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PRESSURE AND TEMPERATURE FORMATION OF A_3B COMPOUNDS

I. Nb_3Si AND V_3Al

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SUMMARY

The formation of the two compounds Nb_3Si and V_3Al has been investigated under high pressures and temperatures (20–70 kbar, 1000–2000°C). In no case was it possible to synthesize a compound with the cubic *A*15 structure, but in both cases a body-centered cubic structure, previously unknown, has been obtained. Other new compounds of vanadium with aluminum are also reported. The appearance of the *A*15 structure is discussed and it is suggested that it may be possible to synthesize cubic *A*15 V_3Al under very high pressures but that cubic *A*15 Nb_3Si should not form at any pressure.

I. INTRODUCTION

The intermetallic compounds of the type A_3B, where A is an element of columns IVB or VB and B an element of columns IIIA or IVA, are well known for their superconducting properties[1,2] when they are formed in the cubic *A*15 structure (also known as β–W). This is the reason why this very peculiar structure has been extensively studied and many attempts have been made to prepare a large number of these A_3B compounds. In the case of V_3Al and Nb_3Si, very little or no success has been achieved by conventional means, so it has been felt that the use of high pressures could be a good way to achieve these syntheses. This can be easily justified: the melting temperatures of the two elements are very far apart; in both cases they differ by at least one thousand degrees centigrade. In addition, pressure displaces equilibrium and one can hope to make, under pressure, a new compound which will be metastable at room temperature and pressure. Furthermore, it has been reported that V_3Al has been synthesized in the *A*15 structure, either by codeposition of the vapors[3] on a heated substrate so as to form a thin film, or by the addition[4] of a small amount of silicon. This also, by analogy with other cases, suggests that pressure could help to stabilize this *A*15 structure.

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In this study on formation of A_3B compounds we mainly looked for the *A*15 structure; however, the different phases we made have also been indexed, and we show below the results of our experiments for the reactions 3Nb + Si and 3V + Al.

II. EXPERIMENTAL

The tetrahedral anvil press developed by H. T. Hall[5] was used to generate the high pressures and temperatures needed for this work. The sample was made of the two powders mixed in the stoichiometric ratio 3 to 1. The starting materials were generally −100 to −200 mesh; the purity was always better than 99.9% except for vanadium which was only 99.9%; for silicon it was better than 99.99%.

The mixed powders were hand compacted in the high pressure cell. This cell is essentially made of a pyrophyllite tetrahedron and a tubular graphite heater, lined with boron nitride to prevent any reaction between the sample and the graphite. At each end there is a small graphite disc and electrical contact with the anvil is made through a molybdenum tab. The temperature was not directly measured but was deduced from the electrical power dissipated in the heater with the help of a calibration curve[6] previously established for different pressures. The pressure itself was also known from a calibration curve[6] made at room temperature in the usual way by monitoring the discontinuities of the electrical resistance of cerium, mercury, bismuth, thallium, ytterbium and barium.

Nb_3In[7] was synthesized some years ago using high pressures and temperatures in a belt-type apparatus. It was then indicated that to obtain the correct stoichiometry and reproducible results, the sample had to be compacted quite strongly and placed in a niobium container. We used the simplified high pressure cell described above (there is no metallic capsule) only after being sure that it was leak proof (a molten metal stays inside the boron nitride tube), and after having verified the reproducibility of results as previously reported.

All the runs were made in the same way. The pressure was first increased up to the desired value (maximum pressure: 70 kbar) then the load was held constant while the temperature was raised. In the runs reported in this work, the temperature was kept constant during two to five minutes, unless otherwise noted, the shortest time corresponding to the highest temperature. This length of time was found to be sufficient; a longer one did not bring any modification nor did it make the reaction more complete. After the time elapsed, the electrical power was suddenly cut off, which quenched the sample and the pressure was then released. The sample was then crushed and X-rayed in 0.5 mm glass capillaries which were rotated during exposure. X-ray data were taken using a G. E. XRD-5 with a Debye–Scherrer powder camera of 143.2 mm diameter. Copper radiation was used and the Nelson–Riley extrapolation applied to determine the lattice constants of cubic structures.

III. RESULTS

The results of our experiments are summarized in the reaction diagrams 1 and 2. They simply mean that under the conditions of pressure and temperature shown, the indicated structure is obtained. The boundaries are not always very well defined because the transitions are sometimes sluggish, and also it is difficult to say exactly

where a new phase appears when one or two others are already present. The boundaries have been shown according to the relative content of the phases. In all runs the reactions were very incomplete and at least diffraction lines of the high-melting metal always appeared on the X-rays films.

