is coordinated by 14 zinc atoms in the form of a cube where all faces are capped. The zinc atoms have a great variety of coordination polyhedra with between 10 and 16 neighbors of which at most two are molybdenum atoms. Many of the atomic positions are in common with the atomic positions occupied in the structures of $Mg_{44}Rh_7$, $Fe_{22}Zn_{78}$, Na_6Tl, and Mg_6Pd. © 1999 Academic Press

INTRODUCTION

We have recently reported on Ti_3Zn_{22} (1), $TiZn_{16}$ (1), Zr_5Zn_{39} (2), and $ZrZn_{22}$ (2). In the course of these studies we have now investigated zinc-rich compounds with niobium and molybdenum as transition metal components.

The binary system niobium–zinc has been thoroughly studied by Meussner and Goode (3), who obtained six binary phases with compositions close to NbZn, $NbZn_{1.5}$, $NbZn_2$, $NbZn_3$, $NbZn_7$, and $NbZn_{15}$. Of these $NbZn_2$ (4) and $NbZn_3$ (5, 6) were found to crystallize with $MgNi_2$- and Cu_3Au-type structures, respectively. The structures of the other compounds have not been reported up to now. The presently communicated structure refinement of $NbZn_3$ is of interest, because we find this phase to have almost the ideal composition at least in a sample annealed at relatively low temperature, whereas for higher temperatures a homogeneity range from $NbZn_{2.87}$ to $NbZn_{2.92}$ had been reported with considerable zinc deficiency (3). The composition of the $TiZn_{16}$-type compound $NbZn_{16}$ characterized here is very close to that of the previously reported phase with the tentative composition $NbZn_{15}$, and we assume that this is one and the same compound.

The binary system molybdenum–zinc has been investigated by Heumann *et al.* (7). These authors found two binary phases with the approximate compositions $MoZn_7$ and $MoZn_{22}$. The X-ray powder pattern of the latter compound reported by Toussaint and Venker (8) corresponds to the phase for which our presently reported structure determination resulted in the composition $MoZn_{20.44}$. Some preliminary results of the work reported here have been presented at a conference (9).

SAMPLE PREPARATION AND LATTICE CONSTANTS

The samples were prepared by reaction of the elemental components under an argon atmosphere in sealed silica tubes of 5 mm inner diameter. Powders of niobium (Serva, 99.8%) and molybdenum (Ventron, >99.9%, 200 mesh), as well as zinc granules (Merck, 99.9%), were used. The samples were rapidly heated to high temperatures and slowly cooled as further described below. To enhance their homogeneity the samples were turned over and shaken in the furnace at least once every day.

We had been aiming at preparing crystals of the compounds reported (3) with the tentative compositions "$NbZn_7$" and "$NbZn_{15}$." For this purpose samples with 98 and 99 at% zinc were heated to 800°C and held at that temperature for 1 h. They were cooled to 500°C at a rate of 3°C/h and held at that temperature for 3 days. The sample with 98 at% zinc was then cooled to 440°C at a rate of 1°C/h, annealed at that temperature for 3 days, and then quenched. The zinc-rich matrix was dissolved in hydrochloric acid, which attacks the second phase at a slower rate. This phase was investigated in a scanning electron microscope, which revealed well-developed crystals. The energy dispersive X-ray fluorescence analyses resulted in the

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composition Nb:Zn = 1:2.9(±0.2). The Guinier X-ray powder diagram of this phase showed only the Cu_3Au-type pattern of $NbZn_3$.

The sample with 99 at% zinc was (after the annealing at 500°C) slowly cooled (1°C/h) to 420°C, annealed at that temperature for 10 days, and quenched in water. The zinc-rich matrix was again dissolved in hydrochloric acid, and the product was investigated in the scanning electron microscope, which revealed crystals of the composition Nb:Zn = 1:15.7(±0.3), up to 100 μm in size.

The crystals of $MoZn_{20.44}$ were prepared in an analogous way. The starting composition was in the atomic ratio Mo:Zn = 1:98. The sample was annealed at 850°C for 60 h, cooled to 650°C at a rate of 5°C/h, further cooled (2°C/h) to 420°C, and quenched in air. The sample was again treated in hydrochloric acid and the resulting crystals were identified by their Guinier powder diagrams.

The crystals of the three compounds are gray with metallic luster; the powders are black. They are stable in air for long periods of time but are slowly attacked by diluted hydrochloric acid. The energy dispersive X-ray fluorescence analyses of the three compounds in the scanning electron microscope did not reveal any impurity elements heavier than sodium.

The lattice constants (Table 1) were determined from least-squares fits of the Guinier powder data recorded with $CuK\alpha_1$ radiation using α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. To assure proper assignment of the indexes the observed patterns were compared with the ones calculated (10) assuming the positional parameters as eventually obtained from the structure determinations.

STRUCTURE DETERMINATION OF $MoZn_{20.44}$ AND STRUCTURE REFINEMENTS OF $NbZn_3$ AND $NbZn_{16}$

Single-crystal intensity data for $NbZn_3$, $NbZn_{16}$, and $MoZn_{20.44}$ were collected on an automated four-circle diffractometer (Enraf–Nonius, CAD-4) using graphite-monochromated $MoK\alpha$ radiation, a scintillation counter with pulse-height discrimination, and $\theta/2\theta$ scans with background counts at both sides of each scan. Empirical absorption corrections were carried out using psi scan data. Further details of the data collections are summarized in Table 1.

