INFLUENCE OF RADIUS RATIO ON THE STRUCTURE OF INTERMETALLIC COMPOUNDS OF THE AB3 TYPE

J. H. N. VAN VUCHT

Philips Research Laboratories, N.V. Philips' Gloeilampenfabrieken, Eindhoven (The Netherlands)

(Received April 30th, 1966)

SUMMARY

Attempts have been made to investigate the factors governing the relative stability of the various structure types found by mixing different kinds of atoms, A or B, in a large number of AB3 intermetallic compounds related to Cu3Au. A geometric factor, leading to the radius-ratio dependent hexagonality of stacking character, as recognized by VAN VUCHT AND BUSCHOW in rare-earth trialuminides, seems to be predominant in many cases and may be used in predicting ternary phases.

This factor has also served as the basis on which trial structures are proposed for three new phases encountered as transition structures between the Cu3Au and the Ni3Sn types, namely, $(Ba_{0.95},Sr_{0.05})Pb_3$ with a rhombohedral unit cell ($a = 12.180$ Å, $\alpha = 34°43'$); $(Ti_{0.97},Nb_{0.03})Ni_3$ with a hexagonal unit cell ($a = 5.10$ Å, $c = 20.80$ Å, $c/a = 4.08$), and $Ti(Ni_{0.11},Pt_{0.89})_3$ with a hexagonal unit cell ($a = 5.482$ Å, $c = 15.65$ Å, $c/a = 2.85$). The geometric factor may even be seen as influencing a transition of the layer type to be stacked. A second factor, the electronegativity difference of the atoms A and B, is recognized as the principal reason why the radius-ratio rule cannot be given in a quantitative manner. In many cases a third factor, the valence-electron concentration prevails.

INTRODUCTION

In a recent paper on the structures of the rare-earth trialuminides[1] it was shown that, depending on the radius of the rare-earth element R, the compound RAl3 may have the cubic Cu3Au type for the smaller R atoms (*viz.* Sc, Tm, Yb, Er), or the hexagonal Ni3Sn type for the larger R atoms (*viz.* Gd, Sm, Nd, Pr, Ce, La). For R metals with radii lying on the border between these two groups (*viz.* Y, Tb, Dy and Ho) structures are found which may be considered as intermediate in character. All these structures are built up from the same type of layer; the stacking sequences of the layers, however, change with increasing R radius from purely cubic, through different types of ordered mixtures of hexagonal and cubic layers, to purely hexagonal. Additional proof for the interdependence of radius ratio and structure type was given by experiments on two groups of ternary trialuminides, $Er_xY_{1-x}Al_3$ and $Er_xGd_{1-x}Al_3$.

When the mean R/Al radius ratio is varied, identical types of stacking varieties occur as are found for the binary trialuminides, and, furthermore, an additional type is observed which fits in at the correct position in the series of intermediate structures with increasing hexagonality.

These results clearly indicate that geometric factors may be very important in determining the type of structure of an RAl₃ compound. In order to demonstrate the more general value of this recognition, a series of investigations was undertaken with various intermetallic compounds known to belong to the structure family in question, using, however, elements that are utterly different from the rare-earth elements and aluminium. By partly or wholly replacing one of the components by an atom of different size, it was hoped to stabilize ternary compounds with intermediate structures as above.

INVESTIGATION PROGRAM

Starting with the AB₃ compounds in the first column of Table I, substitutions are made of the A atoms or the B atoms with elements of like or unlike valency; the latter to find out whether electronic influences (valence-electron concentration) may prevail over the supposed geometric factor. The radius of the substituting atom relative to the radius of the replaced atom is added between brackets. The direction of structure change, predicted on these geometrical grounds, is indicated in column 3, while column 4 anticipates the experimental justification of these predictions.

Experimental details will be given separately in the discussion of each system. The stoichiometry of the AB₃ phases, either binary or ternary, has not been checked. The systems Ni₃(Sn,Ge) and Ni₃(Sn,Si) will be treated in a separate paper[2] because of special complications which, presumably, are related to the fact that Ni₃Sn has a structure transformation. The results from the systems (Ta,Nb)Co₃, (Ta,V)Co₃, (Nb,V)Co₃, (Ta,Mo)Co₃, (Ta,W)Co₃, (V,Mo)Co₃, (V,W)Co₃, (Nb,Mo)Co₃, (Nb,W)Co₃, Ta(Co,Ni)₃ and Ta(Co,Fe)₃ systems will be communicated here in an abbreviated form, in anticipation of a paper[3] describing the investigations in detail.

EXPERIMENTAL DATA

BaPb₃–CaPb₃ system

Starting with hhc-stacked BaPb₃ (hexagonally $a = 7.287$ Å, $c = 25.77$ Å $c/a = 3.54$, or rhombohedrally $a = 9.565$ Å, $\alpha = 44°47'4$) it was expected that upon the gradual replacement of Ba by Ca, less hexagonal structures might become stable. In fact CaPb₃ itself has been shown to belong to the Cu₃Au type compounds by ZINTL AND NEUMAYR[5] with $a = 4.901$ Å.

The samples were prepared by melting mixtures of the metals, weighed in an argon atmosphere, into pure, decarbonized, thick-walled iron crucibles sealed by welding on lids of the same material. These filled bombs were enveloped in silica and heated in this state for one day at 1000°C and subsequently for 3 days at 500°C. After this treatment the bombs were opened in a glove box filled with dry nitrogen; the brittle contents were crushed in this box in an agate mortar and the powder was placed in a special sample holder which allowed an X-ray diffractogram to be made without exposure to the air. The X-ray apparatus consisted of a Philips wide-angle

