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Beta-Wolfram Structure of Compounds Between Transition Elements and Aluminum, Gallium and Antimony

BY E. A. WOOD, V. B. COMPTON, B. T. MATTHIAS AND E. CORENZWIT
Bell Telephone Laboratories, Murray Hill, N. J., U.S.A.

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The compounds Nb_3Al, Nb_3Ga and Cr_3Ga have the β-wolfram structure (*A*15) as determined by the powder method. The space group is O_h^3–$Pm3n$ with 2 formula weights in the unit cell. For Nb_3Al, $a_0 = 5{\cdot}187$ Å; for Nb_3Ga, $a_0 = 5{\cdot}171$ Å; for Cr_3Ga, $a_0 = 4{\cdot}645$ Å.

More complete data are given for Mo_3Ga, V_3Ga, V_3Sb and Nb_3Sb whose preliminary lattice constants were reported previously. For Mo_3Ga, $a_0 = 4{\cdot}943$ Å; for V_3Ga, $a_0 = 4{\cdot}816$ Å; for V_3Sb, $a_0 = 4{\cdot}932$ Å; for Nb_3Sb, $a_0 = 5{\cdot}262$ Å.

The superconducting transition temperature for Nb_3Al is 17·5 °K.; for Nb_3Ga, 14·5 °K. and for V_3Ga, 16·5 °K. The remaining compounds are not superconducting above 1·02 °K.

Three new beta-wolfram compounds have been made in the course of a continuing search for superconductivity in substances with the beta-wolfram structure (Matthias, Geballe, Geller & Corenzwit (1954); Geller, Matthias & Goldstein (1955); Wood & Matthias (1956); Matthias, Wood, Corenzwit & Bala (1956)). These are Nb_3Al, Nb_3Ga and Cr_3Ga. Full data are also given for Mo_3Ga, V_3Ga, V_3Sb and Nb_3Sb whose preliminary lattice constants were reported by Matthias, Wood, Corenzwit & Bala (1956). Our data for Mo_3Al which was assigned the beta-wolfram structure in a report of the Climax Molybdenum Co. of Michigan (1951) are also given.

The lattice constants, interatomic distances and superconductivity data are listed in Table 1. The observed intensities are listed in Table 2, together with the intensities calculated from the formula

$$I \propto p|F_{hkl}|^2\{(1+\cos^2 2\theta)/\sin^2\theta\cos\theta\}\times 10^{-5}\,,$$

where p is the multiplicity factor, F_{hkl} the structure amplitude, and the remaining term is twice the combined Lorentz and polarization factors. The scattering factors for Nb, Mo, Ga, and Sb were obtained from the paper by Thomas & Umeda (1957), for Cr and Al from the paper by Viervoll & Ögrim (1949) and for V from the *International Tables* (1935). Dispersion corrections from Dauben & Templeton (1955) were applied.

The agreement between observed and calculated intensities in Table 2 is satisfactory with the exception of the case of Nb_3Sb which is discussed in the last paragraph of the paper. Absorption most probably accounts for the low intensity of the low angle lines.

The β-wolfram structure belongs to space group

Table 1. *Lattice constants, interatomic distances and superconductivity data for A_3B compounds*

Compound	Lattice constant a_0 Å	Interatomic distances, Å B–A	$(A$–$A)_1$	$(A$–$A)_2$	Superconducting transition temperature °K.
Nb_3Al	$5·187 \pm 0·002$	2·900	2·594	3·175	17·5°
Nb_3Ga	$5·171 \pm 0·002$	2·890	2·586	3·166	14·5°
Mo_3Al	$4·950 \pm 0·001$	2·767	2·475	3·030	Not superconducting above 1·02°
Mo_3Ga	$4·943 \pm 0·002$	2·763	2·472	3·026	Not superconducting above 1·02°
V_3Ga	$4·816 \pm 0·002$	2·692	2·408	2·948	16·5°
Cr_3Ga	$4·645 \pm 0·004$	2·596	2·322	2·844	Not superconducting above 1·02°
V_3Sb	$4·932 \pm 0·002$	2·757	2·466	3·019	Not superconducting above 1·02°
Nb_3Sb	$5·262 \pm 0·002$	2·941	2·631	3·221	Not superconducting above 1·02°

