Acta Cryst. (1959). **12**, 500

The Crystal Structure of VCo_3

By Shozo Saito

Department of Mining & Metallurgical Engineering, University of Illinois, Urbana, Illinois, U.S.A.

(*Received* 8 *December* 1958 *and in revised form* 30 *January* 1959)

The crystal structure of VCo_3 has been determined by X-ray analysis. The structure is ordered close-packed hexagonal, $P\bar{6}m2$, with 24 atoms per unit cell. $a_0 = 5{\cdot}032$ Å and $c_0 = 12{\cdot}27$ Å. This structure is closely related to the ordered cubic structure of the $AuCu_3$-type.

In an investigation of the vanadium–cobalt system, Koster & Schmid (1955) found that in the neighborhood of 25 at.% V the face-centered-cubic solid solution becomes ordered below 1070 °C. and very weak super-lattice lines could be observed. However no detailed information was given for the crystal structure of the ordered phase. The present investigation was undertaken to determine this crystal structure.

Experimental methods

The alloys used in the present work were prepared by arc melting in a water cooled copper crucible under helium atmosphere. Electrolytic cobalt and vanadium, both 99·9% pure, were used as the starting materials. Chemical analyses of the alloys were not made, but the melting losses were not higher than 2% for any alloy. Sealed in evacuated fused silica tubes, the ingots were first homogenized at 1175 °C. for 24 to 48 hrs., quenched, and then annealed at 1000 °C. for 72 hr., followed by quenching in cold water. Powder specimens for X-ray work were made by crushing the heat-treated solid specimens into fine powders and re-annealed at 1000 °C. about 1 hr. and quenched, to remove strains.

X-ray diffraction patterns were taken using an asymmetrical focusing camera. Cr K radiation was used in order to increase the intensity of the superlattice lines as a result of the anomalous scattering of Cr $K\alpha$ radiation by vanadium atoms. The lattice parameters were determined using a symmetrical focusing camera of 60 mm. radius and Cr K radiation. The $(20\bar{2}9)$, $(22\bar{4}0)$ and $(20\bar{2}8)$ reflections, which appeared in the high θ-angle range, were used for the calculation of lattice parameters. Microscopic-examination was carried out in conjunction with the X-ray diffraction work, to determine the number of phases present in each alloy. For this purpose, the polished specimens were etched for about 30 sec. with a 50% nitric acid–water solution.

Experimental results

The alloy with 25 at.% V, homogenized at 1175 °C., showed only the normal diffraction pattern corresponding to the face-centered-cubic structure. After reannealing the same alloy at 1000 °C., however, there appeared additional diffraction lines, as shown in Table 1. Many of the additional reflections were very weak, as reported by Koster & Schmid (1955), but some of them, namely Nos. 18, 21, 49 and 50, were as strong as the 'face-centered cubic' reflections. (The last reflection was observed only in the high angle patterns taken with the symmetrical camera.) It must be taken into account that the intensity varies considerably with increasing Bragg angle as a result of the particular geometry of the asymmetrical focusing camera. Three of the weak lines, Nos. 6, 9+10, and 31, corresponded to the superlattice lines (100), (110) and (210) for the $AuCu_3$-type ordered face-centered-cubic structure. Accordingly, after the 1000 °C. anneal the alloy may have been considered as a two-phase one, consisting of an ordered phase of the $AuCu_3$-type and a second unidentified phase. In order to establish whether or not the alloy in fact consisted of one or two phases, four additional alloys with 22·4, 27·8, 33·1 and 38·4 at.% V were prepared under the same conditions as described above. Metallographic and X-ray study of all five alloys showed, in agreement with Koster & Schmid (1955), that the 25 at.% V alloy consisted of a single phase, while the alloys containing 33·1 and 38·4 at. % V consisted of two phases, namely, the phase based on VCo_3 and σ. The 27·8% V alloy consisted of a single phase, identical with that of the 25 at.% V alloy, while the 22·4 at.% V alloy had, in addition to the phase based on VCo_3, a second phase based on α-cobalt. As a result, it was concluded that the complex X-ray patterns of the 25 and 27·8 at.% V alloys must be interpreted in terms of a single structure.