TABLE I

REVIEW OF INVESTIGATED SYSTEMS AND RESULTS

Starting AB_3	Stacking	Replacement* of A	B	Change expected in direction	Structure types found successively
$BaPb_3$	hhc	Ca(0.88)		cubic	12-layer (hhcc?), Cu_3Au type (c)
		Sr(0.94)		cubic	12-layer (hhcc?), VCo_3 type (hcc), deformed Cu_3Au type (c')
		K(1.05)		hexagonal	no AB_3 type
		La(0.83)		cubic	Cu_3Au (c)
			Tl(0.98)	hexagonal	Ni_3Sn type (h)
			Bi(1.04)	cubic	Cu_3Au (c), deformed Cu_3Au type (c')
$ThAl_3$	h	U(0.86)		cubic	Cu_3Au type (c)
			In(1.10)	cubic	Cu_3Au type (c)
$SnNi_3$	h	Ge(0.88)		cubic	Cu_3Au type (c)
		Si(0.85)		cubic	Cu_3Au type (c)
$TiNi_3$	hc	Al(1.00)		indifferent	Cu_3Au type (c)
		Zr(1.10)		hexagonal	$BaPb_3$ type (hhc)
		Nb(1.01)		hexagonal	10-layer (hhchc?), $BaPb_3$ type (hhc), Ni_3Sn type (h), Cu_3Ti type
		Ta(1.01)		hexagonal	10-layer (hhchc?), $BaPb_3$ type (hhc), Ni_3Sn type (h), Cu_3Ti type
			Cu(1.03)	cubic	10-layer (hhchc?), $BaPb_3$ type (hhc), Cu_3Ti type, Al_3Ti type, two-phase (no AB_3)
			Co(1.02)	cubic	VCo_3 type (hcc), two-phase (no AB_3 type)
			Fe(1.02)	cubic	two-phase (no AB_3 type)
			Pt(1.09)	cubic	7-layer (hchcccc?), Cu_3Au type (c)
$TiPd_3$	hc		Pt(1.01)	cubic	7-layer (hchcccc?), Cu_3Au type (c)
VCo_3	hcc	Nb(1.08)		hexagonal	no AB_3 type
		Ta(1.07)		hexagonal	no AB_3 type
		Mo(1.03)		hexagonal	$BaPb_3$ type (hhc), Ni_3Sn type (h)
		W(1.04)		hexagonal	$BaPb_3$ type (hhc), Ni_3Sn type (h)
			Ni(0.98)	hexagonal	$BaPb_3$ type (hhc), Ni_3Sn type (h), unknown, Al_3Ti type
			Fe(1.01)	cubic	Cu_3Au type (c), two-phase (no AB_3 type)
$TaCo_3$	hhc	Nb(1.00)		indifferent	no AB_3 type
		Mo(0.96)		cubic	Ni_3Sn type (h)
		W(0.96)		cubic	Ni_3Sn type (h)
			Ni(0.98)	hexagonal	Ni_3Sn type (h), Cu_3Ti type
			Fe(1.01)	cubic	no AB_3 type
$GaNi_3$	c		In(1.14)	hexagonal	no AB_3 type
$AlNi_3$	c		In(1.10)	hexagonal	no AB_3 type

* In brackets, the C.N. 12 radius substitution atom/replaced atom is given, as calculated from a table given by LAVES[18].

goniometer with a proportional counter and a pulse-height discriminator; the radiation used was $CuK\alpha$.

On replacement of about 5% of the Ba atoms by Ca a new type of structure became stable, the powder diagram of which is shown in Table II. Indexing is possible on the basis of a hexagonal unit cell with $a = 7.260$ Å and $c = 34.304$ Å, $c/a = 4.72$. From the reflections present it may be concluded that the space group is $R\bar{3}m$. The rhombohedral unit cell has the dimensions: $a = 12.180$ Å, $\alpha = 34°43'$.

There is only one way, using the close-packed AB_3 layers, of constructing a

TABLE II

X-RAY POWDER DIAGRAMS OF NEW AB_3 PHASES

$(Ba_{0.95},Ca_{0.05})Pb_3$			$(Ti_{0.97},Nb_{0.03})Ni_3$			$Ti(Ni_{0.11},Pt_{0.89})_3$		
$10^3 \times sin^2\theta$ CuKα	h k l	I	$10^3 \times sin^2\theta$ CoKα	h k l	I	$10^3 \times sin^2\theta$ CuKα	h k l	I
15.54	1 0 1	1	40.78	1 0 0	<1	36.15	1 0 2	3
17.08	0 1 2	4	42.94	1 0 1	<1	48.11	1 0 3	4
23.08	1 0 4	<1	47.88	1 0 2	<1	65.25	1 0 4	3
27.75	0 1 5	1	122.53	1 1 0	<1	79.15	1 1 0	3
45.46	1 1 0	1	164.27	2 0 0 ⎰ 2 0 1 ⎱	10	87.25	0 0 6	2
60.84	0 2 1	4				105.78	2 0 0	2
61.97	2 0 2	20	170.92	2 0 2 ⎰ 1 1 5 ⎱	15	108.05	2 0 1	2
65.77	1 0 10	6				115.08	2 0 2	20
68.00	0 2 4	8	179.28	2 0 3	15	118.89	0 0 7	100
72.68	0 0 12 ⎰ 2 0 5 ⎱	100*	185.20	0 0 10	>500	127.26	2 0 3	22
			193.00	2 0 4	30	144.41	2 0 4	18
84.61	0 2 7	50	209.08	2 0 5	100	166.21	2 0 5	15
92.41	2 0 8	3	229.15	2 0 6	15	194.10	2 1 2	2
100.68	1 0 13	2	254.4	2 0 7	2	197.26	1 1 7	5
106.96	1 2 2	1	282.7	2 0 8	10	206.10	2 1 3	1
110.66	0 2 10	10	313.3	2 0 9	2			
117.88	1 1 12 ⎰ 1 2 5 ⎱	3	349.5	2 0 10	2	223.45	2 1 4 ⎰ 2 0 7 ⎱ 1 0 9	2
			388.0	2 0 11	2			
121.39	2 0 11	1	430.2	2 0 12	10	237.86	3 0 0	<1
129.72	2 1 7	2	477.3	2 0 13	2	261.11	2 0 8	1
134.92	3 0 0	<1	491.6	2 2 0	15	268.52	1 0 10	1
139.50	3 0 3	2	522.7	2 2 4	1	271.49	2 1 6	1
144.97	1 0 16	1	525.6	2 0 14	7	293.13	0 0 11	1
153.05	3 0 6	1	580.0	2 0 15	55	301.27	2 0 9	10
159.00	2 0 14 ⎰ 1 1 15 ⎱	5	635.3	3 0 12	1	315.94	2 2 0	10
			637.0	2 0 16	5	347.98	2 0 10	10
175.85	3 0 9	2	641.2	2 2 9	1	355.48	3 0 7	2
179.95	2 2 0	20	666.9	0 0 19	1	372.28	1 1 11	<1
189.15	0 2 16	1	675.9	2 2 10	30	374.81	1 0 12	1
194.24	1 3 1	17*	698.6	2 0 17	5	398.00	2 0 11	10
206.11	2 0 17	15	738.1	0 0 20	75	435.08	1 0 13 ⎰ 3 0 9 ⎱ 2 2 7	20
218.96	1 3 7	<1						
242.33	0 2 19 ⎰ 0 4 2 ⎱	15				442.50	4 0 3	3
252.73	2 2 12 ⎰ 0 4 5 ⎱	30				454.34	2 0 12	10
						474.70	0 0 14	30

