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TRANSFORMATIONS IN AB_2 INTERMETALLIC COMPOUNDS

Final Report

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TRANSFORMATIONS IN AB_2 INTERMETALLIC COMPOUNDSAbstract

The crystal structures, crystal chemistry, thermal expansion, and magnetic and mechanical properties of intermetallic compounds which exhibit the KHg_2 -type structure were studied in this program.

Structural data are presented for a number of $REZn_2$ compounds which are very similar to those for other KHg_2 -type compounds. From these, it appears that, while the overall configuration is a result of directional bonding, there is sufficient isotropy in the bonding to allow for atom shifts in the various compounds. The atom positions can be reasonably predicted on the basis of hard sphere packing. The coordination number of the A atoms was found to be 16. The KHg_2 -type structure is closely related to the AlB_2 -, $CaIn_2$ -, and the CdI_2 -type structures in that all contain hexagonal B-atom nets in some form.

The thermal expansion of $HoZn_2$ and $YbZn_2$ were studied and qualitatively interpreted in terms of the structural configuration of the atoms. In the case of $YbZn_2$, crystallographic evidence for a phase change over the range 300° - $600^\circ C$ was found. It appears that the high temperature phase is isostructural with $NdAu_2$, whose structure is yet unknown, although closely related to the $MoSi_2$ -type structure. This structure change may be related to a valence change.

Magnetic susceptibility measurements of $REZn_2$ compounds showed that the rare earth atoms exhibit a +3 valence, except in $CeZn_2$, $EuZn_2$, and $YbZn_2$, where +3 and +2 valences are mixed and temperature dependent.

Mechanical property data are presented for $HoZn_2$. It is a typical brittle material which exhibits a small amount of plastic deformation by twinning.

Crystal structure data are presented for the following related compounds:

YbCuZn, YZn₃, DyZn₃, HoZn₃, ErZn₃, Y₃Zn₁₁, Y₂Zn₉, Er₂Zn₉, YZn₆, and ErZn₆₋₇.

TRANSFORMATIONS IN AB_2 INTERMETALLIC COMPOUNDSIntroduction

As part of a program at Penn State to investigate the crystal structures and properties of intermetallic compounds, a study of AB_2 intermetallic compounds exhibiting the KHg_2 -type crystal structure was initiated. This study had as its objectives the determination of the occurrence of this type of compounds, the determination of their magnetic properties, and an investigation of the relationship of the KHg_2 -type crystal structure to other types of AB_2 structures through a characterization of a phase transformation which was thought to occur in some of the KHg_2 -type compounds. It was hoped that the information generated would illuminate some of the general principles involved in the formation of various types of compounds and in the chemical bonding between the component atoms.

At the beginning of this study, only a few compounds were known to exhibit this type of crystal structure. These were KHg_2 , $CeCu_2$, YCu_2 , and $CaZn_2$. It was possible that many more compounds of this type existed, particularly between group IIA and IIIB metals with group IB and IIB metals. Furthermore, evidence existed for an unusual martensitic phase transformation in YZn_2 , which was suspected to exhibit the KHg_2 -type structure, although this transformation was not well-characterized. If the crystal structure of the low and high temperature forms of this compound could be determined, then the relationship between the KHg_2 -type structure and another structure type would be known.

ResultsCrystal Structure Studies

A large number of AB_2 intermetallic compounds were prepared and found to exhibit the KHg_2 -type structure. The lattice parameters for these

orthorhombic compounds, determined from analyses of Debye-Scherrer x-ray diffraction patterns, are reported in Table I. The balance of the data therein are the results of other independent investigators, and the list represents all of the KHg_2 -type compounds known at the present time. It is unlikely that any more binary intermetallic compounds with this structure exist. It can be seen that, in fact, the occurrence of these compounds is limited to combinations of group IIA and IIIB metals with group IB, IIB, and some IIIA metals. The ternary compounds are an exception. However, if one postulates a transfer of one electron/atom from gallium to nickel, then these compounds, in essence, also fit the limits of occurrence stated above.

A number of these compounds were studied by single crystal x-ray diffraction techniques in order to determine the positions of the atoms within the crystallographic unit cell. The results are given in Table II, along with the results of other independent investigators. It can be seen that many KHg_2 -type compounds remain which have not been so-characterized. However, there are sufficient data to indicate that the positional parameters for the atoms are nearly the same for all the compounds. The variations appear to be adjustments for changes in the sizes of the different component atoms.

Several ideas concerning the crystal chemistry of the KHg_2 -type structure can be drawn from these data. First, while the overall configuration of the KHg_2 -type structure is certainly a result of directional characteristics of the bonding, there must be sufficient isotropic character to this bonding to allow for shifts in the positions of the atoms from compound to compound. That is, space-filling is also a main factor in the formation of the KHg_2 -type structure. If the view is adopted that this structure type is layer-like, in which a basic layer of both A and B atoms, parallel to the b and c crystallographic axes (see Figure 1), is repeated in a direction perpendicular

