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Some Crystal Chemical Aspects of A_3B(β-W) Type Compounds

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All the known A_3B compounds with the A15(β-W) type structure have been compiled. The compilation shows that the formation of the A_3B compounds to be strongly dependent on atomic orbitals of both the A and B elements. Specifically A elements come exclusively from the transition atoms of 4-A 5-A and 6-A groups, whereas B elements come exclusively from 8-A, 9-A, 10-A groups of transition atoms as well as from 1-B, 2-B, 3-B, 4-B and 5-B groups of nontransition atoms.

Roughly, there is a one-to-one correspondence between the population (therefore the stability) of the A_3B compounds and their superconducting critical temperature; the more stable is the compound, the higher is the critical temperature.

Ever since the discovery of superconductivity (*92*) in V_3Si, the A_3B compounds of the A15(β-W) type structure have been found to be the most favorable structures by far for the occurence of superconductivity (*93*). A criterion set forth by Matthias, Geballe, and Compton (*93*) for the critical temperatures as a function of valence electrons to atom ratio, e/a, in these compounds led to discovery of some substituted A_3B compounds with significantly higher critical temperature (e.g., $Nb_3Al_{.8}Ge_{.2}$) (*94*). Nevertheless, Matthias' rule has not led to a better understanding of the reason why good superconductors are found in the compounds of this type. Indeed, the criterion of valence electrons to atom ratio, e/a, is not rigidly followed in that, when the ideal e/a ratio is brought about through substitution of A atom by another A′ atom, it does not lead to a higher critical temperature. In fact, it lowers it (*95*). Only in the substitution of B atoms with another B′ atom such as shown in the case of $Nb_3Al_{.8}Ge_{.2}$, is the e/a ratio criterion obeyed.

We believe that the fact that the A_3B(β-W) type compounds are unique as superconductors should not be an isolated phenomenon, but should also manifest its uniqueness in the area of crystal chemistry and in metallurgy. This belief led us to a compilation of all the A_3B type[1] compounds found to exist (1∼91) thus far as shown in Table I. While there are still a number of systems yet to be investigated, the available data clearly show a number of interesting and unique characteristics associated with the A_3B compounds of this type in term of its crystal chemistry and metallurgy. These interesting characteristics are summarized in Table II and Fig. 1, and described as follows.

1. Element A in the A_3B compounds comes exclusively from 4-A 5-A, and 6-A group transition atoms. These transition atoms never participate in the formation of the A_3B compounds as B element.[2]
2. Among the three group of A atoms, 4-A(d^2), 5-A(d^3), and 6-A(d^4), the 5-A(d^3) group of atoms is most favored in the formation of A_3B compounds as shown in Fig. 1.
3. Element B in the A_3B compounds, on the other hand, comes exclusively from the 8-A, 9-A, 10-A groups of transition atoms as well as from 1-B, 2-B, 3-B, 4-B and 5-B groups of nontransition atoms. Again, these atoms never partake in the formation of A_3B compounds as A elements.[2]

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[1] Unless noted otherwise, the A_3B type refers to those with the A15(β-W) type structure.

[2] This empirical rule was pointed out earlier by M. V. Nevitt in "Electronic Structure and Alloy Chemistry of the Transition Elements" (Paul A. Beck, Ed.), p. 101, Wiley, New York (1963). The nonparticipation rule as stated here excludes the solid solubility range in which A element may substitute for B element and vice versa up to the limit of solid solubility range.