Powder strongly orientated

Hexagonal description
$a = 7.268$ Å
$c = 34.304$ Å
$c/a = 4.72$

Rhombohedral description
$a = 12.180$ Å
$\alpha = 34°43'$

hexagonal unit cell
$a = 5.10$ Å
$c = 20.80$ Å
$c/a = 4.08$

Sample quenched from 1600°C
Powder probably with some preferred orientation

hexagonal unit cell
$a = 5.482$ Å
$c = 15.65$ Å
$c/a = 2.85$

* Coincidence with lines of f.c.c. lead.

12-layered hexagonal unit cell with rhombohedral symmetry, namely

ABCBCABABCACA

c c h h c c h h c c h h

It is presumed therefore that this is the structure of the intermediate (Ba,Ca) Pb_3 compound and it is hoped to give further proof of this in future work.

In all probability, the structure encountered here is the 50% hexagonally-stacked structure which was expected to occur in the systems (Er,Y)Al_3 and (Er,Gd) Al_3, but in these latter cases the Ni_3Ti-type hchc stacking was found instead. This, together with another observation, at that time justified the statement that those stacking sequences were apparently preferred where the alternation of hexagonal and cubic layers is at its maximum. In the light of the present experiments, however, it must be admitted that, although this may be true for the rare-earth trialuminides it apparently does not apply to the alkaline-earth triplumbides.

On the substitution of more barium by calcium in this lattice the Cu_3Au type occurs as the second phase.

$BaPb_3$–$SrPb_3$ system

ZINTL AND NEUMAYR[5] found that $SrPb_3$ is tetragonal with $a = 4.965$ Å, $c = 5.035$ Å, $c/a = 1.014$, and has a slightly deformed Cu_3Au type of structure. Our observations, using identical experimental methods to those for the $BaPb_3$–$CaPb_3$ system, yielded virtually the same result, $a = 4.969$ Å, $c = 5.012$ Å, $c/a = 1.09$. Efforts to index the $SrPb_3$ diagram with a hexagonal unit cell were fruitless.

The composition ($Ba_{0.5}$,$Sr_{0.5}$)Pb_3 provided a diagram that was indexed with a hexagonal unit cell of dimensions $a = 7.164$ Å, $c = 17.199$ Å and $c/a = 2.40$.

The c/a ratio clearly indicates a 6-layer structure, which presumably is identical to the $\frac{1}{3}$-hexagonal VCo_3 or $PuAl_3$ structure (stacking hcc).

This hcc structure is in equilibrium with a 12-layer hhcc structure, similar to ($Ba_{0.95}$, $Ca_{0.05}$)Pb_3 at the Sr-poor side, and with the deformed Cu_3Au type structure at the Sr-rich side.

$BaPb_3$–"KPb_3" system

The replacement of barium in $BaPb_3$ by potassium should lead to the stabilization of a more hexagonal structure, *e.g.* the Ni_3Sn type. However, it appeared experimentally that under the conditions of preparation as detailed for the $BaPb_3$–$CaPb_3$ system no new AB_3 type became stable. A sample of the composition ($Ba_{0.9}$,$K_{0.1}$)Pb_3 showed only the 9-layer diffraction pattern, while ($Ba_{0.5}$,$K_{0.5}$)Pb_3 showed a mixture of a weak 9-layer pattern, very strong lines of f.c.c. Pb and a weak, third pattern of a non identified phase, probably not of AB_3 composition. An intermetallic compound, KPb_3, seems not to be stable at the annealing temperature chosen.

$BaPb_3$–$LaPb_3$ system

Though the radius of lanthanum atoms differs quite considerably from the barium atom radius, a small percentage of Ba was substituted. It was expected in this way to stabilize stackings which were more cubic. However, an inspection of the X-ray diagrams of the samples ($Ba_{0.9}$,$La_{0.1}$)Pb_3 and ($Ba_{0.5}$,$La_{0.5}$)Pb_3 showed no traces of transition types. Besides the peaks of the 9-layered $BaPb_3$ type, lines of Pb were observed, probably due to superficial oxidation of the powdered sample. $LaPb_3$ was found to be of Cu_3Au type with $a = 4941$ Å.

$BaPb_3$–"$BaTl_3$" system

Since the radius of Tl is larger than that of Pb it was expected that, upon

replacing Pb by Tl, the structure of $BaPb_3$ would make room for a still more hexagonal structure. This proved to be justified: a sample of the composition $Ba(Pb_{0.5},Tl_{0.5})_3$ showed the characteristic X-ray diagram of a Ni_3Sn structure with a hexagonal unit cell of $a = 7.392$ Å, $c = 5.475$ Å, $c/a = 0.74$. A compound $BaTl_3$ does not seem to exist.