TABLE I

Crystallographic Data for KHg_2 -type
Intermetallic Compounds

Compound	a (Å)	b (Å)	c (Å)	Reference
YZn_2	$\begin{cases} 4.504 \pm 3 \\ 4.465 \end{cases}$	$\begin{cases} 7.143 \pm 7 \\ 7.110 \end{cases}$	$\begin{cases} 7.664 \pm 6 \\ 7.629 \end{cases}$	Sree Harsha (1964) Veleckis et al. (1967)
LaZn_2	$\begin{cases} 4.67 \\ 4.689 \\ 4.698 \end{cases}$	$\begin{cases} 7.61 \\ 7.638 \\ 7.743 \end{cases}$	$\begin{cases} 7.55 \\ 7.593 \\ 7.749 \end{cases}$	Veleckis et al. (1967) Fornasini and Merlo (1967) Kejriwal, Sree Harsha and Ryba (1964)
CeZn_2	$\begin{cases} 4.633 \pm 5 \\ 4.63 \pm 1 \\ 4.64 \\ 4.639 \pm 1 \\ 4.619 \end{cases}$	$\begin{cases} 7.538 \pm 5 \\ 7.54 \pm 1 \\ 7.53 \\ 7.552 \pm 1 \\ 7.474 \end{cases}$	$\begin{cases} 7.499 \pm 5 \\ 7.50 \pm 1 \\ 7.50 \\ 7.510 \pm 1 \\ 7.533 \end{cases}$	Chiotti and Mason (1965) Lott and Chiotti (1966) Veleckis et al. (1967) DebRay, et al. (1972) Fornasini and Merlo (1967)
PrZn_2	$\begin{cases} 4.61 \\ 4.602 \end{cases}$	$\begin{cases} 7.46 \\ 7.489 \end{cases}$	$\begin{cases} 7.52 \\ 7.450 \end{cases}$	Veleckis et al. (1967) Kejriwal, Sree Harsha and Ryba (1964)
NdZn_2	$\begin{cases} 4.599 \\ 4.58 \\ 4.585 \pm 4 \end{cases}$	$\begin{cases} 7.409 \\ 7.39 \\ 7.404 \pm 4 \end{cases}$	$\begin{cases} 7.566 \\ 7.56 \\ 7.561 \pm 4 \end{cases}$	Fornasini and Merlo (1967) Veleckis et al. (1967) Ryba (1967)
SmZn_2	4.552	7.299	7.590	Fornasini and Merlo (1967)
EuZn_2	4.728	7.650	7.655	Iandelli and Palenzona (1964)
GdZn_2	$\begin{cases} 4.513 \\ 4.487 \pm 3 \end{cases}$	$\begin{cases} 7.214 \\ 7.132 \pm 5 \end{cases}$	$\begin{cases} 7.606 \\ 7.616 \pm 5 \end{cases}$	Fornasini and Merlo (1967) Ryba (1967)
TbZn_2	$\begin{cases} 4.492 \\ 4.502 \pm 3 \\ 4.481 \pm 3 \\ 4.477 \end{cases}$	$\begin{cases} 7.142 \\ 7.133 \pm 5 \\ 7.122 \pm 3 \\ 7.090 \end{cases}$	$\begin{cases} 7.595 \\ 7.624 \pm 5 \\ 7.576 \pm 5 \\ 7.600 \end{cases}$	Fornasini and Merlo (1967) Ryba (1967) DebRay (1972) Fornasini and Merlo (1967)
DyZn_2	4.631 $\pm$ 5	7.103 $\pm$ 7	7.627 $\pm$ 11	Kejriwal, Sree Harsha and Ryba (1964)
HoZn_2	$\begin{cases} 4.456 \pm 1 \\ 4.460 \end{cases}$	$\begin{cases} 7.039 \pm 3 \\ 7.042 \end{cases}$	$\begin{cases} 7.641 \pm 5 \\ 7.612 \end{cases}$	Michel and Ryba (1966a) Fornasini and Merlo (1967)
ErZn_2	4.448	6.984	7.610	Fornasini and Merlo (1967)
TmZn_2	$\begin{cases} 4.433 \pm 2 \\ 4.433 \end{cases}$	$\begin{cases} 6.949 \pm 4 \\ 6.944 \end{cases}$	$\begin{cases} 7.597 \pm 4 \\ 7.604 \end{cases}$	Michel and Ryba (1966b) Fornasini and Merlo (1967)

TABLE I

(continued)

Compound	a (Å)	b (Å)	c (Å)	Reference
YbZn ₂	$\begin{cases} 4.573 \pm 2 \\ 4.570 \pm 1 \end{cases}$	$\begin{cases} 7.325 \pm 5 \\ 7.290 \pm 1 \end{cases}$	$\begin{cases} 7.569 \pm 4 \\ 7.562 \pm 1 \end{cases}$	Michel and Ryba (1965) Mason and Chiotti (1968)
LuZn ₂	4.416	6.886	7.600	Fornasini and Merlo (1967)
CaZn ₂	4.591 $\pm$ 2	7.337 $\pm$ 7	6.667 $\pm$ 4	Schulze and Wieting (1961)
SrZn ₂	4.779 $\pm$ 2	7.795	7.820 $\pm$ 1	Bergman and Schlichta (1964)
CaAg ₂	4.68	7.26	8.14	Calvert (1965)
SrAg ₂	4.83	7.73	8.27	Calvert (1965)
ThAg ₂	7.840	6.680	8.400	Calvert (1965)
EuAg ₂	4.753	7.488	8.164	Köster and Meixner (1965)
SrAg ₂	4.817	7.710	8.263	Köster and Meixner (1965)
BaAg ₂	4.958	8.063	8.453	Köster and Meixner (1965)
EuCd ₂	5.053	7.920	8.447	Köster and Meixner (1965)
SrCd ₂	5.046	8.008	8.451	Köster and Meixner (1965)
LaIn ₂	4.759	7.695	9.092	McMasters and Gschneidner (1974)
ThZn ₂	$\begin{cases} * 4.518 \pm 6 \\ * 4.20 \\ * 4.497 \pm 2 \end{cases}$	$\begin{cases} 7.356 \pm 8 \end{cases}$	$\begin{cases} 7.707 \pm 12 \\ 4.17 \\ 7.718 \pm 2 \end{cases}$	Ryba and Kejriwal (1963) Makarov and Gudkov (1956) Brown (1961)
YCu ₂	$\begin{cases} 4.305 \pm 5 \\ 4.308 \pm 3 \end{cases}$	$\begin{cases} 6.800 \pm 5 \\ 6.891 \pm 8 \end{cases}$	$\begin{cases} 6.315 \pm 5 \\ 7.303 \pm 7 \end{cases}$	Storm and Benson (1963) Kejriwal and Ryba (1963)
LaCu ₂ *	$\begin{cases} 4.340 \\ 4.346 \pm 5 \end{cases}$		$\begin{cases} 3.818 \\ 3.807 \pm 5 \end{cases}$	Iandelli and Palenzona (1968) Storm and Benson (1963)
CeCu ₂	$\begin{cases} 4.43 \pm 1 \\ 4.425 \pm 5 \end{cases}$	$\begin{cases} 7.05 \pm 2 \\ 7.057 \pm 5 \end{cases}$	$\begin{cases} 7.45 \pm 2 \\ 7.475 \pm 5 \end{cases}$	Larson and Cromer (1961) Storm and Benson (1963)
PrCu ₂	4.400 $\pm$ 5	7.024 $\pm$ 5	7.435 $\pm$ 5	Storm and Benson (1963)
NdCu ₂	4.387 $\pm$ 5	7.000 $\pm$ 5	7.420 $\pm$ 5	Storm and Benson (1963)

