PRESSURE AND TEMPERATURE FORMATION OF A₃B COMPOUNDS[*]

II. Nb₃Ge, Nb₃Sn, Nb₃Pb, V-In and V-Pb

JEAN-MICHEL LEGER

Centre National de la Recherche Scientifique, 1, Place Aristide Briand, (92) Bellevue (France)

H. TRACY HALL

Brigham Young University, Department of Chemistry, Provo, Utah 84601, U.S.A.

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SUMMARY

The formation of the compounds Nb_3Ge, Nb_3Sn, Nb_3Pb has been investigated under high pressures and temperatures (20-70 kbar, 800-2200ºC). A new f.c.c. phase of Nb_3Sn has been synthetized; two cubic structures have been obtained from the reaction of niobium with lead and new structures for compounds of vanadium with lead or indium are also reported. The appearance of the $A15$ structure is discussed in terms of the ratios of the atomic radii of the elements and it is concluded that pressure helps its formation when the ratio r_A/r_B is smaller than a critical value.

1. INTRODUCTION

In a previous note[1] we examined the effects of high pressures on the formation of the two A_3B compounds, Nb_3Si and V_3Al. The endeavor to make these compounds in the $A15$ (or β-W) structure was stimulated by the claim[2] that they would possibly have the highest superconducting temperatures known up to now.

Our experiments employing high pressures did not lead to the formation of these compounds in the $A15$ structure but we were able to point out the important role which is played by the size of the atomic radii of the different elements. We concluded that Nb_3Si could not be made under high pressures but that V_3Al could be obtained if a sufficiently high pressure was used.

In the present note we describe the continuation of our investigations on the formation of A_3B compounds under high pressure and give the reaction diagrams for $3Nb + Ge$ and $3Nb + Sn$. Some experiments on the reactions $3Nb + Pb$, $3V + Pb$ and $3V + In$ are reported.

2. EXPERIMENTAL

The tetrahedral anvil press developed by H. T. Hall[3] was used to generate the high pressures and temperatures (20-70 kbar, 800-2200ºC). The sample, made from the powdered elements mixed in the stoichiometric ratio 3 to 1, is heated under pressure and finally quenched by cutting off the electrical power. It is then removed from the high-pressure cell and a Debye-Scherrer X-ray diffraction film obtained from it. Details of the experimental procedure[1], the pressure and temperature calibrations and sample geometry have been previously given.

The experiments on $3Nb + Ge$ and $3Nb + Sn$ were of 2-5 minutes duration and those on $3Nb + Pb$, $3V + In$ and $3V + Pb$ from half-an-hour to two hours duration. The reactions described here were generally incomplete and in all cases, unless otherwise noted, diffraction lines of the high-melting element appeared

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[*] Most of this work has been done while at Brigham Young University.

on the X-ray films.

3. RESULTS

3Nb + Ge (Fig. 1)
   (a) At high temperature a mixture of a hexagonal and cubic structures is obtained:
      (i) The lattice parameters of the hexagonal structure are:

$$a = 7.677 \pm 0.003 \text{ Å} \qquad c/a = 0.691$$
$$c = 5.309 \pm 0.002 \text{ Å}$$

      (ii) The cell constant of the cubic structure is

$$5.163 \pm 0.007 \text{ Å}.$$

   (b) At lower temperatures, but pressures higher than 26 kbar, there is a field widening with pressure where a mixture of three different structures is obtained:
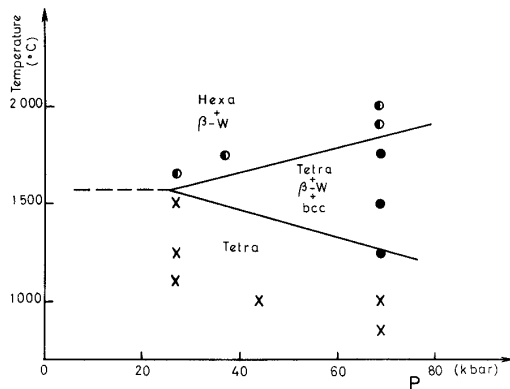

Fig. 1. Reaction diagram for 3Nb + Ge. ◑, hexagonal + β-W structures; ●, β-W, tetragonal and b.c.c. structures; ×, tetragonal structure. The reaction is always incomplete and some unreacted niobium remains in addition to the indicated structures.