It was noted that two diffraction lines, Nos. 18 and 49, were very close to the diffraction lines, Nos. 19 and 48, of the hypothetical '$AuCu_3$-type structure'. This suggested that the actual lattice of VCo_3 may be slightly distorted as compared with the hypothetical 'cubic lattice'. No such splitting was observed for the (200)-line of the 'cubic lattice'. From these observations it was clear that the crystal symmetry of the distorted lattice is not tetragonal as it is in the case of VNi_3. With the help of the hexagonal Bunn chart it was found that all observed reflections may be fitted to a hexagonal unit cell. The lattice para-

Table 1. *X-ray diffraction pattern for* VCo_3 *with* Cr $K\alpha$ *radiation*

Line No.	Tentative cubic indices	Final hexagonal indices	Spacing in Å		Relative intensity		
			Calc.	Obs.	Calc.	Obs.	
1	—	0001	12·27	—	0	—	outside of angle range of camera used
2	—	0002	6·137	—	0	—	
3	—	$10\bar{1}0$	4·358	—	0	—	
4	—	$10\bar{1}1$	4·107	—	1·75	—	
5	—	0003	4·091	—	0	—	
6	100	$10\bar{1}2$	3·553	3·51	4·99	*vw*	
7	—	0004	3·069	—	0	—	
8	—	$10\bar{1}3$	2·983	2·97	6·07	*vw*	
9	110	$11\bar{2}0$	2·516	2·51	8·30	*vw*	
10		$10\bar{1}4$	2·509		4·15		
11	—	$11\bar{2}1$	2·465	—	0	—	
12	—	0005	2·455	—	0	—	
13	—	$11\bar{2}2$	2·328	—	0	—	
14	—	$20\bar{2}0$	2·179	—	0	—	
15	—	$20\bar{2}1$	2·145	2·135	135·4	*m*	
16	—	$11\bar{2}3$	2·143		0		
17	—	$10\bar{1}5$	2·139		1·34		
18	—	$20\bar{2}2$	2·053	2·049	374·4	*s*	
19	111	0006	2·046	2·042	249·6	*s*	
20	—	$11\bar{2}4$	1·946	—	0	—	
21	—	$20\bar{2}3$	1·923	1·919	470·8	*s*	
22	—	$10\bar{1}6$	1·852	—	0	—	
23	200	$20\bar{2}4$	1·777	1·775	324·4	*s*	
24	—	$11\bar{2}5$	1·757	—	0	—	
25	—	0007	1·753	—	0	—	
26	—	$21\bar{3}0$	1·647	—	0	—	
27	—	$21\bar{3}1$	1·633	—	2·50	—	
28	—	$20\bar{2}5$	1·630	1·629	98·4	*w*	
29	—	$10\bar{1}7$	1·627	—	1·25	—	
30	—	$21\bar{3}2$	1·591	—	6·77	—	
31	210	$11\bar{2}6$	1·587	1·584	13·53	*vw*	
32	—	0008	1·534	—	0	—	
33	—	$21\bar{3}3$	1·520	—	9·02	—	
34	—	$20\bar{2}6$	1·491	—	0	—	
35	—	$30\bar{3}0$	1·453	—	5·40	—	
36	—	$21\bar{3}4$	1·451	—	6·77	—	
37	—	$10\bar{1}8$	1·447	—	2·70	—	
38	—	$30\bar{3}1$	1·443	—	0	—	
39	—	$11\bar{2}7$	1·439	—	0	—	
40	—	$30\bar{3}2$	1·414	—	0	—	
41	—	$30\bar{3}3$	1·369	—	0	—	
42	—	$21\bar{3}5$	1·368	—	2·61	—	
43	—	$20\bar{2}7$	1·366	1·367	76·22	*w*	
44	—	0009	1·364	—	0	—	
45	—	$11\bar{2}8$	1·310	—	0	—	
46	—	$10\bar{1}9$	1·303	—	4·33	—	
47	—	$21\bar{3}6$	1·283	—	0	—	
48	220	$22\bar{4}0$	1·258	1·259	403·1	*m*	
49	—	$20\bar{2}8$	1·255	1·256	201·6	*w*	
50	—	$20\bar{2}9$	1·156	1·156	200·8	*w*	

meters $a_0 = 5{\cdot}032$ Å and $c_0 = 12{\cdot}27$ Å for this hexagonal unit cell were determined from three high angle diffraction lines in a pattern taken with a symmetrical focusing camera. These lattice parameters are very closely related to the $a_c = 3{\cdot}55$ Å of the cubic lattice: $a_0 = \surd(2)a_c$, $c_0 = 2\surd(3)a_c$. Table 1 gives the spacings for all diffraction lines observed and the spacings calculated from the above lattice parameters. The agreement is in general quite good, and it is least satisfactory for the diffraction lines at the lowest θ angles, where the accuracy obtainable with the asymmetrical focusing camera is not very great. (See Table 1).