$NbZn_3$ had already been recognized as crystallizing with a Cu_3Au-type structure previously (5, 6). The orthorhombic lattice constants of $NbZn_{16}$ found on the single-crystal diffractometer turned out to be similar to those of $TiZn_{16}$ (1, 11), and the isotypy of the titanium and niobium compounds was eventually proved by the structure refinement of $NbZn_{16}$.

The structure determination of $MoZn_{20.44}$ was much more difficult. Direct methods did not result in atomic positions suitable for the structure determination. Thus, we proceeded by first estimating the cell content from the volume/atom (V/A) plot shown in Fig. 1. From this plot we estimated a V/A ratio of 15.2 ± 0.5 nm$^3 \times 10^3$. This resulted

TABLE 1
Crystal Data of $NbZn_3$, $NbZn_{16}$, and $MoZn_{20.44(2)}$

	$NbZn_3$	$NbZn_{16}$	$MoZn_{20.44}$
Space group	$Pm\bar{3}m$ (No 221)	$Cmcm$ (No 63)	$F\bar{4}3m$ (No 216)
Lattice constants (Guinier powder)			
a (pm)	393.3(1)	769.6(1)	1846.4(1)
b (pm)	—	1143.6(1)	—
c (pm)	—	1166.3(1)	—
V (nm^3)	0.06084	1.0265	6.2947
Formula mass	289.04	1138.9	1432.3
Formula units/cell, (Z)	1	4	18.28
Calculated density (g/cm^3)	7.88	7.35	6.91
Crystal dimensions (μm^3)	45 × 45 × 45	50 × 60 × 60	40 × 40 × 50
Highest/lowest transmission	1.30	1.61	2.21
$\theta/2\theta$ scans up to 2θ (°)	70	80	74
Range in h, k, l	±6, ±6, ±6	0–13, ±20, ±21	±31, ±31, 0–31
Total number of reflections	1044	6740	14451
Unique reflections	45	1800	1371
Internal residual, R_i	0.019	0.037	0.063
Reflections $F_0 > n\sigma(F_0)$:	45 ($n = 3$)	943 ($n = 3$)	768 ($n = 2$)
Number of variables	5	50	64
Conventional residual $R(F)$	0.010	0.021	0.059

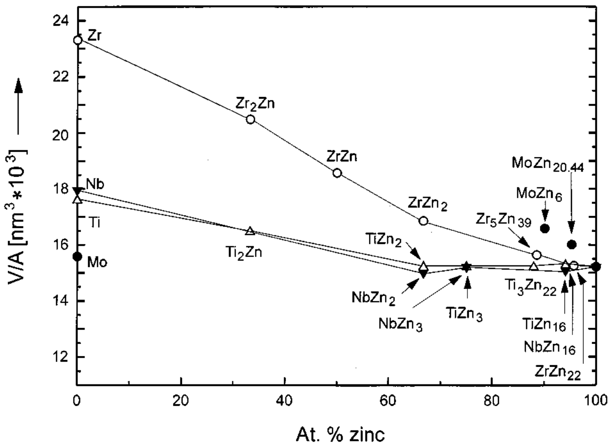

FIG. 1. Average atomic volumes in the binary systems titanium–zinc, zirconium–zinc, niobium–zinc, and molybdenum–zinc.

in a cell content between 400 and 428 atoms. The X-ray intensity data had indicated a face-centered lattice with cubic, high Laue symmetry and no further systematic extinctions. Hence, the space groups $F432$, $F\bar{4}3m$, and $Fm3m$ were possible. With this information we looked into Pearson's Handbook (12) and found the five structure types Mg_6Pd (13), $Fe_{22}Zn_{78}$ (14), $Mg_{44}Rh_7$ (15), Na_6Tl (16), and $Cu_{41}Sn_{11}$ (17) with between 396 and 416 atoms in a face-centered cubic cell of the space group $F\bar{4}3m$. As will be discussed further below, the first four of these are closely related structures. We proceeded by using the positional parameters of $Fe_{22}Zn_{78}$ as starting parameters for the structure determination. By placing zinc atoms at all 14 atomic positions of this structure, we already obtained a conventional residual of $R = 0.12$ in a full-matrix least-squares refinement. Small thermal parameters indicated which positions might be occupied by molybdenum atoms, and difference Fourier syntheses suggested additional atomic positions.

The final full-matrix least-squares refinements of the structures of $NbZn_3$ and $NbZn_{16}$ were carried out with the program MOLEN (18). For the refinement of the $MoZn_{20.44}$ structure we used the program SHELXL-93 (19). These programs also provided the atomic scattering factors and the weighting schemes, which accounted for the counting statistics. Factors which corrected for isotropic secondary extinction were fitted as least-squares parameters.

We refined occupancy parameters for the three structures to check for deviations from the ideal compositions. No significant deviations from the ideal occupancies were found for the structures of $NbZn_3$ and $NbZn_{16}$ (Table 2). Hence, in the final refinement cycles of these structures the ideal occupancy parameters were resumed. The position 4*c* of $MoZn_{20.44}$ turned out to have a scattering power greater than that of zinc and therefore a mixed Mo/Zn occupancy was refined. In contrast, the positions Zn6, Zn9, Zn11, and Zn15 showed occupancy values significantly smaller than 100%. Of these the positions Zn9 and Zn15 are interrelated; i.e., four Zn9 positions form a tetrahedron with the Zn15 at its center. The interatomic distances indicated that either the four Zn9 positions or the Zn15 position can be occupied, but not all five together. This was compatible with the occupancy parameters when both occupancies (that of the Zn9 positions as well as that of the Zn15 position) were refined simultaneously. For this reason these occupancy parameters were refined constrained. In the final refinement cycles the thermal parameters of the positions Mo2/Zn, Zn6, and Zn11 were fixed at reasonable values in order to reduce the standard deviations of the corresponding occupancy parameters. All other atomic positions were refined with the ideal occupancy parameters. The results are summarized in Tables 1, 2, and 3. The anisotropic thermal parameters and the structure factor tables are available (20).