TABLE I

SUMMARY OF ALL THE KNOWN A_3B(β-W) TYPE COMPOUNDS[a]

v.e.	v.e.	8	9	10	1	2	3	4	5	3	4
v.e.	A \ B	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Al	Si
4	Ti	○ 1	○ 2	○ 3	○ 4		●p 5			⊕ 3a	○ 3a
	Zr	○ 3	○ 3	○ 3b	○ 6	○ 3b	●p 7	●p 8		● 9	◐ 3a
	Hf	○ 10	○ 11	○ 12						○ 13	○ 3b
5	V	○ 3a	●p 14	●p 15	I 16	○ 17	●p 18	● 19	● 20	● 21	● 3a
	Nb	○ 3b	○ 22	○ 23	○ 24		●p 25	● 26		●p 27	● 3
	Ta	○ 28	○ 29	○ 30			○ 31	⊕ 32			⊕ 32
6	Cr		○ 3a	○ 33	I 3a	○ 3a	● 34	● 35		○ 3	● 36
	Mo	○ 3a	○ 37				● 18	●p 38		●p 39	●p 3a
	W	○ 3a	○ 3a	○ 3a				○ 3a			
	A \ B	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb		
4	Ti	○ 40	○ 3c	○ 41	⊕ 3	○ 42	○ 7		● 43		
	Zr	○ 40	○ 3c	○ 44	⊕ 3	○ 45	⊕ 7	●p 46	⊕ 32		
	Hf		○ 3c	○ 3b	○ 47			○ 3c	○ 3c		
5	V	○ 48	● 49	●p 50	I 3a	● 19		● 51	● 52		
	Nb		●p 53	○ 54	I 55		● 56	●p 57	● 58		
	Ta	○ 59	○ 60	⊕ 3c	I 59			● 61	● 52		
6	Cr	●p 62	● 49	○ 3a	I 63	○ 42					
	Mo	○ 64	○ 65	○ 3c	I 3a			● 66			
	W	○ 59	○ 67	○ 68	I 55						
	A \ B	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		
4	Ti		● 69	● 70	● 3	● 71	● 71		⊕ 3b		
	Zr		⊕ 3	○ 72	●p 73	● 71	● 71	● 3c			
	Hf		○ 74	○ 3c	○ 75						
5	V	● 40	● 73	● 49	●p 76		● 71	● 19	● 77		
	Nb	● 78	● 79	●p 80	● 41		○ 81	● 21	● 66		
	Ta		⊕ 82	● 3	● 29	I 83					
6	Cr	●p 84	● 85	● 49	○ 86			I 3a			
	Mo	●p 87	●p 88	● 89	○ 90						
	W	○ 91	○ 3b	○ 3a	○ 86			I 3			

[a] (●) Existence of A_3B compound; (○) absence of any compound at the composition; (⊕) existence of a compound with A:B = 3:1 composition, but having a structure other than β-W type; (I) The system is immiscible at this composition. (p) The A_3B compound has been confirmed to be formed through either a peritectic or peritectoid reaction. Number in right upper corner is reference number.

4. Transition atoms of 3-A(d^1) and 7-A(d^5) do not participate in the formation of A_3B compounds either as A or B elements. Two exceptions to this rule are found in the formation of Mo_3Tc characterized by Darby and Zegler (*96*) and W_3Re identified by Federer and Steele (*97*) to be the β-W type.

5. For the given group of A atoms, the probability (or population) of the A_3B compound formation increases as B element (either a transition atom with *d*-orbital or nontransition atom with *s*-orbital) goes from 3*d* to 4*d* to 5*d* or from 4*s* to 5*s* to 6*s*.

6. On the other hand, for the given group of A atom, the probability (measured in term of population) of the formation of A_3B compounds decreases as B element (nontransition atom with *p*-orbital) goes from 4*p* to 5*p* to 6*p*.

7. Wherever the phase equilibrium diagram is definitely characterized, the A_3B compounds are shown to be formed consistently through either a peritectic or a peritectoid reaction (i.e., compound with incongruent melting point).

The electrochemical and/or size factors have been recognized or utilized as an explanation (*98*) in the formation of intermetallic compounds involving transition atoms. However, as shown above, the A_3B compounds formation is completely independent of these known factors. For example, Au and Ag react quite differently even though their atomic sizes are about the same. Indeed, the dominant, if not the only factor recognizable in Table I appears to be in the atomic orbital (e.g., stringent restriction on what type of atom can or cannot serve as A element). Inasmuch as the atomic orbital requirement is far more stringent in covalent bond than in metallic bond, it must be assumed that the degree of covalency in the A_3B compounds is high. This assumption is also in keeping with the observed "A-chain integrity" (straight chain of A atoms) found in the crystal structure of A_3B compounds.