Table 2. *Comparison of calculated with observed intensities (visually estimated)*

hkl	Nb_3Al		Nb_3Ga		Mo_3Al		Mo_3Ga		V_3Ga		Cr_3Ga		V_3Sb		Nb_3Sb	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
110	12.4	s	2.03	Abs.	11.7	s	2.2	w	0.8	m	0.4	vw	6.1	m	1.8	vw
200	8.5	s	13.8	s[a]	7.1	m	12.9	s	1.8	s	2.1	s	4.3	m	27.1	m-s
210	57.1	vvs	56.4	vvs[b]	50.1	vvs	52.1	vvs	2.2	vs	3.8	vs	2.5	m	60.1	s
211	18.6	vs	30.9	s	15.7	vs	27.7	vs	3.2	vvs	4.3	vs	8.9	s	59.2	s
220	1.7	vw	0.3	Abs.	1.5	w	0.3	vvw	0.1	w-m	0.05	vvw	0.9	vw	0.3	Abs.
310	2.3	w-m	0.5	m-s[b]	2.0	m	0.5	w[a]	0.2	m	0.09	vw	1.6	w	0.4	Abs.
222	8.4	m-s	6.0	w-m[a]	7.0	vs	5.7	m-s	0.05	vw	0.3	w	0.1	Abs.	3.5	w
320	12.1	s	11.8	m	9.9	vs	11.0	s	0.7	m-s	1.8	s	0.7	vw	12.6	m-s
321	9.1	m-s	14.5	m	7.2	vs	13.1	s	3.6	vvs	6.4	vvs	9.2	s	29.6	s
400	5.8	m	7.0	w-m	4.7	m-s	6.5	m-s	1.7	s	6.0	vvs	2.9	m	10.2	m-s
411,330	1.2	vw	0.3	Abs.	1.2	w	0.3	vw[a]	-	-	-	-	7.7	m-s	0.3	vw[a]
420	2.6	w-m	4.1	vw	2.1	m	3.8	m	-	-	-	-	-	-	8.4	m
421	11.2	s	11.1	m	9.9	vs	10.8	s	-	-	-	-	-	-	11.8	m-s
332	2.3	w-m	3.6	vw	1.9	m	3.4	m	-	-	-	-	-	-	7.4	m
422	0.6	vvw	0.1	Abs.	0.6	vvw	0.2	Abs.	-	-	-	-	-	-	0.1	Abs.
510,431	1.6	w	0.4	Abs.	1.8	m	0.5	w[a]	-	-	-	-	-	-	0.4	vvw[a]
520,432	13.0	s	12.9	m	13.4	vvs	14.2	vs	-	-	-	-	-	-	13.0	m-s
521	3.8	w-m	5.9	w	3.6	m-s	6.4	m-s	-	-	-	-	-	-	11.7	m-s
440	6.1	m	7.4	w-m	6.4	s	9.1	s	-	-	-	-	-	-	10.2	m-s
530,433	1.1	vw	0.3	Abs.	1.5	m	0.4	vw	-	-	-	-	-	-	0.2	Abs.
600,442	2.7	w-m	4.2	vw	3.0	m-s	5.5	m-s	-	-	-	-	-	-	8.1	m
610	5.2	m	5.2	w	7.0	vs	7.5	s	-	-	-	-	-	-	5.0	w-m
611,532	7.1	m	11.2	m	9.2	vs	16.8	vs	-	-	-	-	-	-	21.3	s
620	0.8	vvw	0.2	Abs.	1.9	m	0.5	vw	-	-	-	-	-	-	0.2	w
541	1.9	vw	0.6	Abs.	-	-	-	-	-	-	-	-	-	-	0.4	Abs.
622	23.1	vs	19.8	m-s	-	-	-	-	-	-	-	-	-	-	6.2	m
630,542	-	-	-	-	-	-	-	-	-	-	-	-	-	-	34.9	vs
631	-	-	-	-	-	-	-	-	-	-	-	-	-	-	50.7	vvs

$a = \beta$ line coincident; $b =$ Nb line coincident.

The intensities of the various substances are not comparable with each other because of differences in exposure (*vs* = very strong; *s* = strong; *m* = medium; *w* = weak).

O_h^3–$Pm3n$. The formula is A_3B in which the A atoms occupy position $6(c)$: $\pm(\frac{1}{4}, \frac{1}{2}, 0;\ \circlearrowleft)$; the B atoms occupy positions $2(a)$: $(0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Each B atom is coordinated to twelve A atoms at the distance B–$A\,(\frac{1}{4}a_0\sqrt{5})$. Each A atom is coordinated to two A atoms at the distance $(A$–$A)_1$, $(\frac{1}{2}a_0)$; to eight A atoms at distance $(A$–$A)_2$, $(\frac{1}{4}a_0\sqrt{6})$; and to four B atoms at distance B–A. The structure has been described in the above papers and by Hägg & Schönberg (1954).