      (i) The previous cubic structure.
      (ii) A tetragonal structure with the following lattice parameters:

$$a = 10.192 \pm 0.010 \text{ Å} \qquad c/a = 0.505.$$
$$c = 5.146 \pm 0.005 \text{ Å}$$

      (iii) A body-centered cubic structure which has a cell constant equal to 3.333 ± 0.003 Å, just slightly larger than that of pure niobium (3.307 Å).
   (c) At lower temperatures only the previously mentioned tetragonal structure was obtained.
      The lattice constants and the *c/a* ratio of the hexagonal or tetragonal structures are quite close to those of the hexagonal or tetragonal Nb_5Ge_3 compounds which are already known at normal pressure:

Nb_5Ge_3 Hex. (Mn_5Si_3 type)	$a = 7.718$ Å	$c/a = 0.696.$
	$c = 5.370$ Å	
Nb_5Ge_3 Tetr. (W_5Si_3 type)	$a = 10.148$ Å	$c/a = 0.508.$
	$c = 5.152$ Å	

      It has been shown that the *A*15 compounds formed at atmospheric pressure are not stoichiometric and that the parameter varies slightly with composition[4]:

5.177 Å for $Nb_3Ge_{0.45}$,
5.167 Å for $Nb_3Ge_{0.66}$.

It seems that the cubic structure which we made under pressure ($a = 5.163$ Å) probably corresponds to an $A15$ compound closer to the stoichiometry than those obtained at normal pressure.

3Nb + Sn (Fig. 2)

(a) At high temperatures a face-centered cubic structure, was obtained, no extra lines being present on the X-ray film. The lattice parameter of this f.c.c. Nb_3Sn phase is 4.412 Å ± 0.003 Å. This f.c.c. structure has been obtained alone only on one occasion when undertaking some temperature cycles between 1400 and 2200°C at 64 kbar. In the other runs in the absence of such cycling, we again obtained this f.c.c. structure but admixed with the cubic structure described below.
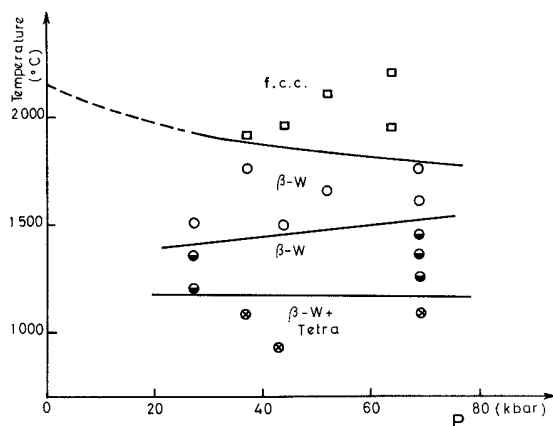

Fig. 2. Reaction diagram for 3Nb+Sn. □, f.c.c. Nb₃Sn; ○, pure β-W Nb₃Sn; ◖, β-W Nb₃Sn mixed with unreacted Nb and Sn; ⊗, β-W Nb₃Sn and tetragonal structure mixed with unreacted Nb and Sn.

(b) At temperatures between 1500 and 1800°C we obtained one other pure cubic structure, no extra line appearing on the X-ray film. The cell parameter of this cubic phase of Nb_3Sn is 5.300 ± 0.004 Å. From the experiment reported above it appears that this cubic phase is only metastable at higher temperatures and the boundary shown on Fig. 2 is certainly close to the equilibrium phase boundary.

(c) At temperatures between 1200 and 1500°C the latter cubic phase is still obtained but the reaction is now far from being complete.