* AlB₂(C32) type structure (hexagonal)

TABLE I

(continued)

Compound	a (Å)	b (Å)	c (Å)	Reference
SmCu ₂	4.360±5	6.925±5	7.375±5	Storm and Benson (1963)
EuCu ₂	$\begin{cases} 4.434 \\ 4.45 \pm 1 \end{cases}$	$\begin{cases} 7.250 \\ 7.25 \pm 1 \end{cases}$	$\begin{cases} 7.553 \\ 7.54 \pm 1 \end{cases}$	$\begin{cases} \text{Iandelli and Palenzona (1968)} \\ \text{Storm and Benson (1963)} \end{cases}$
GdCu ₂	4.320±5	6.858±5	7.330±5	Storm and Benson (1963)
TbCu ₂	4.310±5	6.825±5	7.320±5	Storm and Benson (1963)
DyCu ₂	4.300±5	6.792±5	7.300±5	Storm and Benson (1963)
HoCu ₂	4.280±5	6.759±5	7.290±5	Storm and Benson (1963)
ErCu ₂	4.275±5	6.726±5	7.265±5	Storm and Benson (1963)
TmCu ₂	4.266±5	6.695±5	7.247±5	Storm and Benson (1963)
YbCu ₂	$\begin{cases} 4.286 \\ 4.28 \pm 1 \end{cases}$	$\begin{cases} 6.894 \\ 6.76 \pm 1 \end{cases}$	$\begin{cases} 7.382 \\ 7.40 \pm 1 \end{cases}$	$\begin{cases} \text{Iandelli and Palenzona (1968)} \\ \text{Storm and Benson (1963)} \end{cases}$
LuCu ₂	4.245±5	6.627±5	7.220±5	Storm and Benson (1963)
KHg ₂	5.16	8.10	8.77	Duwell and Baenziger (1955)
YNiGa	4.296	6.901	7.319	Dwight (1967)
SmNiGa	4.347	6.972	7.413	Dwight (1967)
GdNiGa	4.322	6.931	7.367	Dwight (1967)
TbNiGa	4.302	6.884	7.347	Dwight (1967)
DyNiGa	4.284	6.850	7.343	Dwight (1967)
HoNiGa	4.279	6.829	7.329	Dwight (1967)
ErNiGa	4.262	6.789	7.315	Dwight (1967)
TmNiGa	4.247	6.750	7.305	Dwight (1967)
YbNiGa	4.25	6.76	7.33	Dwight (1967)
LuNiGa	4.216	6.678	7.290	Dwight (1967)

TABLE II

Atom Positions in KHg_2 -type CompoundsA atoms in 4(e): $0, 1/4, z_A$; etc.B atoms in 8(h): $0, y_B, z_B$; etc.

Compound	z_A	y_B	z_B	Reference
YZn_2	0.537 ± 3	0.047 ± 1	0.166 ± 3	Sree Harsha (1964)
LaZn_2	0.542	0.056	0.165	Sree Harsha (1964)
CeZn_2	0.536 ± 7	0.058 ± 5	0.160 ± 5	Debray, Sougi & Meriel (1972)
SmZn_2	0.532	0.054	0.166	Fornasini & Merlo (1967)
EuZn_2	0.552	0.059	0.165	Iandelli & Palenzona (1964)
TbZn_2	$\begin{cases} 0.541 \pm 3 \\ 0.530 \end{cases}$	$\begin{cases} 0.043 \pm 3 \\ 0.044 \end{cases}$	$\begin{cases} 0.154 \pm 3 \\ 0.166 \end{cases}$	$\begin{cases} \text{Debray, Sougi \& Meriel (1972)} \\ \text{Fornasini \& Merlo (1967)} \end{cases}$
HoZn_2	0.5281 ± 4	0.0410 ± 9	0.1663 ± 8	Michel and Ryba (1966)
TmZn_2	0.5061 ± 7	0.0386 ± 9	0.1672 ± 9	Michel (1966)
YbZn_2	0.5503 ± 5	0.0587 ± 9	0.1641 ± 9	Michel and Ryba (1965)
CaZn_2	0.553 ± 2	0.057 ± 1	0.165 ± 2	Wieting (1961)
SrZn_2	0.552	0.061	0.165	Bergman & Schlichta (1964)
CaAg_2	0.55	0.06	0.16	Calvert (1965)
SrAg_2	$\begin{cases} 0.55 \\ 0.545 \end{cases}$	$\begin{cases} 0.05 \\ 0.051 \end{cases}$	$\begin{cases} 0.16 \\ 0.164 \end{cases}$	$\begin{cases} \text{Köster \& Meixner (1965)} \\ \text{Calvert (1965)} \end{cases}$
BaAg_2	0.56	0.05	0.17	Köster & Meixner (1965)
EuAg_2	0.54	0.06	0.17	Köster & Meixner (1965)
EuCd_2	0.05	0.56	0.33	Köster & Meixner (1965)
SrCd_2	0.55	0.055	0.165	Köster & Meixner (1965)
YCu_2	0.546 ± 2	0.052 ± 2	0.162 ± 2	Kejriwal & Ryba (1963)
CeCu_2	0.5377 ± 6	0.0510 ± 11	0.1648 ± 10	Larson & Cromer (1961)
KHg_2	0.547 ± 6	0.60 ± 3	0.173 ± 3	Duwell & Baenziger (1955)