DISCUSSION

$NbZn_3$ has already been reported to crystallize with the cubic Cu_3Au-type structure, and the lattice constant of $a = 393.4$ pm determined by Vold (5) is in excellent agreement with the one found presently ($a = 393.3$ pm). Our structure refinement for this compound resulted in occupancy parameters corresponding to a composition $Nb_{1.0034(15)}Zn_{2.9895(42)}$. If we assume the niobium position to be fully occupied with niobium atoms, we obtain the formula $NbZn_{2.979(7)}$. Thus, within three standard deviations our structure refinement corresponds to the ideal composition $NbZn_3$. On the other hand, a chemical analysis of a single-phase sample of this compound had resulted in the composition $NbZn_{2.968}$ (3). No error limits have been reported for this analysis. However, from our results we cannot rule out the possibility that this phase is slightly zinc deficient.

Meussner and Goode (3) reported two compounds with a zinc content higher than $NbZn_3$. Electron-microprobe analyses of the two phases resulted in compositions close to $NbZn_7$ and $NbZn_{15}$. Hence, the latter phase most likely corresponds to the one for which we find the composition $NbZn_{16}$ from our structure refinement. $NbZn_{16}$ is isotypic with the structure reported previously for the compound $TiZn_{16}$ (11). This structure has recently been refined from single-crystal X-ray data and it was pointed out that this structure contains relatively large voids, which are believed to be occupied by nonbonding electrons (1). This was further supported by a comparison of the structures of Zr_5Zn_{39} and Ce_5Mg_{41} (2). The coordination polyhedra of $NbZn_{16}$ are shown in Fig. 2.

TABLE 2
Atomic Parameters of $NbZn_3$, $NbZn_{16}$, and $MoZn_{20.44(2)}$

Atom	Site	Occup.	x	y	z	B_{eq}
$NbZn_3$ ($Pm\bar{3}m$)						
Nb	1*a*	1.0034(15)	0	0	0	0.238(2)
Zn	3*c*	0.9965(14)	0	$\frac{1}{2}$	$\frac{1}{2}$	0.479(4)
$NbZn_{16}$ ($Cmcm$)						
Nb	4*c*	1.006(2)	0	0.04803(5)	$\frac{1}{4}$	0.316(8)
Zn1	16*h*	1.002(1)	0.16808(6)	0.18677(4)	0.06950(4)	1.016(7)
Zn2	16*h*	0.998(1)	0.20370(7)	0.44792(4)	0.13402(4)	1.225(7)
Zn3	8*g*	0.998(2)	0.33619(9)	0.14394(6)	$\frac{1}{4}$	1.00(1)
Zn4	8*f*	0.997(2)	0	0.17564(5)	0.64080(5)	1.18(1)
Zn5	8*f*	0.999(2)	0	0.62026(6)	0.03172(5)	0.90(1)
Zn6	4*c*	1.011(3)	0	0.28941(8)	$\frac{1}{4}$	1.21(2)
Zn7	4*a*	0.990(3)	0	0	0	1.00(1)
$MoZn_{20.44(2)}$ ($F\bar{4}3m$)						
Mo1	16*e*	0.96(3)	0.6485(1)	0.6485	0.6485	0.50(5)
Mo2/Zn	4*c*	0.57(10)/0.43	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0.8*
Zn1	48*h*	1.03(3)	0.0475(1)	0.0475	0.6528(2)	1.30(5)
Zn2	48*h*	1.03(3)	0.0760(2)	0.0760	0.2649(2)	2.62(8)
Zn3	48*h*	1.04(3)	0.1049(1)	0.1049	0.7786(2)	1.45(6)
Zn4	48*h*	1.04(3)	0.1542(2)	0.1542	0.0234(2)	1.79(6)
Zn5	48*h*	1.05(3)	0.1910(1)	0.1910	0.5162(2)	1.35(6)
Zn6	24*g*	0.70(1)	0.0935(4)	$\frac{1}{4}$	$\frac{1}{4}$	1.8*
Zn7	24*g*	1.08(3)	0.6433(2)	$\frac{1}{4}$	$\frac{1}{4}$	1.02(6)
Zn8	24*f*	0.94(3)	0.1644(6)	0	0	2.7(1)
Zn9	16*e*	0.35(3)	0.0543(7)	0.0543	0.0543	2.1(5)
Zn10	16*e*	1.01(3)	0.1656(2)	0.1656	0.1656	1.58(9)
Zn11	16*e*	0.44(2)	0.3324(4)	0.3324	0.3324	1.8*
Zn12	16*e*	1.09(4)	0.4128(3)	0.4128	0.4128	1.3(1)
Zn13	16*e*	1.04(3)	0.9156(2)	0.9156	0.9156	0.64(7)
Zn14	4*b*	1.14(8)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1.7(2)
Zn15	4*a*	0.65	0	0	0	0.7(3)

Note. The third column contains the occupancy parameters obtained in previous least-squares cycles. In the final cycles these parameters were assumed to be ideal with the exception of the Zn6 and Zn11 positions of $MoZn_{20.44(2)}$. The Zn9 and Zn15 sites of this structure are too close to each other. Hence, only one of these sites can be occupied. For this reason their occupancy parameters were constrained. The last column contains the equivalent isotropic displacement parameters B_{eq} (10^4 pm^2). Those marked with an asterisk were held constant during the last refinement cycles. Standard deviations in the place values of the last listed digits are given in parentheses throughout the paper.