$BaPb_3$–$BaBi_3$ system

Since bismuth is smaller than lead, the replacement of lead atoms in $BaPb_3$ by bismuth should lead to structures with less than two-thirds hexagonal character. The tendency to such a shift appears immediately from the fact that $BaBi_3$ has a structure, according to ZHURAVLEV et al.[6], of the Cu_3Au type although it is slightly tetragonally deformed ($a = 5.188$ Å, $c = 5.157$ Å). In fact it is found that 90% of a sample of composition $Ba(Pb_{0.91}, Bi_{0.09})_3$ consists of a (non-deformed) Cu_3Au type with $a = 5.159$ Å.

$ThAl_3$–$ThIn_3$ system

The Ni_3Sn-type $ThAl_3$ was expected, if some Al atoms at random could be replaced by indium atoms, to change into one of the more cubically-stacked transition structures. However, using as-cast argon-arc welded specimens, we did in fact find that the ternary samples with the compositions $ThAl_2In$ and $ThAlIn_2$ consisted of the phases $ThAl_3$ (Ni_3Sn type), $ThAl_2$ (AlB_2 type) and indium metal.

Only the total replacement of Al succeeded: $ThIn_3$ proved to have the Cu_3Au type structure with $a = 4.96$ Å. Apparently the great stability of the heterogeneous $ThAl_2$–In mixture makes it impossible to stabilize the ternary AB_3 compound.

$ThAl_3$–UAl_3 system

Neither was this system succesful in yielding ternary transition structures. The compositions $ThUAl_6$ and ThU_2Al_9 were investigated. The first was mainly single-phase and showed a Ni_3Sn type with $a = 6.43$ Å, $c = 4.61$ Å, $c/a = 0.717$ (pure $ThAl_3$ has $a = 6.499$ Å, $c = 4.626$ Å, $c/a = 0.712$), the second was mainly two-phase and consisted of a Ni_3Sn type with $a = 6.38$ Å, $c = 4.60$ Å, $c/a = 0.72$, and a Cu_3Au type with $a = 4.32$ Å (pure UAl_3 has been reported[7] to have $a = 4.287$ Å). Both samples contained traces of additional $MgCu_2$ type $(U,Th)Al_2$, and of $(U,Th)Al_4$.

Ni_3Ti–Ni_3Al system

Ni_3Ti has a 50% hexagonal structure. The unit cell is hexagonal with $a = 5.109$ Å and $c = 8.299$ Å $(c/a = 1.624)$; the stacking sequence is ABACA (hchc). Upon replacement of Ti by Al, which has a somewhat smaller radius, it was expected that the hexagonal character would diminish. In fact, Ni_3Al itself is Cu_3Au type (with values varying with vacancy concentration from $a = 3.557$ Å to $a = 3.565$ Å according to TAYLOR AND FLOYD[8]. Disappointingly, however, the investigation of the intermediate compositions showed no transition structures. In an as-cast sample of composition $Ni_3(Ti_{0.75},Al_{0.25})$ a Ni_3Ti-type unit cell with $a = 5.09^5$ Å, $c = 8.30$ Å, $c/a = 1.63$ was found in addition to the Cu_3Au type with $a = 3.595$ Å. This is in qualitative agreement with the result of TAYLOR AND FLOYD who state that about $\frac{2}{3}$ of the Al atoms in Ni_3Al can be replaced by Ti.

Ni_3Ti–"Ni_3Zr" system

Substitution of Ti by the larger atom Zr should lead according to our scheme,

to a more hexagonal stacking. Total replacement should lead to a compound Ni_3Zr, which, however, does not occur in the Ni–Zr equilibrium diagram as given by KRAMER[9]. It was expected that an Ni_3Sn type would be encountered between Ni_3Ti and a hypothetical Ni_3Zr. Instead our as-cast, argon-arc-melted alloys showed, in the compositions ranging from $Ni_3(Ti_{0.75},Zr_{0.25})$ to $Ni_3(Ti_{0.5},Zr_{0.5})$, a 9-layered $BaPb_3$ structure (hhc) with some homogeneity region. With the composition $Ni_3(Ti_{0.67},$ $Zr_{0.33})$ the lattice constants were $a = 6.961$ Å, $\alpha = 43°30'$ (the hexagonal unit cell $a = 5.158$ Å, $c = 18.875$ Å, $c/a = 3.66$). Annealing, however, at temperatures below 1300°C resulted in a decomposition of this phase into a Ni_3Ti-type structure and an unknown structure which has an X-ray diagram isotypic with the one obtained for the composition Ni_3Zr (which deviates from KRAMER's data). It was possible to find the single-phase 9-layered structure again, by quenching the samples from about 1500°C in water.

Ni_3Ti–Ni_3Nb system

Although Ni_3Nb has the Cu_3Ti structure, which is built up from close-packed layers structurally different from those of Ni_3Ti, it was thought interesting to find out whether a substitution of Ti by Nb in Ni_3Ti would lead to intermediate ternary phases of the Cu_3Au family and if so, how the transition to the Cu_3Ti type takes place. The predicted direction for a structure change, starting with Ni_3Ti, is the hexagonal one because the radius of Nb is larger than that of titanium. As-cast, argon-arc-melted buttons of compositions progressively increasing in Nb content were investigated with $CoK\alpha$ radiation. The following structure types were encountered:

Ni_3Ti	hexagonal Ni_3Ti type, $a = 5.109$ Å, $c = 8.299$ Å, $c/a = 1.624$
$Ni_3(Ti_{0.97},Nb_{0.03})$	hexagonal, $a = 5.106$ Å, $c = 20.81$ Å, $c/a = 4.08$ (probably 10 layers)
$Ni_3(Ti_{0.89},Nb_{0.11})$	rhombohedral $BaPb_3$ type, $a = 6.930$ Å, $\alpha = 43°18'$ (hexagonal, $a = 5.115$ Å, $c = 18.809$ Å, $c/a = 3.68$)
$Ni_3(Ti_{0.67},Nb_{0.33})$	hexagonal Ni_3Sn type, $a = 5.130$ Å, $c = 4.211$ Å, $c/a = 0.82$
$Ni_3(Ti_{0.25},Nb_{0.75})$	orthorhombic Cu_3Ti type, $a = 5.11$ Å, $b = 4.53$ Å, $c = 4.21$ Å

Between the compositions mentioned, the appropriate two-phase regions were found. Some unidentified peaks (weak or very weak) present in the diagrams of samples having compositions between the last two mentioned, presumably indicate a more gradual transition of the structure than is given by the list above. For this reason this list is probably not complete.