Figure 1. (100) Layers in HoZn_2 and YbZn_2 . All circles represent C.N. 12 radii.

to that layer, then it is possible to nearly predict the atom positions in the following way. Consider the A and B atoms to be hard spheres in contact in the layer. The A atoms form parallel zig-zag chains within the layer, which has an angle β that is a function of the relative sizes of the A and B atoms. This relationship, expressed as the variation of the parameter $\sin \beta/2$ versus the Goldschmidt CN12 radius ratio r_A/r_B , is shown in Figure 2, along with the points derived from the actual atom positions for the compounds for which structural data are known. It can be seen that, in general, the experimental results confirm this relationship.

From the crystallographic data, it is, of course, possible to determine the coordination number of the A atom in the KHg_2 -type structure. Because of the somewhat complex nature of the structure, however, the coordination number has to be defined rather strictly. The criterion of Frank and Kasper (1958) was used. Here, the domain of an atom is defined as the smallest polyhedron formed around it by the perpendicular bisecting planes of the connections of that atom to all its surrounding atoms. The planes forming this smallest polyhedron denote, then, which atoms are directly coordinated to the central atom. The A atom domains were found for TmZn_2 , HoZn_2 , and YbZn_2 and are shown in Figure 3. Only one-fourth of each domain is shown, since the A atoms are located at the intersection of two perpendicular mirrors. In Figure 4, are shown the resulting coordination polyhedra for the rare earth atoms for these three compounds. It can be seen that they are essentially the same, and that the coordination number is 16 (4RE + 12Zn). The coordination polyhedra contain some 4- and 5-sided faces, and therefore do not fit the geometrical classification scheme of Frank and Kasper which is based on triangulated coordination shells.

The KHg_2 -type structure appears to be closely related to several other

VARIATION OF A-ATOM CHAIN ANGLE WITH RELATIVE ATOM SIZES

Figure 2.

Fig 2

Figure 3. DOMAINS OF Tm, Ho, AND Yb ATOMS

Figure 4. COORDINATION POLYHEDRA OF Tm, Ho, AND Yb ATOMS

AB_2 compound structure types. These are: the AlB_2 -type, exhibited by all $REGa_2$ compounds except $YbGa_2$ and $EuGa_2$; the CdI_2 -type, exhibited by all $RECd_2$ and $REHg_2$ compounds; and the $CaIn_2$ -type exhibited by $YbGa_2$, $EuGa_2$, $YbIn_2$, and $EuZn_2$. The relationship is shown in the configuration of hexagonal B-atom nets in these structures, as shown in Figure 5. In each there is a deviation from planarity of the B-atom nets (except for AlB_2 , Figure 5c). In the CdI_2 -type and $CaIn_2$ -type structures, the B atoms are positioned three up and three down in antiprism form. In the KHg_2 -type structure, the B atoms in the nets are in chair form. This strongly suggests that the directionality of the bonding between the B atoms controls the structure type, except when the A atoms have a larger size, as in some europium and ytterbium compounds. But the existence of hexagonal B-atom nets in some form is a key feature of all of these structure types.

Phase Transformations in KHg_2 -type Compounds

There are a number of experimental observations which indicate that these compounds may undergo a phase transformation at elevated temperatures. Extensive twinning is observed in the compounds. Upon cooling there is considerable sonic activity. Thermal arrests and resistivity changes have been observed in the following compounds and their neighboring alloys: YZn_2 (Chiotti, Mason & Gill, 1963), $SmZn_2$ (Chiotti & Mason, 1967), and $YbZn_2$ (Mason & Chiotti, 1968).

In this program, efforts were made to detect and elucidate this phase transformation, with the objective of determining the crystal structure of the high temperature form. Thermal analyses were performed on all the $REZn_2$ compounds, with the results shown in Figure 6. The secondary arrests shown therein, all very weak, were eventually found to correspond to eutectic

Figure 5.

- A. The CdI_2 -type structure.
- B. The CaIn_2 -type structure.
- C. The AlB_2 -type structure.
- D. The KHg_2 -type structure.

a

b

c

Figure 6. Melting points of REZn_2 intermetallic compounds.

reactions in these alloys, and not to any phase transformation. Since the thermal studies produced no information on the phase transformations, high temperature powder x-ray diffraction studies were carried out on HoZn_2 and YbZn_2 . In order to accomplish this, a special encapsulating procedure was developed (Michel & Ryba, 1967) to prevent oxidation of the powdered samples.