The compound for which our structure determination resulted in the composition $MoZn_{20.44}$ is certainly identical with the compound reported with the approximate composition $MoZn_{\sim 22}$ by Toussaint and Venker (8). Our X-ray powder diagram of $MoZn_{20.44}$ agrees very well with the diagram reported for $MoZn_{\sim 22}$, and the othorhombic lattice constants $a_0 = 651.0(2)$ pm, $b_0 = 1063.3(2)$ pm, $c_0 = 920.5(2)$ pm reported earlier are related to the cubic constant a_c found by us in the following way: $a_0 = a_c/(2\sqrt{2}) = 652.8$ pm, $b_0 = a_c/\sqrt{3} = 1066.0$ pm, $c_0 = a_c/2 = 923.2$ pm.

As already mentioned above, the structure determination of $MoZn_{20.44}$ was difficult. The content of the unit cell was at first estimated from a plot of the average atomic volume vs composition (Fig. 1). Generally, such plots are smooth and independent of the structures. The V/A ratio of $MoZn_{20.44}$ calculated eventually from the refined structure seems to be slightly too high. However, small deviations from the smooth functions are found occasionally. An even higher V/A ratio is obtained for the cubic face-centered structure recently reported for $MoZn_6$ (21), a compound which seems to be identical with the cubic phase of the tentative composition "$MoZn_7$", observed during the phase diagram study by Heumann *et al.* (7).

The atoms in the structure of $MoZn_{20.44}$ occupy 17 atomic sites. If these sites were fully occupied, the face-centered cell would contain 420 atoms, corresponding to the Pearson symbol *cF*420. However, not all of these sites can be fully occupied for steric reasons, as was discussed above

TABLE 3
Interatomic Distances in NbZn$_3$, NbZn$_{16}$, and MoZn$_{20.44}$

					NbZn$_3$						
Nb:	12Zn	278.1	Zn:	4Nb	278.1						
				8Zn	278.1						
					NbZn$_{16}$						
Nb:	1Zn6	276.0	Zn2:	1Nb	288.8	Zn4:	1Nb	285.7	Zn6:	1Nb	276.0
	2Zn3	281.0		1Zn5	260.8		1Zn4	254.7		4Zn1	273.6
	2Zn4	285.7		1Zn3	263.6		1Zn7	259.5		4Zn2	275.2
	4Zn2	288.8		1Zn4	268.4		1Zn5	265.8		2Zn3	307.6
	4Zn1	293.6		1Zn2	270.5		2Zn2	268.4		(2Zn5	344.4)
	2Zn7	296.7		1Zn6	275.2		2Zn3	273.3	Zn7:	2Nb	296.7
Zn1:	1Nb	293.6		1Zn5	278.7		2Zn1	277.6		2Zn4	259.5
	1Zn1	251.2		1Zn7	282.8		2Zn1	311.3		4Zn1	262.5
	1Zn3	251.9		1Zn1	299.7	Zn5:	2Zn2	260.8		4Zn2	282.8
	1Zn1	258.7		1Zn1	300.0		1Zn4	265.8			
	1Zn7	262.5		1Zn1	309.2		2Zn1	270.2			
	1Zn5	270.2		1Zn2	313.5		2Zn2	278.7			
	1Zn6	273.6		1Zn2	334.5		2Zn1	281.7			
	1Zn4	277.6	Zn3:	1Nb	281.0		1Zn5	284.8			
	1Zn5	281.7		2Zn1	251.9		2Zn3	285.4			
	1Zn2	299.7		1Zn3	252.1		(1Zn6	344.4)			
	1Zn2	300.0		2Zn2	263.6						
	1Zn2	309.2		2Zn4	273.3						
	1Zn4	311.3		2Zn5	285.4						
				1Zn6	307.6						
					MoZn$_{20.44}$						
Mo1:	3Zn1	263.8	Zn3:	1Zn13	258.6	Zn6:	2Zn5	254.4	Zn10:	3Zn6	257.5
	3Zn7	265.1		1Mo1	265.8		2Zn11	255.0		3Zn4	264.2
	3Zn3	265.8		1Zn1	276.2		2Zn10	257.5		1Mo2/Zn	269.9
	3Zn5	268.3		2Zn5	279.7		2Zn4	281.7		3Zn2	297.2
Mo2/Zn:	4Zn11	263.5		2Zn7	282.2		1Mo2/Zn	288.8		3Zn11	308.0
	4Zn10	269.9		2Zn4	282.4		4Zn2	324.0		(1Zn9	355.8)
	6Zn6	288.8		1Zn8	293.3	Zn7:	2Mo1	265.1	Zn11:	3Zn6	255.0
Zn1:	1Zn1	248.2		2Zn3	304.4		4Zn7	278.4		1Zn12	257.0
	1Mo1	263.8		(2Zn2	347.5)		2Zn5	280.7		1Mo2/Zn	263.5
	2Zn1	274.8	Zn4:	1Zn10	264.2		4Zn3	282.2		3Zn2	269.7
	1Zn3	276.2		1Zn9	266.8	Zn8:	2Zn9	247.8		3Zn10	308.0
	2Zn2	279.0		2Zn2	268.4		2Zn13	265.3		(3Zn5	344.8)
	2Zn5	280.2		1Zn13	269.7		2Zn2	271.6	Zn12:	1Zn11	257.0
	2Zn12	286.2		1Zn6	281.7		4Zn4	288.4		3Zn2	274.5
	1Zn14	308.2		2Zn3	282.4		2Zn3	293.3		1Zn14	278.9
	(1Zn8	359.6)		2Zn8	288.4		1Zn15	303.5		6Zn1	286.2
Zn2:	2Zn4	268.4		2Zn5	302.8		2Zn1	359.6		3Zn5	331.5
	1Zn11	269.7		(2Zn4	341.3)	Zn9:	(1Zn15	173.7)	Zn13:	3Zn3	258.6
	1Zn8	271.6	Zn5:	1Zn6	254.4		3Zn8	247.8		3Zn8	265.3
	1Zn12	274.5		1Mo1	268.3		3Zn4	266.8		3Zn9	267.8
	2Zn1	279.0		2Zn3	279.6		3Zn13	267.8		3Zn4	269.7
	2Zn5	284.0		2Zn1	280.2		3Zn9	283.6		1Zn15	269.8
	1Zn10	297.2		1Zn7	280.7		(1Zn10	355.8)	Zn14:	4Zn12	278.9
	2Zn6	324.0		2Zn2	284.0					12Zn1	308.2
	2Zn3	347.5		2Zn4	302.8				Zn15:	(4Zn9	173.7)
				1Zn5	307.9					4Zn13	269.8
				1Zn12	331.5					6Zn8	303.5
				1Zn11	344.8						