(d) At temperatures below 1200°C a tetragonal structure is obtained; the cell constants are:

$a = 5.169 \pm 0.005$ Å $c/a = 2.04$.
$c = 10.539 \pm 0.009$ Å

At atmospheric pressure the f.c.c. phase of Nb_3Sn has never been reported. This phase probably exists only under pressure, just below the melting curve. No tetragonal structures with parameters close to those given here have been previously described.

The second cubic phase of Nb_3Sn corresponds, without any doubt, to the well known β-W phase which is stable up to the melting point at normal pressure; the lattice constants are in good agreement (5.30 instead of 5.28-5.29 Å).

3Nb + Pb

Below 850°C it has been impossible to detect any trace of reaction, of niobium with lead. At higher temperatures, and pressures greater than 20 kbar, we have been able to identify two cubic structures which have the following lattice parameters:

$a_1 = 4.208 \pm 0.004$ Å,
$a_2 = 5.319 \pm 0.005$ Å.

The smaller cubic structure is stable at higher temperatures (1500ºC) than the larger one and was previously completely unknown. At normal pressure only one compound of niobium with lead has been reported[5], claimed to be an $A15$ Nb_3Pb compound with a lattice parameter ($a = 5.270$ Å) which is smaller than that of β-W Nb_3Sn (5.28-5.30 Å). This seems quite unlikely and is presumed[5] to come from a lead deficiency. The compound was prepared by sintering the niobium powder mixed with lead pellets in a graphite container (200 atm, 1500ºC) and was followed by annealing at 1100ºC. The larger parameter we report is in good agreement with what would be expected from a steady increase over the complete column of the Periodic Table. It is possible that some carbon contamination may explain the stabilization of a structure which otherwise can be made only at high pressures, but it is surprising that the smaller cubic structure was not found at ordinary pressure.

V_3Pb

At normal pressure the existence of a β-W compound, V_3Pb, has also been claimed[5]. It was prepared in the same way as Nb_3Pb but, here again, the cell parameter ($a = 4.937$ Å) appears to be too small, being just equal to that of V_3Sn. The explanation is likely to be the same as in the previous case.

We investigated the reaction $3V + Pb$ under high pressures and temperatures. Up to 1400ºC we did not find any trace of reaction; at 1700ºC some reaction seems to occur but it is too slight to be identified. From two runs at 25 or 50 kbar and around 2000ºC we have been able to detect a tetragonal structure:

$a = 6.175 \pm 0.010$ Å $c/a = 1.51.$
$c = 9.344 \pm 0.015$ Å

Such a structure has never been reported; no cubic β-W structure could be found.

V_3In

We also investigated the reaction $3V+In$. Up to 1000ºC, there was not the slightest trace of reaction. At 2000ºC and 45 kbar we have been able to make a tetragonal structure:

$a = 6.153 \pm 0.011$ Å $c/a = 1. 54.$
$c = 9.477 \pm 0.017$ Å

No compound of vanadium was known up to now but no cubic structure could be found under pressure.

4. DISCUSSION

The syntheses of Nb_3In[6], Nb_3Bi[6], and probably Nb_3Pb are possible by the use of high pressures but this is not the case for Nb_3Si, V_3In or V_3Pb. The reason for this difference calls for consideration.

In our previous note on Nb_3Si and V_3Al we pointed out that the key factor was not the value of the cell parameter in the β-W structure but the ratio of the atomic radii of the two elements. This is confirmed by the experiments reported here. For example, it is possible to compute the lattice parameter of V_3In in the β-W structure using Geller's technique[7]. This yields a value of 4.92 Å which lies between values of already existing compounds but, nevertheless, the compound could not be made under pressure.

If we now look at the ratio of the atomic radii (the atomic radius is taken as half the shortest distance of approach in the element) we see that the values for the compounds which can be made at normal pressure are such that (see Table I):

$0.99 \le r_A/r_B \le 1.17$ $A = $ niobium,
$0.94 \le r_A/r_B \le 1.12$ $A = $ vanadium.