In a recent paper by Beck & Dwight (1959) it has been pointed out that the close-packed ordered structures of the $MgCd_3$-type and the $AuCu_3$-type may be described by suitable stacking of the same ordered layers first used by Laves & Wallbaum (1939) to describe the $TiNi_3$ structure. The unit cell of this ordered layer contains four atoms (see Fig. 1), one A atom (black circle) and three B atoms (empty circles). The dimension of the unit cell in the layer is equal to the sum of the diameters of atoms A and B: $a_0 = 2(r_A+r_B)$. For VCo_3 this sum is equal to 5·24 Å, if the Goldschmidt atomic radii for coordination number 12 are used. Compared with this value, there is a large contraction in the observed a_0-value. However such contractions were observed to occur in several structures of the $MgCd_3$ or $TiNi_3$ type (Beck

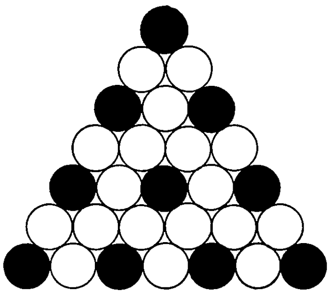

Fig. 1. Close-packed ordered layer of composition AB_3. A atoms are black circles and B atoms are empty circles.

& Dwight, 1959). It was, therefore, considered quite possible that the structure of VCo_3 may also be described in terms of the same layers.

The stacking scheme for the $MgCd_3$ structure may be designated (Beck & Dwight, 1959) as *abab*. The cubic $AuCu_3$-type structure and the hexagonal $TiNi_3$-type structure are three- and four-layer close-packed structures, respectively. Their stacking sequences are *abcabc* and *abacabac*.

In the case of VCo_3, the stacking sequence should be composed of 6 layers, since the c_0-axis of the hexagonal lattice corresponds approximately to six times the d_{111} value for the 'cubic lattice'. Thus the stacking sequence *abcacbabcacb* was considered as a possible one. Intensities of all the reflections were calculated on the basis of this atomic arrangement. The calculated and observed intensities are in good agreement, as shown in Table 1.

Discussion

The atomic positions in the unit cell are determined by the stacking scheme mentioned above. They are as follows:

Stacking of layer	Positions of V atoms	Positions of Co atoms
a	$0\,0\,0$	$\frac{1}{2}\,0\,0,\ 0\,\frac{1}{2}\,0,\ \frac{1}{2}\,\frac{1}{2}\,0$
b	$\frac{2}{3}\,\frac{1}{3}\,\frac{1}{6}$	$\frac{1}{6}\,\frac{1}{3}\,\frac{1}{6},\ \frac{2}{3}\,\frac{5}{6}\,\frac{1}{6},\ \frac{1}{6}\,\frac{5}{6}\,\frac{1}{6}$
c	$\frac{1}{3}\,\frac{2}{3}\,\frac{1}{3}$	$\frac{5}{6}\,\frac{2}{3}\,\frac{1}{3},\ \frac{1}{3}\,\frac{1}{6}\,\frac{1}{3},\ \frac{5}{6}\,\frac{1}{6}\,\frac{1}{3}$
a	$0\,0\,\frac{1}{2}$	$\frac{1}{2}\,0\,\frac{1}{2},\ 0\,\frac{1}{2}\,\frac{1}{2},\ \frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$
c	$\frac{1}{3}\,\frac{2}{3}\,\frac{2}{3}$	$\frac{5}{6}\,\frac{2}{3}\,\frac{2}{3},\ \frac{1}{3}\,\frac{1}{6}\,\frac{2}{3},\ \frac{5}{6}\,\frac{1}{6}\,\frac{2}{3}$
b	$\frac{2}{3}\,\frac{1}{3}\,\frac{5}{6}$	$\frac{1}{6}\,\frac{1}{3}\,\frac{5}{6},\ \frac{2}{3}\,\frac{5}{6}\,\frac{5}{6},\ \frac{1}{6}\,\frac{5}{6}\,\frac{5}{6}$