Note. All distances shorter than 385 pm (NbZn$_3$ and MoZn$_{20.44}$) and 350 pm (NbZn$_{16}$) are listed. All standard deviations are 0.1 pm or less in NbZn$_3$ and NbZn$_{16}$, and less than 0.3 pm in MoZn$_{20.44}$. Atoms with interatomic distances listed in parentheses are not shown in the drawings of the coordination polyhedra of Fig. 4.

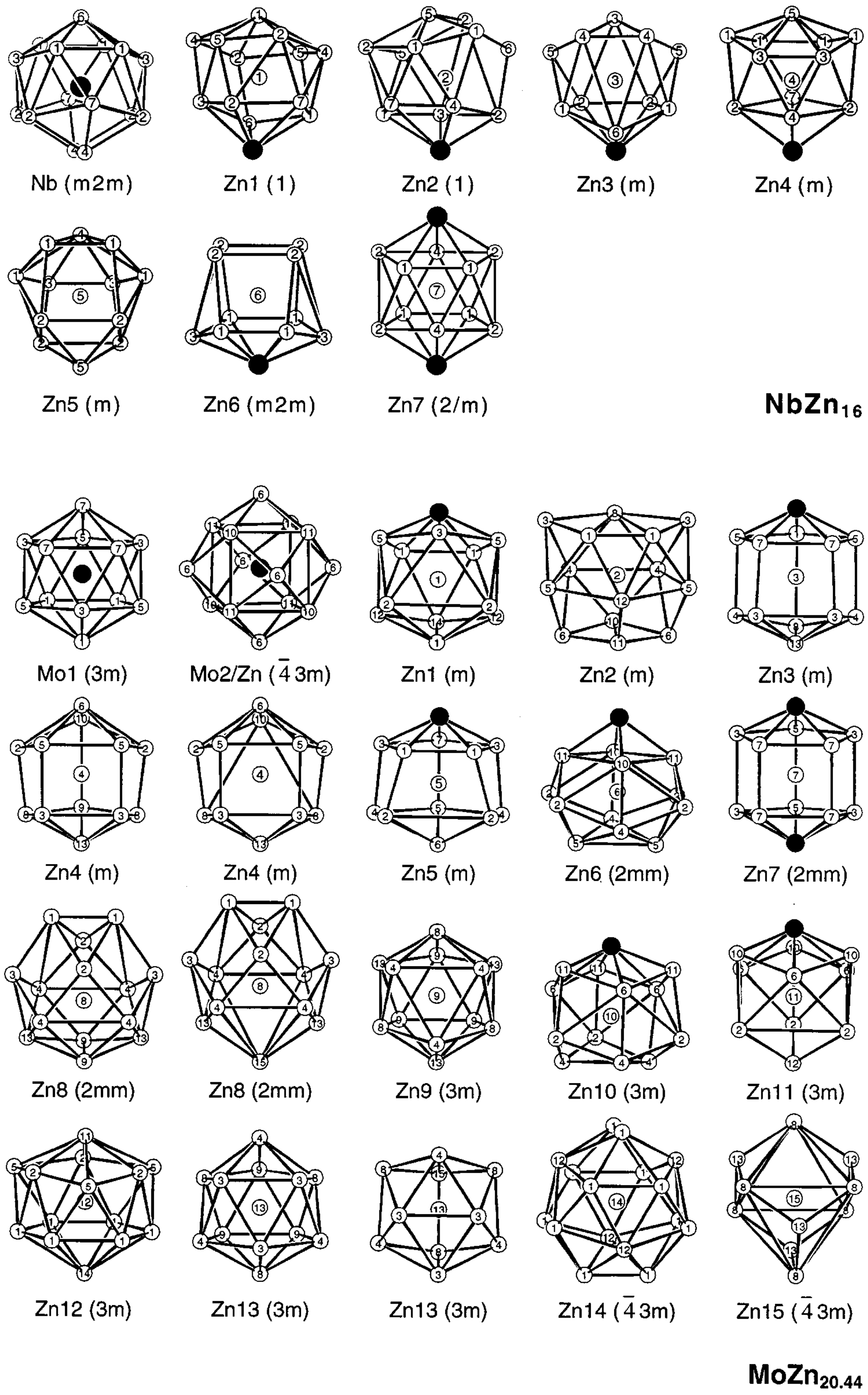

FIG. 2. Coordination polyhedra in the structures of $NbZn_{16}$ and $MoZn_{20.44}$. In the structure of $MoZn_{20.44}$ only the Zn15 site or the four neighboring Zn9 sites can be occupied. This results in two somewhat differing coordination polyhedra for the Zn4, Zn8, and Zn13 atoms. The site symmetries of the central atoms are indicated in parentheses.