The first transition phase, the 10-layered one, is likely to be intermediate in hexagonality between hc Ni_3Ti and hhc Ni_3 ($Ti_{0.89},Nb_{0.11}$). Its stacking mode may then be one of the following alternatives for the 60% hexagonal type with a 5-layer repeat period hhchc (ABABCBABACA) and hhhcc (ABABACBCBCA). Other possibilities (with 10-layer repeat periods) are

hhhhhcchcc   (ABABABACBCA ...),
hhhchchchc   (ABABACABACA ...),
hchhhhchcc   (ABACACACBCA ...)

and hhhchhchcc (ABABACACBCA...).

In view of the experiences with the rare-earth trialuminides the first possibility, hhchc, is to be preferred as a trial structure. A structure determination is in progress. In the meantime a list of the reflections is given in Table II.

Annealing experiments at 1000°C showed that both the 10-layered and 9-layered structures are stable only at temperatures close to the melting points of the specimens. This, together with the strong inclination to a preferred orientation of the X-ray powder specimens for the hexagonal basal planes, is an extra experimental difficulty in the structure determination.

$Ni_3Ti–Ni_3Ta$ system

After the investigation of the system $Ni_3Ti–Ni_3Nb$, similar behaviour was expected in the system $Ni_3Ti–Ni_3Ta$. In fact, the following phases were encountered in the as-cast, argon-arc melted buttons:

$Ni_3(Ti_{0.96},Ta_{0.04})$ hexagonal $a = 5.104$ Å, $c = 20.83$ Å, $c/a = 4.08$, 10-layered (probably hhchc stacked).

$Ni_3(Ti_{0.83},Ta_{0.17})$ rhombohedral $BaPb_3$ type, $a = 6.939$ Å, $\alpha = 43°16'$ (hexagonal, $a = 5.116$ Å, $c = 18.837$ Å, $c/a = 3.68$) hhc.

$Ni_3(Ti_{0.67},Ta_{0.33})$ hexagonal Ni_3Sn type, $a = 5.126$ Å, $c = 4.208$ Å, $c/a = 0.82$.

In compositions beyond those containing the Ni_3Sn type, a series of intermediate structures is observable (among which is the Cu_3Ti type, analogous to the $Ni_3(Ti,Nb)$ system) until at about $Ni_3(Ti_{0.35},Ta_{0.65})$ the ultimate room-temperature Ni_3Ta type is present.

The structure of Ni_3Ta was originally reported[10] to be of the Cu_3Ti type (like Ni_3Nb) but NOWOTNY et al.[11] have recently reported the existence of another modification, namely the related Al_3Ti type. In the course of our investigations into the ternary systems of tantalum with Ni, Co and Fe it was discovered that pure $TaNi_3$ (from arc-melted buttons, as well as from the alloys melted in Al_2O_3 crucibles) underwent a structural transformation, probably diffusionless, at about 300°C. High-temperature X-ray diffractometry showed that above this temperature the structure was of the Cu_3Ti type. This type could be stabilized to room temperature by the replacement of very little of the nickel by iron or cobalt atoms. Below the transformation temperature the diffractogram showed a pattern which was not that of an Al_3Ti type, but which looked rather similar to that of $TaPt_3$, which is a monoclinic structural relative of Cu_3Ti with the stacking sequence hhcc or ABABCACABCBCA...[12-14].

$Ni_3Ti–Cu_3Ti$ system

This system shows, at least at small substitution percentages, similar behaviour to the $Ni_3Ti–Ni_3Nb$ (or Ni_3Ta) system, though here the majority atom is replaced. The change in structure is towards a more hexagonal character, again opposite to the expectation on geometrical grounds.

At the composition $(Ni_{0.97},Cu_{0.03})_3Ti$, a ten-layered hexagonal structure with $a = 5.112$ Å, $c = 20.840$ Å, $c/a = 4.08$ (probably hhchc stacked) becomes stable. At $(Ni_{0.93},Cu_{0.07})_3Ti$, a $BaPb_3$-type hhc stacking occurs with cell dimensions (hexagonal) $a = 5.112$ Å, $c = 18.871$ Å, $c/a = 3.69$ or, (rhombohedral) $a = 6.948$ Å, $\alpha = 31°24'$.

At the approximate composition $(Ni_{0.67},Cu_{0.33})_3Ti$ an unknown structure

becomes stable, probably based on close packing of somewhat modified layers. When ultra-rapidly cooled from the liquid state this specimen appeared to be single-phase Cu_3Ti type with $a = 5.067$ Å, $b = 4.216$ Å and $c = 4.495$ Å. The as-cast specimen $(Ni_{0.33},Cu_{0.67})_3Ti$ was two-phase, showing a mixture of virtually pure copper, f.c.c., with $a = 3.615$ Å and tetragonal Al_3Ti type with $a = 3.114$ Å, $c = 7.955$ Å, $c/a = 2.55$. Ultimately the specimen with composition "Cu_3Ti" was found to be also two-phase. Indications are that pure Cu_3Ti, has paradoxically, no simple Cu_3Ti-type structure and indeed, does not exist at this composition. Instead we observed a phase with a very narrow homogeneity range of presumably the composition $Cu_{15}Ti_4$ with an orthorhombic unit cell of the dimensions $a = 4.531$ Å, $b = 12.929$ Å and $c = 4.343$ Å. A recheck on the binary Cu–Ti phase diagram is in progress.