Nb_3Si (Fig. 1)

(a) At high temperature a compound which has an hexagonal structure is formed. The lattice parameters are:

$a = 7.536 \pm 0.006$ Å

$c = 5.257 \pm 0.004$ Å

(b) At low temperatures and low pressures a body-centered cubic structure mixed with a tetragonal one is obtained. The cell parameter of the b.c.c. structure is 3.377 Å, just slightly larger than that of pure niobium ($a = 3.306$ Å). The lattice parameters of the tetragonal structure are:

$a = 6.593 \pm 0.010$ Å

$c = 12.652 \pm 0.015$ Å

(c) At higher pressures the b.c.c. structure has disappeared. In no case have we been able to synthesize the cubic *A*15 structure we were looking for.

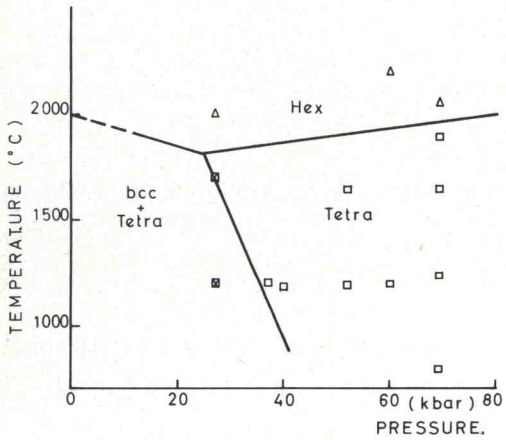

Fig. 1. 3Nb+Si reaction diagram. △, hex; □, tetra; ×, b.c.c. The reaction is always incomplete and some unreacted niobium remains in addition to the indicated structures.

As can be seen from Fig. 1, our data seem to indicate the existence of three different structures at atmospheric pressure: above 2000°C there is one hexagonal structure but below this temperature a tetragonal structure mixed with a b.c.c. one appears. It is worth noticing that among the different compounds which are known at normal pressure there is one, Nb_5Si_3, which is hexagonal ($a = 7.52$ Å, $c = 5.24$ Å) above 2000°C and tetragonal ($a = 6.570$ Å, $c = 11.884$ Å) below, but no b.c.c. structure with a parameter close to the one described here has been previously reported.

V_3Al (Fig. 2)

At ordinary pressure the reaction of vanadium with aluminum is very small, and only aluminum-rich compounds are known with, perhaps, the exception of a metastable b.c.c. V_3Al. At low temperatures ($T \leqslant 1300°C$) the reaction is very limited and longer runs do not make it more complete. In some cases we extended the time to four hours under pressure and temperature but this did not make any difference. Above 1500°C, the reaction is much faster but also very incomplete, and experiments were made as previously discussed.

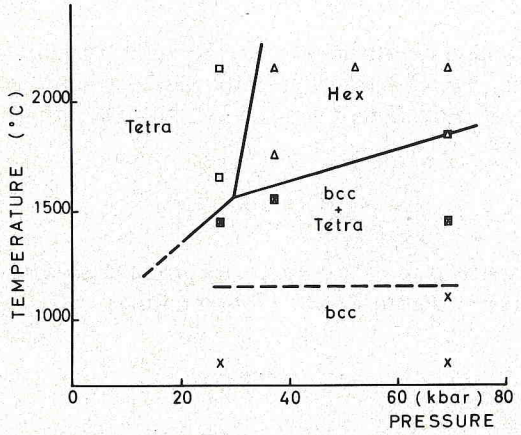

Fig. 2. 3V+Al reaction diagram. △, hex; □, tetra; ×, b.c.c. The reaction is always incomplete and some unreacted vanadium remains in addition to the indicated structures.

(a) At high temperatures and high pressures an hexagonal structure is obtained; the lattice parameters are:

$a = 7.070 \pm 0.006$ Å

$c = 9.565 \pm 0.008$ Å

(b) At lower pressures the lattice cell is quite different and becomes tetragonal with the following parameters:

$a = 6.167 \pm 0.009$ Å

$c = 9.481 \pm 0.013$ Å

(c) At lower temperatures a body-centered cubic structure mixed with the above tetragonal one is obtained. The cell parameter of the b.c.c. structure is 3.075 ± 0.002 Å, just slightly larger than the one of pure vanadium (3.030 ± 0.003 Å, as given by our measurements). In the low temperature region we obtained very little reaction but some traces of the b.c.c. phase seemed to be present.

A b.c.c. metastable phase, V_3Al, has been previously reported[9] with a lattice parameter equal to 4.92 Å, but its binary character was not firmly established. In our experiments no such phase has been found. The tetragonal and hexagonal structures we prepared under pressure were not previously known. Unfortunately, as in the previous case, we have not been able to synthesize the cubic *A*15 structure.