The space group of highest symmetry allowing such an atomic arrangement is $D^1_{3h}(P\bar{6}m2)$. The 24 atomic positions in the unit cell may be classified into 8 kinds of crystallographically equivalent sites: 1*a*, 1*b*, 2*h*, 2*i* (for V atoms) 3*j*, 3*k*, 6*n*, 6*n*′ (for Co atoms). There are no general conditions limiting the possible reflections for this space group, but when the structure factors are calculated, using the above atomic arrangement, special extinction rules are obtained, which are quite consistent with the experimental results. These are shown in Table 2. When the observed lines are indexed with reference to the hexagonal unit cell, it is noted that all the reflections for which $h-k = 3n$ and $l \neq 6n$ or $h-k \neq 3n$ and $l = 6n$ are missing from the diffraction patterns. Table 2 shows that the structure factor for these reflections is zero.

Table 2. *Calculated structure factors*

	$h-k = 3n$	$h-k = 3n+1$	$h-k = 3n-1$
$l = 6n$	$6F_{\text{tot}}$	0	0
$l = 6n\pm 1$	0	$-\sqrt{(3)}iF_{\text{tot}}$	$\sqrt{(3)}iF_{\text{tot}}$
$l = 6n\pm 2$	0	$3F_{\text{tot}}$	$3F_{\text{tot}}$
$l = 6n\pm 3$	0	$2\sqrt{(3)}iF_{\text{tot}}$	$2\sqrt{(3)}iF_{\text{tot}}$

$F_{\text{tot}} = f_V + 3f_{Co}$ if h and k are even.
$F_{\text{tot}} = f_V - f_{Co}$ if h and k are odd or mixed.

In calculating the X-ray line intensities for the proposed ordered hexagonal close packed structure, only the structure factor and multiplicity factor were taken into account. The various geometrical factors were not included, because they are not very simple in the case of the asymmetrical camera of the focusing type. The atomic scattering factors were determined as a function of $\sin\theta/\lambda$, and correction was made for the anomalous scattering of Cr $K\alpha$ radiation by V atoms, using Hönl's formula (James, 1948), especially in order to estimate the intensity of weak lines.

When the value $c/2a = 1{\cdot}219$ is compared with the ratio of the corresponding atomic distances in the cubic lattice, namely $(\frac{3}{2})^{\frac{1}{2}} = 1{\cdot}225$, it is clear that a slight contraction takes place along the c-axis when the disordered face-centered-cubic arrangement of the atom changes to the ordered VCo_3 structure.

The stacking scheme *abcacbabcacb* is composed of the paired sequences *abc* and *acb*, both of which correspond to the $AuCu_3$ structure, but with orientations in twin relation to each other. Thus the hexagonal structure may be thought of as composed of alternating nearly cubic twin-related bands, each of which consists of three ordered atomic layers.

Summary

X-ray photographs were taken for the 25 at.% V alloy annealed at 1000 °C. for 72 hr. and quenched in cold water. Analysis of the powder patterns showed that the crystal structure of VCo_3 is ordered close-packed hexagonal, $P\bar{6}m2$, $a_0 = 5{\cdot}032$ and $c_0 = 12{\cdot}27$ Å, with 24 atoms in the unit cell. The structure may be described by stacking of ordered close-packed layers in the sequence *abcacbabcacb*, and it is closely related to the $AuCu_3$-type structure.

The author is indebted to Prof. P. A. Beck for his valuable advice and encouragement. This work was supported by the U.S. Air Force under Contract No. 33(616)-3789.

References

Beck, P. A. & Dwight, A. E. (1959). *Trans. M. S. of A.I.M.E.* To be published.

James, R. W. (1948). *The Optical Principles of the Diffraction of X-rays*. London: Bell.

Koster, W. & Schmid, H. (1955). *Z. Metallk.* **46**, 195.

Laves, F. & Wallbaum, H. J. (1939). *Z. Kristallogr.* A, **101**, 78.