For HoZn_2 no phase transformation could be detected in the x-ray diffraction studies. The high temperature patterns showed no change in crystal structure at temperatures up to 800°C . The thermal expansion of this compound, as shown in Figure 7, is nearly linear over this temperature range. The expansion coefficients are: $\alpha_a = 1.66 \cdot 10^{-5}/^\circ\text{C}$, $\alpha_b = 1.59 \cdot 10^{-5}/^\circ\text{C}$, and $\alpha_c = 2.10 \cdot 10^{-5}/^\circ\text{C}$.

In the case of YbZn_2 , however, abnormal behavior was observed. Beginning at about 300°C , additional x-ray reflections appeared in the pattern whose intensities increased as the temperature was raised to 650°C . These additional reflections persisted even when the samples were cooled to room temperature. In addition, abnormal changes with temperature in the intensities of a number of x-ray reflections were observed, as shown in Figure 8. This behavior was considered to be due to a phase transformation.

The expansion coefficients for YbZn_2 were calculated from the data up to 300°C . The results are: $\alpha_a = 1.56 \cdot 10^{-5}/^\circ\text{C}$, $\alpha_b = 1.90 \cdot 10^{-5}/^\circ\text{C}$, and $\alpha_c = 2.78 \cdot 10^{-5}/^\circ\text{C}$. Upon noting that the thermal expansion of both HoZn_2 and YbZn_2 along the a and b directions is nearly the same and the expansion along the c direction is much larger, it was necessary to adopt a new view of the KHg_2 -type structure. The KHg_2 -type structure was considered to be layer-like with layers as shown in Figure 1. In these layers, the parallel zig-zag chains of A atoms running along the b direction are separated by double rows of zinc atoms. However, the nearly isotropic expansion around the c direction indicates that the atom connections along the a and b directions

Figure 7. Lattice parameters versus temperature for HoZn_2 .
Shading denotes limits of error.

Figure 8. Relative integrated intensity of the (022), (103) and (112) YbZn₂ reflections versus temperature.

must be quite similar. Upon further consideration of the structure, parallel zig-zag A atom chains were also found running along the a direction, and these two sets of chains form puckered A atom nets, shown in Figure 9, parallel to the a-b plane. These A atom nets are separated by puckered double layers of Zn atoms. The distances between the A atoms are $4.060\text{\AA}$ and $3.546\text{\AA}$, respectively, for the chains running along the a and b directions in HoZn_2 , and $3.790\text{\AA}$ and $3.741\text{\AA}$ in YbZn_2 . These are close enough in both cases to be considered nearest neighbors. The thermal expansion data, then, suggest that the A-A bonding is stronger than the bonding between zinc atoms in adjacent layers, so that most of the expansion occurs through the lengthening of the bonds between the zinc atoms in the puckered double layers between the A atom nets, perpendicular to the c direction.

If it is assumed that the lengthening of these zinc-zinc bonds is responsible for the major portion of the thermal expansion, then it is possible to explain the relative magnitudes of the expansion coefficients for both HoZn_2 and YbZn_2 . In Figure 1, note that the zinc-zinc bond in question is tilted with respect to the c direction. This means that as it lengthens the structure should expand a small amount along the b direction in addition to a large expansion along the c direction, while the expansion along a is unaffected. Thus, one expects that $\alpha_b > \alpha_a$, as in YbZn_2 . However, the angle of tilt of the zinc-zinc bond with respect to the c direction decreases as the size of the A atom decreases. For HoZn_2 , then, α_b should be more nearly equal to α_a , which is so. The contribution of the various bonds to the thermal expansion is certainly quite complex, and shifts in atom positions with increasing temperature need to be determined in order to give a more exact picture. However, it is felt that the lengthening of the zinc-

Figure 9. Ho atom nets in HoZn_2 .

zinc bond is a key feature of the expansion.

Some support for this interpretation is given by Gschneidner (1969), who investigated the relationship between melting points and lattice parameters for several series of lanthanide compounds, including the REZn_2 series. From his studies, Gschneidner expects that the melting points of rare earth compounds should increase with increasing atomic number if the contraction in the size of the unit cell is greater than in the pure metals. This was not found to be true in the REZn_2 compounds, and Gschneidner suggests that either the thermal expansion of the REZn_2 compounds exhibits anomalous behavior within the series or that primarily zinc-zinc bonds are probably the weakest in the structure at the melting point. It is reasonable to expect, then, that they are also weak at lower temperatures and are responsible for the major part of the thermal expansion.

It is possible to show the trends in the thermal expansion coefficients amongst all the REZn_2 compounds. A convenient parameter to show this is the C.N. 12 radius of the rare earth atom. This choice of independent variable is reasonable because the positions of the zinc atoms in the structure appear to be almost completely dependent upon the size of the A atom as discussed previously. The results are given in Figure 10, where the trends are arbitrarily shown by straight lines due to the lack of sufficient data. It is interesting to note that the A atom distances in the puckered net in the a and b directions vary with C.N. 12 radius in a manner quite similar to that of α_a and α_b (see Figure 11).

Numerous attempts were made to interpret the high temperature x-ray diffraction pattern for YbZn_2 . To eliminate the possibilities that the alloy had oxidized or decomposed, or that it had reacted with the encapsulation material, x-ray powder patterns were calculated for Yb_2O_3 , YbBe_{13} ,

Figure 10. Trends in thermal expansion behavior for MZn_2 compounds.