IV. DISCUSSION

One purpose of this study was the synthesis of a cubic *A*15 structure which would have probably shown an interesting superconducting temperature. The lack of success in both cases led us to look at the conditions required to make such a structure.

Using Geller's technique[10] it is possible to compute the lattice parameter of a A_3B compound in the *A*15 structure (Table I). For already known compounds the agreement is generally quite good.

TABLE I

CALCULATED LATTICE PARAMETER OF THE A_3B COMPOUNDS IN THE *A*15 STRUCTURE

The *A*15 radius of aluminum (1.39 Å) is deduced from the lattice parameter of Nb_3Al. It is then easy to deduce the cell constant of V_3Al.

a(Å)	Nb_3Si	Nb_3Ge	Nb_3Ga	Nb_3Sn	Nb_3Al
	5.06	5.12	5.15	5.30	5.19
a(Å)	V_3Si	V_3Ge	V_3Ga	V_3Sn	V_3Al
	4.72	4.77	4.82	4.94	4.83

Among the niobium series, Nb_3Si would have the smallest lattice parameter, and this is also true when all known *A*15 compounds[1] involving niobium are considered. This could explain why this compound does not exist or is not stable. It is not so for V_3Al for which the calculated lattice parameter falls between the values of the parameters of two already existing compounds. This could indicate that it should be possible to synthesize V_3Al in the cubic *A*15 structure.

It has also been known[1] for a long time that a condition of formation of this structure in the A_3B compounds is that the ratio of the atomic radius of the elements A and B should not be too different from unity.

In effect, for testing the possibility of formation of a compound A_3B, it seems much more natural to use the radius of an element itself rather than a specialized radius such as this β-W radius which is only usable to compute the lattice parameter of a compound A_3B once it is made in the β-W structure.

From Table II, it can be seen that the ratio rA/rB is the highest for Nb_3Si and the smallest for V_3Al. We are, indeed, in two extreme cases. If we consider that the condition to synthesize a cubic compound A_3B with the *A*15 structure is to obtain a ratio closer to unity, it is then easy to determine what will be the effect of pressure. The compressibilities[11] of the different elements have been measured: silicon is more compressible than niobium and in the same way aluminum is more compressible than vanadium. So in both cases pressure will increase the ratio rA/rB.. But for Nb_3Si the ratio at ordinary pressure is already larger than one, so pressure will make it even more different from unity. It is exactly the opposite for V_3Al because at room pressure the ratio is smaller than one. So it can be thought that pressure would prevent the formation of *A*15 Nb_3Si but would help the formation of

*A*15 V_3Al. One can try to make a rough evaluation of the pressure which would be necessary to synthesize β-W V_3Al by noting that this structure exists as soon as $rA/rB = 0.935$ (V_3Sn). A quick calculation shows that the required pressure to reach this value in the case of V_3Al is approximately 120 kbar. Perhaps it is not necessary to go up to this ratio (0.935); in this case the required pressure would be lower; but on the other hand it is necessary to heat to get some reaction, and as the thermal expansion coefficient of the low melting element (Al) is larger than that of the other element (V), this contributes strongly to increase the pressure. Anyway, it appears that pressure could lead to the synthesis of V_3Al but not of Nb_3Si.

TABLE II

ATOMIC RADII OF ELEMENTS AND THEIR RATIO FOR THE A_3B COMPOUNDS

The atomic radius of an element is taken as being half the value of the shortest distance.

*r*A	*V*	*Nb*			
	1.31	1.43			
*r*B	*Si*	*Ge*	*Ga*	*Sn*	*Al*
	1.17	1.22	1.22	1.40	1.43
*r*A/*r*B	Nb_3Si	Nb_3Ge	Nb_3Ga	Nb_3Sn	Nb_3Al
	1.22	1.17	1.17	1.02	1.00
*r*A/*r*B	V_3Si	V_3Ge	V_3Ga	V_3Sn	V_3Al
	1.12	1.074	1.074	0.935	0.916

The comparison of the two reaction diagrams is also very interesting. In both cases we find the same phases, only the boundaries are displaced. The two systems are very close, the main difference being that for 3Nb + Si the b.c.c. phase is stable at low pressures and that for 3V + Al the b.c.c. phase is stable at high pressures. The study of the reaction diagrams of similar compounds[7–12] shows that the β-W phase is often mixed with, or close to the b.c.c. phase. This adds evidence to the previous discussion: Nb_3Si in the *A*15 structure could not be made under pressure while V_3Al could possibly be made.

The study of the reaction diagrams of A_3B compounds is very useful to better understand the formation of the cubic *A*15 structure and will be continued in another paper. This understanding is quite necessary if we want to make superconductors with high transition temperatures.

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