The composition of alloys prepared in the arc furnace is not precisely known since losses cannot readily be avoided. Chemical analyses of the samples were not made because more than one phase was present in all cases. In some cases the lattice constant was invariant throughout a series of specimens with different initial proportions of components, indicating constant composition of the phase in question. Where a range of lattice constant was observed, this is reported. When the reactants were sealed in silica tubes, no attempt was made to evacuate the tubes because of the large volume of sample relative to the amount of air in the tube. A rough calculation shows that the amount of oxide or nitride formed would be negligibly small. No nitride or oxide diffraction lines are observed in the films.

X-ray diffraction powder photographs were taken of the resulting product, using a Norelco camera of 114·6 mm. diameter with Cu K radiation for the niobium and molybdenum compounds and Cr K radiation for the vanadium and chromium compounds.

Nb_3Al (Corenzwit, 1958) has a transition temperature to the superconducting state of 17·5 °K. This is the highest transition temperature of any substance known to date except that of Nb_3Sn (18·05 °K.). It was prepared by heating an aluminum–niobium pressed pellet in a helium arc furnace. The lattice constant ranged from 5·185 Å to 5·194 Å. This niobium–aluminum compound was accompanied by a very small amount of impurity which was probably another niobium–aluminum phase.

Nb_3Ga was prepared by melting gallium with niobium powder in a sealed fused silica tube at 1200 °C. and subsequently fusing the product in the arc furnace in a helium atmosphere. Without the arc furnace fusion, the β-W structure was not obtained. The specimen with the constants reported in Table 1 was made by the reaction of niobium and gallium in atomic proportions of 2:1, but preferential loss of gallium certainly took place during the arc furnace fusion. The powder pattern showed a small amount of niobium and a very small amount of gallium present. No variation of lattice constant was observed although initial proportions of components were varied from 4:1 to 2:1.

Mo_3Al was formed by the arc furnace reaction of the stoichiometric amounts of the constituents in a helium atmosphere. Molybdenum was present as an impurity, indicating some aluminum loss in the furnace. The lattice constant was unchanged in a melt containing 58 atomic% Al. Here in addition to the β-W phase and Mo, a third phase was present which was not identified. Mo_3Al was previously reported by the Climax Molybdenum Co. of Michigan (1951), as having the β-W structure with a lattice constant of 4·951 Å which agrees with the value reported in Table 1.

Mo_3Ga, unlike Nb_3Ga, can be formed by reaction in a sealed fused silica tube at 1200 °C. A small amount of free molybdenum was present, indicating some loss of gallium to the walls of the tube. No variation of lattice constant was observed although initial proportions of components were varied from 4:1 to 1:1.

V_3Ga, was formed by causing the elements to react in stoichiometric proportions in the helium arc furnace. A small amount of a second phase, not yet identified, was present in all cases. No variation in lattice constant was observed when the initial proportions of reactants were varied from 3:1 to 5:1. In one sample made from initial proportions 2V:1Ga, a third phase was present. The unidentified phases are not VN, V_2O_3, V_2O_5, GaN, nor any of the gallium oxides. The V_xN_y structures described by Hahn (1949) are not present.

Cr_3Ga forms in the β-W phase when the components are heated to 1200 °C. in a sealed fused silica tube. When more than the stoichiometric amount of chromium is present, the product is inhomogeneous and may contain crystals with the β-W structure ranging in lattice constant from 4·632–4·649 Å. When the proportions of chromium and gallium are 2:3 a very interesting structure results. The strongest lines in the powder diagram can be indexed on a primitive cubic cell with $a_0 = 2{\cdot}82$ Å. However, weaker lines require a larger unit cell and the true unit cell has not yet been determined. An attempt is now being made to obtain a satisfactory single crystal for further work on this compound.

The two antimony compounds presented the greatest preparative and analytical difficulties of any of the compounds herein reported. They were prepared in sealed fused silica tubes and could not be obtained without the presence of other phases. There appears to be only one other phase accompanying the β-W V_3Sb phase. Its pattern is closely similar, though not identical, with that of the unidentified phase accompanying the V_3Ga. Since only one sample of V_3Sb was available, no information concerning the constancy of the lattice constant could be obtained.

In all of the foregoing cases, the film used for the data in Tables 1 and 2 showed very few relatively weak lines in addition to those of the β-W phase. In the case of Nb_3Sb there are about 32 extra lines, some of which are of weak to medium strength. Nearly all of the stronger lines can be identified as NbO, primitive cubic, $a_0 = 4{\cdot}210$ Å (Brauer (1941) and Andersson & Magnéli (1957)). The remaining lines are not those of Nb, NbO_2 or any of the forms of Nb_2O_5, Sb, or Sb_2O_3. Because of the large number of unidentified lines in this pattern, some of which might be superimposed on those of the Nb_3Sb compound, the identification of this structure as β-W is less well-established. The presence of impurities may account for the discrepancy between the calculated and observed intensity for the {620} reflection.

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