Figure 11. M-M distances in MZn_2 compounds versus Goldschmidt C.N. 12 radii of the M atoms.

YbZn , $\text{Yb}_3\text{Zn}_{11}$, and Yb_5Zn_7 (a hypothetical compound). The latter three compounds could be formed if one of the following reactions occurred:

The patterns for none of these compounds satisfactorily explained the high temperature x-ray diffraction pattern for YbZn_2 , as shown in Figures 12 and 13. Next, x-ray diffraction patterns were calculated for a number of closely related structure types: the AlB_2 -, the CdI_2 -, and the CaIn_2 -, and the MoSi_2 -types. The MoSi_2 -type structure is exhibited by many of the REAg_2 and REAu_2 compounds. These patterns were calculated by using detailed metallic size and geometry arguments to obtain the lattice parameters and atom positions for YbZn_2 if it exhibited these structure types at high temperatures. Referring again to Figure 12, it is seen that none of these patterns satisfactorily explained that for YbZn_2 at 650°C . The patterns shown were calculated using a computer program called POWD (Smith, 1967).

Finally, it was found by McMasters, Gschneidner, Bruzzone & Palenzona (1971) and Iandelli & Palenzona (1968) that a transition in structure type occurs for REAg_2 and REAu_2 compounds. The lighter rare earth compounds exhibit the KHg_2 -type structure and the heavier rare earth compounds exhibit the MoSi_2 -type structure. However, SmAg_2 , PrAu_2 , NdAu_2 , and SmAu_2 exhibit complex tetragonal structures with lattice parameters on the order of $a \approx 16$, $c \approx 9\text{\AA}$. The structure of these compounds, although not yet determined, must be intermediate between the KHg_2 - and MoSi_2 -type structures. When the calculated powder pattern for NdAu_2 was compared with the high temperature

Figure 12.

- A. The calculated YbZn_2 powder pattern.
- B. The experimental (650°C) YbZn_2 powder pattern.
- C. The calculated YbBe_{13} powder pattern.
- D. The calculated Yb_2O_3 pattern.
- E. The calculated MoSi_2 -type structure powder pattern.
- F. The calculated AlB_2 -type structure powder pattern.
- G. The calculated CaIn_2 -type structure powder pattern.
- H. The calculated CdI_2 -type structure powder pattern.

Figure 13.

- A. The calculated YbZn_2 powder pattern.
- B. The experimental (650°C) YbZn_2 powder pattern.
- C. The NdAu_2 powder pattern.
- D. The $\text{Yb}_3\text{Zn}_{11}$ powder pattern.
- E. The " Yb_5Zn_7 " powder pattern.

pattern of YbZn_2 , a good match was obtained for the extra reflections which occur, as shown in Figure 13 and Table III. It appears then that, upon heating, YbZn_2 transforms to the NdAu_2 -type structure.

A number of attempts were made to solve the structure of NdAu_2 , using data supplied by K. A. Gschneidner, Ames Laboratory, without success. The structure will certainly contain some type of hexagonal B-atom nets. Because of the tetragonal symmetry, these B-atom nets will lie parallel to both the $\underline{a-c}$ and $\underline{b-c}$ planes to conform to the required 4-fold symmetry for the tetragonal system. This arrangement of double hexagonal B-atom nets is a key feature of the MoSi_2 -type structure.

The close relationship of the NdAu_2 -type to that of MoSi_2 can also be confirmed by extrapolating the lattice parameters for the REAu_2 compounds which exhibit the MoSi_2 -type structure as a function of the CN12 radius of the A-atom, as shown in Figure 14. For NdAu_2 , the extrapolated values are $a = 3.76$, $c = 9.10\text{\AA}$. A "supercell" with four cells along the a and b axes would give $a = 15.08$, $c = 9.10\text{\AA}$, which are near the measured parameters of $a = 15.94$, $c = 9.33\text{\AA}$.

The change in crystal structure in YbZn_2 may be related to a valence change. Wernick, Haszko & Dorsi (1962) noted that the structure change from C14 to C15 in the REMn_2 compounds beyond Er was probably due to a transfer of an electron from manganese to the rare earth atoms. The results of Dwight, Downey & Conner (1967) show that in YbAu_2 the ytterbium atom must be nearly trivalent, since its metallic radius is much smaller than the metallic radius of the divalent ion. Furthermore, paramagnetic susceptibility measurements on YbZn_2 showed that the temperature dependence is not linear. At low temperatures, the valence of ytterbium was found to be +3, and as the temperature was increased there appeared to be a mixture

TABLE III

The Observed and Calculated d-values for YbZn_2
 at 650°C , YbZn_2 (KHg_2 -type Structure) and NdAu_2

YbZn ₂ Pattern at 650°C Observed d-Values	YbZn ₂ (KHg ₂ -type) Room temperature d (hkl)		NdAu ₂ d (hkl)	
3.992			3.995	231
3.966			3.985	400
3.948	3.914	101		
3.855	3.785	002		
3.682	3.663	020		
3.667			3.664	401
3.566			3.564	420
3.490			3.485	331
3.336			3.329	421
3.140			3.126	510
3.025			3.017	341, 501
2.964			2.964	511
2.821			2.821	521
2.816			2.817	440
2.761	2.709	112	2.733	530
2.696			2.697	441
2.692	2.674	121		
2.668			2.657	600
2.661	2.632	022		
2.616			2.623	531
2.612			2.621	610

TABLE III (continued)

YbZn ₂ Pattern at 650°C Observed d-Values	YbZn ₂ (KHg ₂ -type) Room temperature d (hkl)		NdAu ₂ d (hkl)	
2.547			2.555	621
2.427			2.523	611
2.523			2.520	620
2.431			2.433	621
2.418	2.385	013		
2.336	2.324	031		
2.298			2.302	631
2.293	2.286	200		
2.244			2.254	710,550
2.233	2.209	103		
2.154			2.210	640
2.191			2.191	711,551
1.992			1.994	651
1.971	1.957	202		
1.949			1.949	801
1.934			1.934	811,741
1.933			1.933	820
1.850			1.853	570
1.842			1.842	661
1.784	1.755	033		
1.738	1.726	222		
1.729	1.701	114		
1.708	1.681	024		

TABLE III (continued).