In an attempt to better understand the mechanism of superconductivity, the A-chain integrity has been utilized as a boundary condition for a number of theoretical calculations, either based on a tight binding approximation (*99*) or aug-

TABLE II

SUMMARY OF A AND B ELEMENTS LISTED ACCORDING TO THE ATOMIC PERIODIC TABLE[a]

transition atom								non-transition atom				
▨	A			▨	B			B				
▨ 3-A	4-A	5-A	6-A	▨ 7-A	8-A	9-A	10-A	1-B	2-B	3-B	4-B	5-B
▨				▨						Al	Si	
▨ Sc	Ti	V	Cr	▨ Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
▨ Y	Zr	Nb	Mo	▨ Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
▨	Hf	Ta	W	▨ Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi

[a] The 3-A and 7-A group of atoms which do not participate in the formation of $A_3B(\beta\text{-W})$ type compound are shaded.

mented plane wave approach (*100*) or in term of molecular orbital theory (*101*). It is believed, from the observations made here that the A-chain integrity while important, is not sufficient and that other boundary conditions such as that described here must be added. This is to say that for any theoretical model of A_3B compounds to be aesthetically satisfying or physically significant, it must embrace within its framework, the principal manifestations observed in points 1 through 7.

The valence electron to atom ratio, e/a, for all the possible combinations of A_3B compounds are summarized in Table III. Comparison of Table I vs Table III shows that with the exception[3] of cases where B element is an 1-B or 2-B atom, there is roughly a one-to-one correspondence between the population of A_3B compounds and the superconducting critical temperature curve given by Matthias, Geballe, and Compton (*93*) in terms of the e/a ratio (maxima at $e/a = 6.5$ for B = transition atom and at $e/a = 4.7$ for B = nontransition atom). This observation indicates an intimate relationship between the crystal chemistry of A_3B compounds and their superconducting property; the more stable is the compound, the higher is the critical temperature. It follows therefore, once the crystal chemistry of the A_3B compounds is understood, the same understanding should also shed light on the mechanism of superconductivity.

Finally, it should be noted that metallurgically, the observation (7) tells us that the annealing of A_3B compounds must be carried out with extra care. In particular, the selection of annealing temperature must be made with a full knowledge of the peritectic temperature.

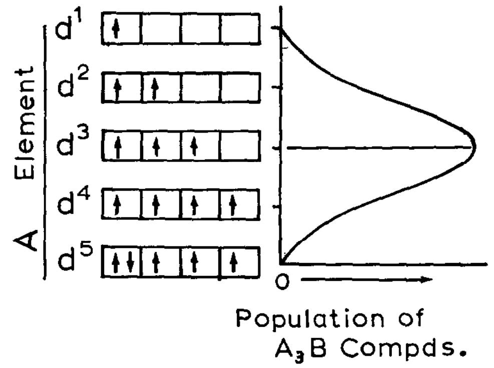

FIG. 1. Population of $A_3B(\beta\text{-W})$ type compounds vs d-orbitals of A element. The five independent energy levels in d-orbital are reduced to four by the fact, K, Ca are counted as 1-A 2-A whereas Cu, Zn are counted as 1-B and 2-B, respectively.

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TABLE III

THE AVERAGE VALENCE ELECTRON TO ATOM RATIO[a]

B:	*d*			*s*		*p*		
A	8	9	10	1	2	3	4	5
d								
4	5.00	5.25	5.50	3.25	3.50	3.75	4.00	4.25
5	5.75	6.00	6.25	4.00	4.25	4.50	4.75	5.00
6	6.50	6.75	7.00	4.75	5.00	5.25	5.50	5.75

[a] Arranged in the same way as Table I.

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[3] In cases of B = Au or Hg, this exception disappears if the valence electrons of these two atoms are taken as 11 and 12, respectively.

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