Ni_3Ti–"Co_3Ti" system

The compound Co_3Ti is not stable according to the handbooks[15,16]. Because cobalt is slightly larger than nickel it was hoped that a gradual substitution in Ni_3Ti would give rise to related AB_3 structures before the ultimate instability interfered. In fact it is found that the Ni_3Ti type stays intact until about the composition $(Ni_{0.6}, Co_{0.4})_3Ti$. At the composition $(Ni_{0.5},Co_{0.5})_3Ti$, however, the VCo_3-type, six-layered hcc structure becomes stable and stays so until at about $(Ni_{0.25},Co_{0.75})_3Ti$ the $MgCu_2$ type Laves phase ($a = 6.706$ Å) appears, probably to be identified with Co_2Ti.

Ni_3Ti–"Fe_3Ti" system

The solubility of Fe in hc-type Ni_3Ti is found to extend to about $(Ni_{0.9},Fe_{0.1})_3Ti$ in the as-cast, argon-arc melts. Upon substitution of more iron, a $MgZn_2$-type Laves phase appears, which is probably to be identified with Fe_2Ti with some nickel dissolved in it.

Ni_3Ti–Pt_3Ti system

According to the literature[15,16], Pt_3Ti has the cubic Cu_3Au-type structure ($a = 3.898$ Å). Since Pt is larger than Ni this is in agreement with the radius-ratio rule. A partial substitution of Ni in Ni_3Ti seemed to yield no new compounds at first sight. On closer investigation, however, the X-ray diffractograms of the as-cast, argon-arc-melted alloys showed some reflections which belonged neither to the Ni_3Ti(hc)-type, nor the Cu_3Au(c)-type phase.

It was possible to demonstrate that these extra reflections are due to a new ternary phase with the approximate compositions $(Ni_{0.11},Pt_{0.89})_3Ti$. This phase becomes stable at relatively high temperatures (about 1250°C, the melting point is higher than 1500°) and its X-ray diagram can be indexed on the basis of a hexagonal unit cell with $a = 5.482$ Å and $c = 15.65$ Å ($c/a = 2.85$). Clearly it constitutes another extension of the family of polytypes of the AB_3 intermetallic compounds. According to the c/a ratio the hexagonal unit cell has 7 layers.

This means that the following three stacking modes are possible,

ABABABCA

h h h h c c c   ($\frac{4}{7}$ hexagonal),

or   ABABCBCA

h h c h h c c   ($\frac{4}{7}$ hexagonal),

or   ABACABCA

       h c h c c c c   ($\frac{2}{7}$ hexagonal).

In view of the hitherto useful rule for interchange of metals of like valency, that a radius-ratio decrease results in a less-hexagonal stacking, it seems justified to reject the first two possibilities as trial structures. Table II gives observed and calculated spacings and intensities for a composition $(Ni_{0.11},Pt_{0.89})_3Ti$. A full structure determination is in progress.

VCo_3–VNi_3 system

Argon-arc-melted buttons of various compositions were annealed in Al_2O_3 *in vacuo* (enveloped in SiO_2) for 60 h at 950°C. They were then polished and the flat surfaces were used to make X-ray diagrams ($CoK\alpha$). As expected, it was found that the shift in structural character took place in the hexagonal direction, in agreement with the fact that nickel is somewhat smaller than cobalt. The hcc VCo_3-type has made way for the hcc $BaPb_3$-type already at the composition $V(Co_{0.67},Ni_{0.33})_3$ with $a = 5.02$ Å and $c = 18.40$ Å, $c/a = 3.66$ (or rhombohedrally $a = 6.77^5$ Å, $\alpha = 43°30'$).

The composition $V(Co_{0.33},Ni_{0.67})_3$ is (at this temperature) two-phase, *viz.* Ni_3Sn type ($a = 5.040$ Å, $c = 4.089$ Å, $c/a = 0.812$) and f.c.c. (Ni,Co,V) solid solution. VNi_3 is, in agreement with literature data[17], $TiAl_3$ type. At the composition $V(Co_{0.17}, Ni_{0.83})_3$ an unknown structure is found.

VCo_3–"VFe_3" system

A substitution of iron atoms in VCo_3 was expected to yield structures with less hexagonal character, for the radius of iron (C.N.12) is somewhat larger than the cobalt radius[18]. This was expected only at the beginning of the series, because VFe_3 does not exist as an intermetallic compound.

The specimens (treated similarly to the previously referred to VCo_3–VNi_3 alloys) show only one structure related to hcc VCo_3.

According to the occurrence of one extra peak (for $hkl = 100$) in the X-ray diagram of the polished specimen $V(Co_{0.83},Fe_{0.17})_3$ it must be concluded that this specimen is single-phase Cu_3Au type with $a = 3.567$ Å. In the more iron-rich specimens annealed at 950°C, a disordered f.c.c. structure occurs as one of the phases present (no AB_3 structures).

Pd_3Ti–Pt_3Ti system

Pd_3Ti has, according to the literature[16], the Ni_3Ti-type structure with $a = 5.486$ Å, $c = 8.976$ Å, $c/a = 1.636$.

A substitution of Pd by Pt atoms was therefore expected to yield similar results to those of the system Ni_3Ti–Pt_3Ti. This proved to be correct: a 7-layered hexagonal-phase was observed in rapidly-cooled specimens of compositions $(Pd_{0.33}, Pt_{0.67})_3Ti$ and $(Pd_{0.17},Pt_{0.83})_3Ti$. The dimensions of the unit cell are $a = 5.52$ Å, $c = 15.77$ Å, $c/a = 2.85$. Efforts made to isolate the new phase by rapid quenching were unsuccessful. It is possible therefore that the new structure represents a state which is metastable at all temperatures.

Ni_3In–Ni_3Ga system

Since Ni_3In was reported to have the Ni_3Sn type structure $a = 5.32$ Å, $c = 4.24$ Å,

$c/a = 0.798$ and Ni_3Ga the Cu_3Au type structure $a = 3.58$ Å[16], a pseudobinary series of compositions was made to determine whether intermediate types occur. The result was negative. In each specimen (melted in Al_2O_3 crucibles in argon by high-frequency induction) even annealing at 750°C for one week failed to produce AB_3-type phase. Instead, mixtures of f.c.c. nickel solid solutions and Ni_2In-type ternary phases were found, though at the far Ga side traces of superstructure were found in the f.c.c. nickel.