for the Zn9 and Zn15 sites. Furthermore, the Zn6 and Zn11 sites show considerable deviations from the full occupancies with occupancy factors of 0.70(1) and 0.44(2), respectively. Considering all deviations from the ideal occupancy, the recommended (22) Pearson symbol for $MoZn_{20.44}$ is $cF420\text{-}27.96 \cong cF420\text{-}28$.

Apparently, it is favorable for the stability of $MoZn_{20.44}$ to leave some zinc sites partially unoccupied, since the crystals of this compound were isolated from a sample with excess zinc. We believe that these sites accommodate nonbonding electrons by using atomic functions of adjacent zinc atoms, somewhat similar to the well-known lone pairs of main group elements in their lower oxidation states. This has been discussed for $TiZn_{16}$ as already mentioned above (1, 2). Another striking example was found with Ni_3Sn_4, which has an ordered defect CoGe (Co_4Ge_4)-type structure (23).

Most of the molybdenum atoms are situated on site 16*e* with almost perfect icosahedral zinc coordination. The remaining molybdenum atoms occupy site 4*c*, which has a mixed Mo2/Zn occupancy of 0.57(10)/0.43. This site has the coordination number (CN) 14, where eight zinc atoms form a cube with six additional zinc atoms outside the cube faces (Fig. 2). This is the same coordination as is found in a simple cubic body-centered structure (W type). In the present case the coordination of the Mo2/Zn site is formed by 4 Zn11 (263.5 pm), 4 Zn10 (269.9 pm), and 6 Zn6 (288.8 pm) atoms. Since the Zn6 and Zn11 positions are not fully occupied, the real average coordination number of the Mo2/Zn site is lower: 0.44×4 Zn11 + 4 Zn10 + 0.70×6 Zn6 = 9.96 Zn. It seems possible that some neighboring zinc sites of the Mo2/Zn site are unoccupied when this site is occupied by zinc atoms, while it might have a complete coordination shell when the central atom is molybdenum.

The remaining zinc atoms of $MoZn_{20.44}$ occupy 15 atomic sites with coordination numbers varying between 10 and 16. The coordination polyhedron of the Zn7 atom contains two molybdenum atoms; the Zn1, Zn3, Zn5, Zn6, Zn10, and Zn11 atoms have one molybdenum neighbor; and the other zinc atoms have none. Since some of the zinc sites are not fully occupied, it is not very meaningful to calculate average distances. However, generally the average Zn–Zn distances reflect the different coordination numbers; e.g., the Zn15 atom has 10 zinc neighbors at an average Zn–Zn distance of 290.0 pm, while the Zn14 atom has 16 zinc neighbors with the considerably greater average Zn–Zn distance of 300.9 pm. As already mentioned above, neighboring Zn9 and Zn15 positions cannot both be occupied, since the Zn9–Zn15 distance is impossibly short (173.7 pm). When both positions were refined with variable occupancy parameters we obtained occupancy values of 33(3) and 62(5)%. Since these values add up to almost 100% we constrained their sum to 100% in the final refinement cycles. Interestingly, the Zn15 site (Wyckoff position 4*a*) is located in the center of a tetrahedron formed by Zn9 atoms (position 16*e*). Hence, either the four neighboring Zn9 positions are occupied (Zn9–Zn9 distance 283.0 pm) or the center of that tetrahedron contains a Zn15 atom.

In Table 4 we list the positional parameters of $MoZn_{20.44}$ together with those of the related compounds $Mg_{44}Rh_7$ (15), $Fe_{22}Zn_{78}$ (14), Na_6Tl (16), and Mg_6Pd (13), all of which