YbZn ₂ Pattern at 650°C Observed d-Values	YbZn ₂ (KHg ₂ -type) Room temperature d (hkl)		NdAu ₂ d (hkl)	
	d	(hkl)	d	(hkl)
1.668	1.648	231		
1.599			1.595	491
1.578			1.587	771
1.569			1.571	0101
1.545			1.548	590
1.508	1.482	015		
1.438	1.422	134		
1.424	1.410	143		
1.414	1.388	312		
1.390	1.384	321		
1.377			1.383	1131
1.373	1.354	224		
1.346	1.337	242		
1.314	1.305	303		

Figure 14. The lattice parameters vs. the metallic
CN12 radii for the MoSi_2 -type structure
compounds.

of both Yb^{+3} and Yb^{+2} in this compound.

Any further discussion of the crystal chemical relations between the KHg_2^- , NdAu_2^- , and MoSi_2^- -type structures must await the solution of the structure of NdAu_2 .

Magnetic Susceptibilities

The magnetic susceptibility of most of the REZn_2 compounds was measured over the temperature range 4-300°K. The results are given in Table IV. It can be seen that most of the compounds undergo some type of magnetic ordering at low temperatures. The effective magnetic moments are in good agreement with the corresponding +3 free-ion values for PrZn_2 , NdZn_2 , and TbZn_2 , lower for CeZn_2 and HoZn_2 , and higher for GdZn_2 . In CeZn_2 , the reduced magnetic moment can be attributed to crystal field effects and possible valence changes. These valence changes are common to cerium inter-metallic compounds, and involve a partial loss of a 4f electron to the conduction band. The higher magnetic moment in GdZn_2 is due to an exchange interaction between the spins of the Gd^{+3} ions and the conduction electrons.

In EuZn_2 , the susceptibility measurements indicate that a mixture of Eu^{+2} and Eu^{+3} states exist, and that a conversion to only Eu^{+2} takes place as the temperature is lowered. The situation is the same for YbZn_2 , except that ytterbium becomes completely trivalent at low temperatures.

Mechanical Properties

The mechanical properties of HoZn_2 were studied in this program. Specifically, the elastic constants and the compression properties of this compound were measured. In order to make these measurements it was necessary to develop a technique for the production of sound, solid specimens through powder metallurgy. Powders of -325 mesh size were compressed in a special

TABLE IV
Magnetic Data of RZn_2 Intermetallic Compounds*

Compound	$T_N(^{\circ}K)$	$\theta(^{\circ}K)$	μ_{eff}	$g\sqrt{J(J+1)}$	$\mu_{sat.}$	gJ
$LaZn_2$	Pauli paramagnet					
$CeZn_2$	7	24	2.25	2.54	--	2.14
$PrZn_2$	--	14	3.56	3.58	--	3.20
$NdZn_2$	24**	28	3.40	3.62	1.82	3.27
$SmZn_2$	45	t.d.		0.82	--	0.71
$EuZn_2$	20	t.d.		0	--	0
$GdZn_2$	68**	70	8.48	7.94	6.91	7.00
$TbZn_2$	55 25	58	9.62	9.72	--	9.00
$HoZn_2$	12	26	9.71	10.60	--	10.00
$YbZn_2$	--	t.d.		4.54	--	4.00

* T_N is the Néel temperature, θ is the Weiss constant. μ_{eff} and μ_{sat} are expressed in μ_B per formula unit.

** Curie temperature

t.d. = Temperature dependent

Saturation moment at 4.2°K obtained by extrapolation to infinite field using the customary $1/H$ plot.

fall-away die shown in Figure 15. The green compacts were sealed in tantalum tubes under an inert atmosphere to prevent oxidation during sintering. The optimum compaction pressure was found to be 95,000 psi and the optimum sintering temperature was $T/T_{mp} \approx 0.84$ for 14 days. This resulted in a density of nearly 100% theoretical density, as shown in Figure 16.

The elastic constants of these specimens were measured by ultrasonic techniques over the temperature range 90-298°K. The variation of C_{11} and C_{44} is linear over this range and the values at 0°K and 298°K are (10^{12} dynes/cm²)

	0°K	298°K
C_{11}	1.176	1.088
C_{44}	0.334	0.305

The bulk modulus at 298°K is $0.681 \cdot 10^{12}$ dynes/cm², and the Debye temperature is 247°K.

Specimens prepared by the above powder metallurgy technique were tested in compression, and stress-strain plots were obtained using strain gages. Linear behavior was observed with little or no ductility. The elastic modulus obtained from these measurements was $0.76 \cdot 10^{12}$ dynes/cm², and the failure stress was about 58-59,000 psi. The mode of failure was explosive, along the direction of loading. Metallographic examination of the specimens just below the fracture surface revealed a marked change in the twin structure of HoZn₂, as shown in Figure 17. This is believed to be direct evidence for a small amount of localized plastic deformation; that is, a limited amount of plastic deformation can occur in HoZn₂, according to some twinning mode.