Ni_3In–Ni_3Al system

This system too yielded negative results. Even after annealing for one week at 750°C, a sample of composition $Ni_3(Al_{0.75},In_{0.25})$ showed a mixture of Ni_2In type and a Cu_3Au type with $a = 3.573$ Å.

DISCUSSION

The experimental results demonstrate that AB_3 transition structures may occur in systems that vary widely as regards the nature and character of their components. Whether they do occur and in which of the possible structures they crystallize, can only be predicted if their stability is known relative to all the other possible structures in the system.

This is not possible in the present state of knowledge, but the experiments reported here have demonstrated that the structures that occur always form a logical series as far as their stacking character is concerned. This enables us henceforth to predict possible intermediate phases when both the starting- and the end-phases are known and may help to suggest trial structures when new types are found.

Analysis of the results shows furthermore, that the radius-ratio rule, as deduced from the rare-earth trialuminides[1], applies to all those substitutions in which the valency of the atoms remains constant. In most of the cases where atoms of unlike valency are interchanged, an increase of valency electrons leads to increase of hexagonality. To this well-known rule[19,20] exceptions are found in the systems $BaPb_3$–$LaPb_3$, $BaPb_3$–$BaTl_3$ and $BaPb_3$–$BaBi_3$, but this is probably due to the size effect.

Electronegativity differences of the interchanging metals may play a role, *e.g.* in the systems $TaCo_3$–$MoCo_3$ and $TaCo_3$–WCo_3, because tantalum undoubtedly has a somewhat smaller radius in $TaCo_3$ than the normally listed C.N.12 value. Substitution of molybdenum for Ta results then, in a less than linear decrease of the apparent radius ratio A/B. Two of the systems studied by SADAGOPAN AND GIESSEN[19] may also be examples of this case. In the first system $ZrPt_3$–$NbPt_3$ they observed successively the types (hc) Ni_3Ti, (hhc) $BaPb_3$, (h) Ni_3Sn, Cu_3Ti and $NbPt_3$. In the second system, YPt_3–$NbPt_3$, they found successively the types (c) Cu_3Au, (hchcc) $HoAl_3$, (hc) Ni_3Ti, (h) Ni_3Sn, Cu_3Ti and $NbPt_3$. In both cases the electronegativity difference of the substitution partners is rather large and helps the electronic influence to obscure the size effect considerably. VAN VUCHT AND BUSCHOW[1] have pointed out that, in the rare-earth trialuminides, the metallic bond is mixed to some extent with an ionic character because of the electronegativity difference of the rare-earth metals and aluminium. In the meantime, the measurement of magnetic properties at low temperatures on $PrAl_3$ and $ErAl_3$ has provided independent experimental evidence for the existence of a crystal field in these lattices corresponding to an effective negative charge of roughly 0.1 electron per Al atom[21]. In view of this the correction of the

tabulated radius for yttrium due to an undoubtedly even larger ionic admixture in the binding character in YPt_3, must be considerable.

While the electron-concentration influence on structure has been attributed to the filling of Brillouin zones no explanation has hitherto been given for the size effect. We may try the following qualitative approach. Let us consider a close-packed lattice of equally sized atoms A and B in the composition AB_3. At higher temperatures the entropy of mixing stabilizes a random mixture of A and B but, on cooling we note a tendency to order, because the interaction energy $\frac{1}{2}(E_{AA} + E_{BB})$ is less than the inter-action energy E_{AB}. It will immediately be clear that, when directional bonds are absent, the ordered lattice prefers the maximum symmetry, such as is found in the cubic Cu_3Au type, in which each A-atom is surrounded by 12 B-atoms as first neigh-bours and 6 A-atoms as next neighbours. A somewhat less symmetrical surrounding is found in the hexagonal Ni_3Sn type, built up from the same close-packed AB_3 layers, where the number and distance of the neighbouring B-atoms and next-neighbouring A-atoms is the same, but where two of the next-next neighbouring A-atoms are closer than in the Cu_3Au type lattice. This is a small, second-order effect which causes the Cu_3Au type to be stable when $r_A/r_B = 1$ but it may easily be overruled when r_A/r_B increases. The reason for this is the increasing bad fit of the atoms, which means an increase of potential energy. Naturally, the atoms tend to seek their potential minima, but they can achieve this only at the expense of the lattice symmetry. Given the high symmetry of the space group of the Cu_3Au type, the size of each atom in the lattice is defined, with no free parameter left. At a certain r_A/r_B value the bad fit "potential energy" is so large that it becomes energetically profitable to stack the AB_3 layers hexagonally, notwithstanding the disadvantageous closer approach of the A-atoms in next-neighbouring layers. The lower symmetry of the hexagonal space group allows the clustering of the smaller atoms in the layers (see Fig. 1(a)), thus admitting a better packing when the larger A-atoms of both adjoining layers profit from the open spaces (Fig. 1(b)). The c/a ratio per stacked layer must then be smaller than in the cubic arrangement of AB_3 layers.
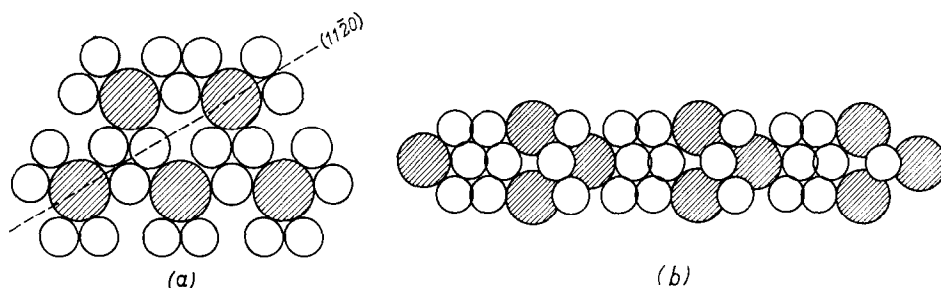

Fig. 1. (a) Layer of a Ni_3Sn-type AB_3 compound. Note the clustering of the smaller atoms. (b) Projection of Ni_3Sn-type layers on the $11\bar{2}0$-plane. The larger atoms fit in the holes formed by the clustering in the layers.