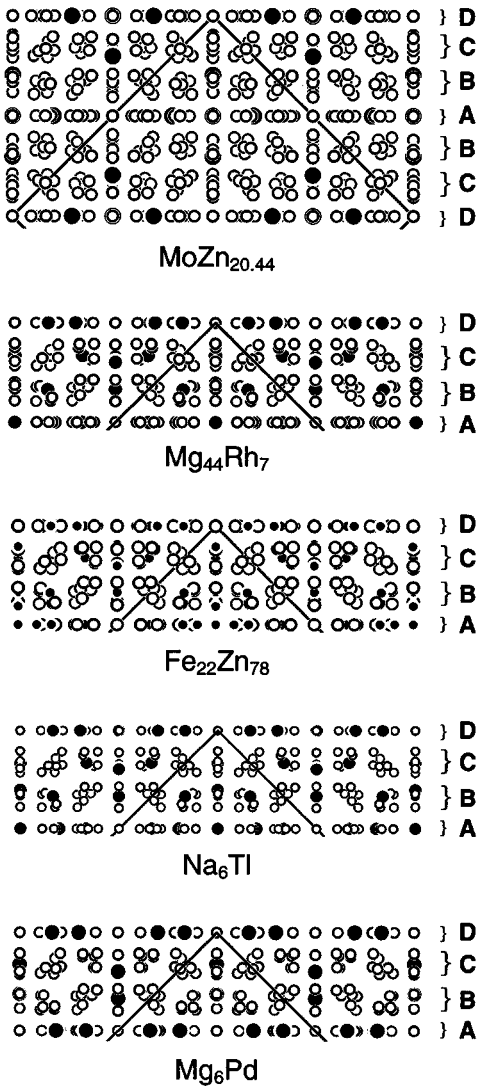

FIG. 3. Comparison of the five face-centered cubic crystal structures of $MoZn_{20.44}$, $Mg_{44}Rh_7$, $Fe_{22}Zn_{78}$, Na_6Tl, and Mg_6Pd. The structures are projected along the edges of the cubic cells. The origins of the cells as standardized with the program STRUCTURE TIDY (24) are indicated. For $MoZn_{20.44}$, only one-half of the cell is shown, and for the other structures, only one-quarter of the cell is shown. The structures may be considered to be stackings of four different atomic layers, of which **A** and **D** as well as **B** and **C** correspond to each other. These layers are shown in Fig. 4.

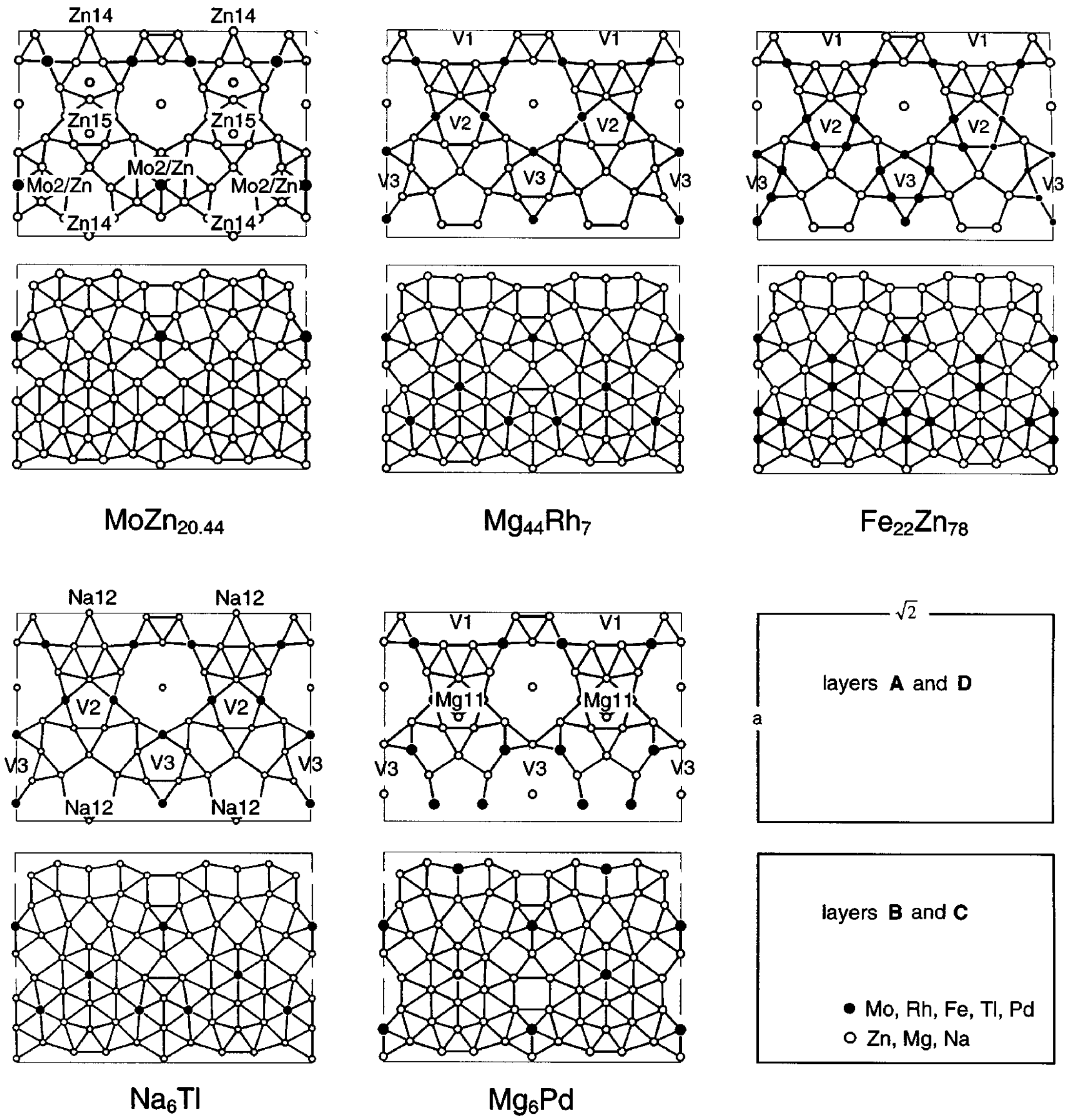

FIG. 4. The atomic layers **A** and **B** of Fig. 3 viewed along [1 1 0]. The positions Zn15, V2, and Mg11 correspond to the lattice points $\frac{1}{2}, 0, \frac{1}{2}$ and $0, \frac{1}{2}, \frac{1}{2}$ of the cubic face-centered lattice. The layers **D** of Fig. 3 are equal to the layers **A**, if the origin of the enframed cell is placed at the atomic positions Zn15, V2, and Mg11; the analogous shifts also transform the layers **B** to **C**. It can be seen that the five structures differ mainly in the layers **A** and **D**.

crystallize in the same cubic space group $F\bar{4}3m$. We have standardized the positional parameters of these structures with the program STRUCTURE TIDY (24) to facilitate comparisons. It can be seen that most of the positional parameters of the five structures are quite similar. The atoms in $MoZn_{20.44}$ occupy 17 different atomic sites, while the other structures have a smaller number of occupied sites. Vacant atomic sites are labeled V1, V2, and V3. In the structures of $Mg_{44}Rh_7$ and $Fe_{22}Zn_{78}$ the same atomic sites are occupied, but the atom distribution is different. The other structures differ in the atom distribution as well as in the number of different occupied atomic sites.