Specimens of HoZn₂ were thinned and examined by transmission electron microscopy in order to study the crystallographic aspects of the twinning. However, particles small enough to be so-examined no longer exhibited any

Figure 15. Die used to prepare HoZn_2 specimens.

- (a) Disassembled die showing the four pieces which form the specimen cavity and the bottom pressure piece.
- (b) Fully assembled die ready for use.

(a)

(b)

Figure 16. Microstructures of sintered HoZn_2 specimens.

- (a) Compacted at 67,000 psi;
Sintered for two days; % TD = 72.5%.
- (b) Compacted at 95,000 psi;
Sintered for six days; % TD = 86.6%.
- (c) Compacted at 95,000 psi;
Sintered for 14 days; % TD = 99.8%.

Magnification: 100 X; unetched.

(a)

(b)

(c)

Figure 17. Twinning in HoZn_2 sintered specimens.

- (a) Specimen not subjected to compression testing.
- (b) Specimen compression tested to failure 5% Nital etch; magnification 400X, enlarged approximately four times for reproduction.

(a)

(b)

twinning.

Crystal Structures of Related Compounds

During the course of this investigation, a number of other intermetallic compounds were studied. One of these was YbCuZn, a compound which melts congruently at 642°C. YbCuZn was found to be orthorhombic, space group Pnma, with $a = 7.097 \pm 2$, $b = 4.417 \pm 2$, $c = 7.486 \pm 2 \text{ \AA}$. The structure of this compound must be very close to the KHg_2 -type structure. A cursory metallographic study of the pseudobinary system YbCu_2 - YbZn_2 was made and, contrary to expectations, extended solubility of these compounds in one another does not occur. In addition, considerable effort was expended in trying to prepare YbCu_2 as a single phase alloy, without success. The significance of these results is not yet understood.

The crystal structures of YZn_3 , DyZn_3 , and HoZn_3 were completely determined, and ErZn_3 was found to be isostructural with YZn_3 . The lattice parameters and atom positions for these compounds are given in Table V. The YZn_3 -type structure is closely related to the KHg_2 -type structure. Both are layer-like, with groups of B atoms interposed between zig-zag chains of A atoms. In YZn_3 , the Zn groups are pentagons rather than trapezoids as in YZn_2 (see Figure 18).

Crystallographic data for other compounds characterized in this work are listed in Table VI. The structure of Y_3Zn_{11} was completely determined, and this structure further shows the tendency of zinc to form hexagonal rings in rare earth compounds.

TABLE V

Crystallographic Data for REZn_3 CompoundsSpace group: Pnma Equipoints: all atoms in $4(c)$: $x, \frac{1}{4}, z$; etc.

	<u>Lattice parameters ($\text{\AA}$)</u>		
	a	b	c
YZn_3	6.690 ± 5	4.405 ± 3	10.111 ± 9
DyZn_3	6.700	4.398	10.06
HoZn_3	6.697 ± 3	4.3655 ± 14	10.099 ± 3
ErZn_3	6.669 ± 10	4.36	10.014 ± 8

<u>Positional parameters</u>			
		x	z
<u>YZn_3</u>	Zn(1)	0.2152 ± 14	0.0449 ± 9
	Zn(2)	0.9162 ± 14	0.8549 ± 9
	Zn(3)	0.5362 ± 13	0.8956 ± 9
	Y	0.2773 ± 9	0.3387 ± 6
<u>DyZn_3</u>	Zn(1)	0.216	0.042
	Zn(2)	0.961	0.853
	Zn(3)	0.535	0.897
	Dy	0.279	0.336
<u>HoZn_3</u>	Zn(1)	0.2169 ± 8	0.0432 ± 5
	Zn(2)	0.9177 ± 7	0.8524 ± 5
	Zn(3)	0.537 ± 8	0.8966 ± 5
	Ho	0.2796 ± 3	0.3370 ± 2

Figure 18. Arrangement of atoms in (010) Plane in YZn₃.

TABLE VI

Crystallographic Data for Various RE-Zn Compounds

	$\overset{\circ}{a}(\text{\AA})$	$\overset{\circ}{c}(\text{\AA})$
$\text{Y}_2\text{Zn}_{\sim 9}$	14.283 ± 7	14.080 ± 13
$\text{Er}_2\text{Zn}_{\sim 9}$	14.14	13.95

Space group: $P\bar{6}2c$, $P6_3mc$, or $P6_3/mmc$

$\text{YZn}_{6.1 \pm 3}$	8.902 ± 4	9.232 ± 4
ErZn_{6-7}	8.82	9.19

Space group: $P\bar{6}2c$, $P6_3mc$, or $P6_3/mmc$

	$\overset{\circ}{a}(\text{\AA})$	$\overset{\circ}{b}(\text{\AA})$	$\overset{\circ}{c}(\text{\AA})$
Y_3Zn_{11}	4.402 ± 6	8.906 ± 7	12.934 ± 10

Space group: $Immm$

Atom positions:

	<u>Equipoint</u>	$\overset{\circ}{x}$	$\overset{\circ}{y}$	$\overset{\circ}{z}$
Y(1)	2(a)	0	0	0
Y(2)	4(i)	0	0	$.2926 \pm 5$
Zn(1)	4(h)	0	0.1840 ± 11	$\frac{1}{2}$
Zn(2)	8(l)	0	0.3630 ± 7	0.3438 ± 5
Zn(3)	8(e)	0	0.2843 ± 8	0.1405 ± 5
Zn(4)	2(d)	$\frac{1}{2}$	0	$\frac{1}{2}$

$R = 12.1\%$

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