The fitting of the atoms in the diverse possible AB_3 lattices may be roughly compared by calculating the space filling per AB_3 unit using the hard-spheres model. Figure 2 shows the result for the Cu_3Au and the Ni_3Sn type lattices, both homogeneous stackings of the same layer types, but the first purely cubic and the second purely

hexagonal. It seems plausible that, by varying gradually the radius ratio A/B (and nothing more) structures may become stable that are to be considered as mixtures of both stacking types. These mixtures apparently prefer to order for the same reason as ordering in the layer occurs.
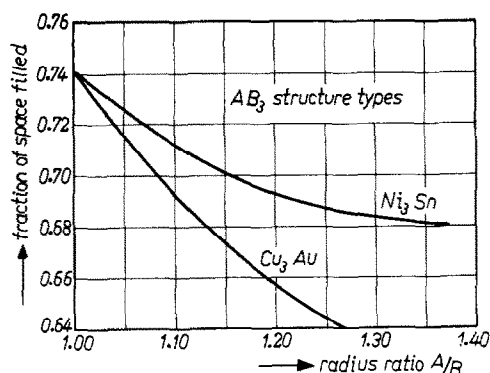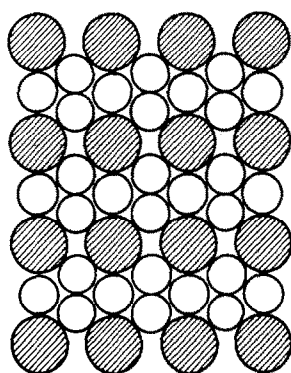

Fig. 2. The maximum packing density as a function of the radius ratio of the participating atoms, calculated for the structure types Cu_3Au and Ni_3Sn (hard-spheres model).

$Cu_3 Ti$ type layer

Fig. 3. Schematic drawing of a Cu_3Ti-type layer. Note the tendency for the larger atoms to approach each other.
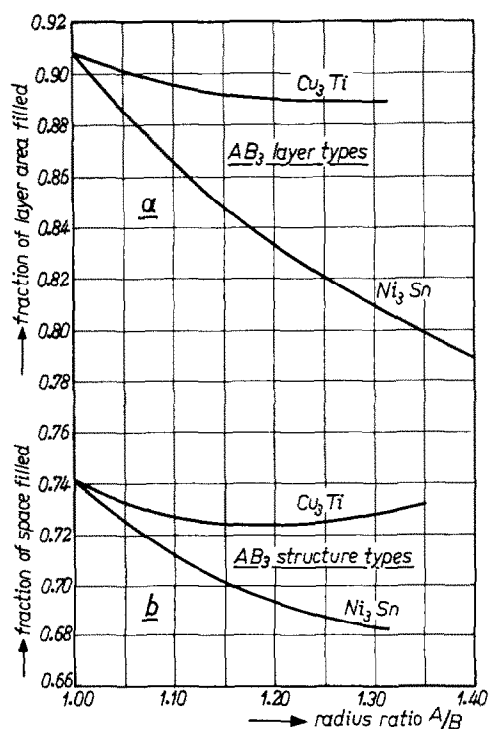
Fig. 4. (a) The maximum packing density (two dimensional) as a function of radius ratio, calculated for layers of the Ni_3Sn and Cu_3Ti types. (b) Three-dimensional maximum packing density as a function of radius ratio, calculated for the Ni_3Sn and Cu_3Ti types.

In the ternary AB_3 compounds a radius change of A or B is simulated by adding a third kind of atom that is likely to mix randomly with the A- or the B-atoms respectively. For many elements this is possible only at higher temperatures; at lower temperatures they may tend to order (on the A or the B sites in the AB_3 lattice) or to separate (giving a mixture of two AB_3 structures). In those AB_3 compounds where the energy gained by ordering A and B mutually is low (i.e. in AB_3 compounds that disorder below their melting point e.g. Cu_3Au and VCo_3), such a partially-random mixture of atoms may be difficult to realize.

Several of the pseudo-binary systems studied show a more or less systematic succession of AB_3-structure types beyond the Ni_3Sn type. These structures are built up by stacking AB_3 layers of a different type (shown in Fig. 3). This layer is commonly characterized by its so-called "shift density" $\frac{1}{2}$ which indicates the fractional number of its ABAB atom rows shifted with respect to their positions in the purely hexagonal layer of maximum symmetry discussed hitherto (shift density o). Though we did not find experimental evidence for the occurrence of these types in those pseudobinary systems, where only size effects are assumed to be effective, it can be shown that the idea of the ordering energy/packing density antagonism may also explain such a continuation beyond the Ni_3Sn type. Giving away some symmetry (disadvantageous in terms of ordering energy because the larger A atoms approach each other) the Cu_3Ti-type layer may be much more densely-packed compared with the Ni_3Sn-type layer with the higher symmetry (see Figures 1 (a) and 3). This applies also to purely hexagonal stacking of the Cu_3Ti-layer type compared with the same stacking of the Ni_3Sn-type layers. Figure 4 shows the maximum packing density in both the two-dimensional and the three-dimensional case. It must be pointed out that with regard to the structure parameter the maximum attainable three-dimensional "space" gain does not coincide with the maximum two-dimensional "space" gain in the layer. Following the above general line of thought a logical succession of types seems to demand that between the hh-stacked Ni_3Sn type (shift density o) and the hh-stacked Cu_3Ti type (shift density $\frac{1}{2}$), other types may occur, viz. hh-stacked with intermediate shift densities (see also ref. 20). Indications of the existence of such types seem to be found in the structure sequences of the systems Ni_3Ti–Ni_3Nb and Ni_3Ti–Cu_3Ti.

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