Because of their large unit cells, the structures are not easy to visualize. In Fig. 3 we show projections of the five structures along one of the cubic cell edges. At the top of Fig. 3 — representing the structure of $MoZn_{20.44}$ — two full translation periods of the other two directions are outlined. In this projection atoms hidden behind others are not indicated. Four different atomic layers can be discerned; they are labeled A, B, C, and D. If the origin of the cell is allowed to move, the layers A can be transformed to the layers D, and B to C. Thus, only two layers are needed to compare the five related structures (Fig. 4). The correspondence of the occupied sites is striking.

TABLE 4
Comparison of the Atomic Parameters ($\times 10^2$) of $MoZn_{20.44}$, $Mg_{44}Rh_7$, $Fe_{22}Zn_{78}$, Na_6Tl, and Mg_6Pd

		$Mo_{18.3}Zn_{373.7}$ $Mo_{4.66}Zn_{95.34}$ $\mathbf{MoZn_{20.44}}$				$Mg_{352}Rh_{56}$ $Mg_{86.3}Rh_{13.7}$ $Mg_{6.30}Rh$ $\mathbf{Mg_{44}Rh_7}$			$Fe_{90}Zn_{318}$ $\mathbf{Fe_{22}Zn_{78}}$ $FeZn_{3.55}$			$Na_{352}Tl_{56}$ $Na_{86.3}Tl_{13.7}$ $Na_{6.30}Tl$ $\mathbf{Na_6Tl}$			$Mg_{340}Pd_{56}$ $Mg_{85.9}Pd_{14.1}$ $Mg_{6.07}Pd$ $\mathbf{Mg_6Pd}$		
$F\bar{4}3m$				*x*	*z*		*x*	*z*		*x*	*z*		*x*	*z*		*x*	*z*
48*h*	(*x x z*)	Zn1	1	05	65	Mg1	05	66	Zn1	05	66	Na1	05	66	Mg1	05	66
48*h*	(*x x z*)	Zn2	1	08	27	Mg2	10	28	Zn2	10	29	Na2	10	28	Mg2	10	28
48*h*	(*x x z*)	Zn3	1	10	78	Mg3	11	79	Zn3	11	78	Na3	11	78	Mg3	11	78
48*h*	(*x x z*)	Zn4	1	15	02	Mg4	16	02	Zn4	16	02	Na4	16	02	Mg4	16	02
48*h*	(*x x z*)	Zn5	1	19	52	Mg5	20	52	Zn5	19	52	Na5	19	52	Mg5	19	52
24*g*	($x\frac{1}{4}\frac{1}{4}$)	Zn6	(0.7)	09		Rh1	09		Fe1	09		Tl1	09		Mg6	13	
24*g*	($x\frac{1}{4}\frac{1}{4}$)	Zn7	1	64		Mg6	64		Zn6	64		Na6	64		Mg7	64	
24*f*	(*x* 0 0)	Zn8	1	16		Mg7	18		Zn7	19		Na7	18		Mg8	19	
16*e*	(*x x x*)	Zn9	(0.4)	05		Mg8	05		Fe2	05		Na8	05		Mg9	05	
16*e*	(*x x x*)	Zn10	1	17		Mg9	17		Fe3	17		Na9	17		Pd1	16	
16*e*	(*x x x*)	Zn11	(0.5)	33		Mg10	30		Fe4	30		Na10	31		—		
16*e*	(*x x x*)	Zn12	1	41		Mg11	44		Zn8	44		Na11	42		Pd2	42	
16*e*	(*x x x*)	Mo1	1	65		Rh2	65		Fe5	65		Tl2	65		Pd3	65	
16*e*	(*x x x*)	Zn13	1	92		Rh3	92		Fe6	92		Tl3	92		Mg10/Pd (0.5/0.5)	92	
4*c*	($\frac{1}{4}\frac{1}{4}\frac{1}{4}$)	Mo2/Zn	(0.6/0.4)			V3			V3			V3			V3		
4*b*	($\frac{1}{2}\frac{1}{2}\frac{1}{2}$)	Zn14	1			V1			V1			Na12($<$0.2)			V1		
4*a*	(0 0 0)	Zn15	(0.6)			V2			V2			V2			Mg11		

Note. Several formulas are listed in the first rows of the table. The first formula ($Mo_{18.3}Zn_{373.7}$) corresponds to the cell content, the second formula ($Mo_{4.66}Zn_{95.34}$) lists the composition as a percentage, and the third ($MoZn_{20.44}$) gives the composition with the minority component set to unity. The most frequently used formula of the literature is printed bold face. The positional parameters were standardized with the program STRUCTURE TIDY (24); they are listed in hundredths. Some atomic sites were found with partial occupancy or with mixed occupancy; these values (full occupancy ≡ 1) are listed in parentheses after the atom designations. Nonoccupied (void) positions, shown in Fig. 3, are designated as V1, V2, and V3.

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