From Table I it can be understood why we have not been able to synthetize V_3In or V_3Pb under pressure. The values of their ratios, r_A/r_B (0.81, 0.75), are too far from the values of already existing compounds ($r_A/r_B \ge 0.94$) and the increase due to pressure is not sufficient to reduce the gap effectively. This increase comes from the larger compressibility of the low-melting element (B) with respect to the high-melting element (A). For V_3Al we found that the pressure required to shift the ratio from 0.92 to 0.94 would be at least 120 kbar; much higher pressures would be needed for V_3In or V_3Pb.

TABLE I

ATOMIC RADIUS OF EACH ELEMENT (TAKEN AS BEING HALF THE SHORTEST DISTANCE OF APPROACH IN THE PURE ELEMENT), THEIR RATIOS FOR THE DIFFERENT COMPOUNDS AND THE LATTICE PARAMETER OF THE A₃B COMPOUNDS IN THE A15 STRUCTURE

		B												
		Al	*Ga*	*In*	*Tl*	*Si*	*Ge*	*Sn*	*Pb*	*As*	*Sb*	*Bi*	*Se*	*Te*
$r(Å)$		1.43	1.22	1.62	1.71	1.17	1.22	1.40	1.75	1.21	1.40	1.46	1.17	1.37
	A													
r_A/r_B	Nb	1.00	1.17,	0.88**	0.84	1.22	1.17	1.02	0.82**	1.18	0.99	0.98**	1.22	1.04
	V	0.92	1.07	0.81	0.77	1.12	1.07	0.94	0.75	1.08	0.94	0.90		0.96
$a(Å)$	Nb	5.19	5.15	5.30**	--	5.06*	5.17	5.30	5.32**	5.10*	5.26	5.32**	--	--
A_3B	V	4.83*	4.82	4.92*	--	4.72	4.77	4.94	4.96*	4.75	4.92	4.95*	--	--

* Calculated (unknown compound)
** Compound made under pressure
-- Unknown compound

For the niobium compounds, pressure has extended the range of ratios for which a β-W structure can be obtained; the limits are now:

$$0.82 \leq r_A/r_B \leq 1.17 \quad A = \text{niobium.}$$

This increase is toward the small values of the ratio, as would be expected from the size effect, but it is also too large to be explained solely by this effect. It is noteworthy that the outer electronic shells are different: in niobium the s shell is incomplete: $4d^4, 5s^1$ but is filled in vanadium $3d^3, 4S^2$.

From Table I it can also be seen which A_3B compounds it should be possible to produce in the β-W structure under high pressures; these compounds should have a ratio included between the values previously given. It is seen that:

Nb_3Tl	$r_A/r_B = 0.84.$	This compound should be easier to make than Nb_3Pb.
V_3Tl	$r_A/r_B = 0.96.$	
		This compound should also be producible under pressure but many compounds of vanadium with tellurium are known, and the β-W structure is not necessarily the most stable one.
Nb_3Te	$r_A/r_B = 1.04.$	
		This compound is not formed at normal pressure but high pressures could help its formation because of the large difference in the melting temperatures.

The ratio of the atomic radii determines the formation of the A_3B compounds in the β-W structure but their formation seems also to be correlated with the pressure reaction diagrams. In effect, the same structures appear and the phase boundaries are somewhat similar in the diagrams obtained for 3Nb+Si[1] and 3Nb+Ge, the differences being the fields where the b.c.c. structures can be made, and the appearance of the β-W Nb_3Ge phase simply admixed with a structure already existing. The two reaction diagrams are similar and the ratios r_A/r_B are then very close together (1.22 and 1.17). This is not so for the diagram for 3Nb+Sn but the ratio is much lower (1.02) and the structures which are formed are quite different. Moreover, it is precisely when the ratio is quite close to 1 that we have been able to obtain, under pressure, a β-W structure which is not admixed with anything else. The reaction of niobium with lead is always much smaller than in the previous case and the β-W structure appears only above 20 kbar but the ratio is now very low. Unfortunately, it is impossible to make the same correlations for the compounds containing vanadium because their reaction diagrams have not been determined. Nevertheless, we obtained tetragonal structures with similar c/a values in the three reactions we studied.

It would be interesting to study the superconducting properties of the compounds made under pressure. This could enable the exact compositions to be determined and may possibly lead to higher transition temperatures.

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