A Study of the Vanadium Tellurides

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The existence of two intermediate phases, β and γ, has been established in the system vanadium tellurium. None of these phases have a simple stoichiometric composition, corresponding to the mono- or ditelluride.

The β-p h a s e has a composition close to V_5Te_4 and no appreciable homogeneity range. The structure is monoclinic with the lattice constants:

$$a = 13.48 \text{ Å}, b = 3.91_3 \text{ Å}, c = 13.82 \text{ Å}, \beta = 93.5_8°$$

when quenched from 1 000°C.

The γ-*phase* has a homogeneity range between about 53 and 62 atomic per cent tellurium in samples quenched from 1 000°C, and between 55.6 and 64.9 atomic per cent tellurium in samples quenched from 750°C. For slowly cooled samples the vanadium rich limit of the γ-phase is at about 56.5 atomic per cent tellurium. Within the γ-phase region four structurally related phases are recognized:

1. The γ_1-phase with a hexagonal NiAs-like structure and composition around 53 atomic per cent tellurium in samples quenched from 1 000°C only. The lattice constants of the hexagonal structure as determined from the two-phase preparation with 52.38 atomic per cent tellurium are:

$$a = 3.942 \text{ Å}, \quad c = 6.126 \text{ Å}, \quad c/a = 1.55_3$$

2. The γ_2-phase with a related monoclinic structure and composition between 55.5 and 63.0 atomic per cent tellurium in samples quenched from 750°C. In this range the lattice constants vary continuously between the limits:

$$a = 6.763 \text{ Å}, \quad b = 3.807 \text{ Å}, \quad c = 2\times6.225 \text{ Å}, \quad \beta = 91.52°$$

at 55.56 atomic per cent tellurium, and

$$'a = 6.460 \text{ Å}, \quad b = 3.685 \text{ Å}, \quad c = 2\times6.335 \text{ Å}, \quad \beta = 90.3°$$

at 62.96 atomic per cent tellurium.

For samples quenched from 1 000°C the tellurium-rich limit of the γ_2-phase is close to 62 atomic per cent tellurium.

3. The γ_3-phase with a hexagonal NiAs-Cd(OH)$_2$-like structure and a narrow composition range in samples quenched from 750°C. The lattice constants for this structure at the composition 63.96 atomic per cent tellurium are:

$$a = 3.689 \text{ Å}, \quad c = 6.405 \text{ Å}, \quad c/a = 1.736$$

This phase was neither observed in samples quenched from 1 000°C nor in slowly cooled.

4. The γ_4-phase with an orthorhombic $Cd(OH)_2$-like structure and composition between 64.3 and 64.9 atomic per cent tellurium. For a sample with 64.91 atomic per cent tellurium, quenched from 750°C, the lattice constants are:

$$a = 6.333 \text{ Å}, \quad b = 3.618 \text{ Å}, \quad c = 2 \times 6.427 \text{ Å}$$

Density measurements show that the solid solution within the γ-phase takes place by subtraction of vanadium atoms as the tellurium content increases.

Only a few references to vanadium tellurides are present in the literature and the earliest work seems to be by Hoschek and Klemm [1]. The tellurides prepared by these authors by the reaction between vanadium (III) oxide or chloride with hydrogen telluride generally had a composition close to the ratio V:Te = 1. Hoschek and Klemm were not able to establish the composition or structure of any of the tellurides formed in their experiments and the tellurium was reported to be relatively weakly bonded. Montignie [2] was not successful in preparing vanadium tellurides by heating vanadium (V) oxide and tellurium under hydrogen.

The first description of a well defined vanadium telluride is due to Ehrlich [3], who obtained the monotelluride by heating the elements in evacuated, sealed silica tubes at 800 to 1 000°C. The compound was found to have a structure of the NiAs-type with unit cell dimensions * $a = 3.81_3$ Å, $c = 6.13_2$ Å and $c/a = 1.60_8$. The X-ray powder photograph of the compound contained, however, some weak reflections which could not be explained on basis of a simple NiAs-like structure. Whether these additional reflections were due to a superstructure or to other phases could not be decided by Ehrlich.

Gal'perin and Perekalina [4] found that the structure of vanadium mono-telluride was not of the NiAs-type, but were unable to interpret it.

Ehrlich [5] has indicated the existence of a compound with structure of the $Cd(OH_2)$-type in the system vanadium tellurium, without giving any experimental evidence for the existence of such a phase.

EXPERIMENTAL

The alloys used in this study were synthesized by heating the elements in the desired ratio in evacuated and sealed silica tubes. In a few cases preparations were made also by adding tellurium to previously prepared alloys containing less tellurium.

The metallic *vanadium* was supplied by the Vanadium Corporation of America and reported to contain 99.6—99.8 % vanadium. The impurities were specified as follows: iron 0.05 %, silicon 0.05 %, aluminium less than 0.05 %, nitrogen less than 0.001 %, and oxygen balance.

The *tellurium* was from the British Drug Houses Ltd. and purified further by distillation *in vacuo*. A spectrographic analysis, which was kindly carried out by siv.ing. S. Rutlin at the Central Institute for Industrial Research, Norway, showed that the puri-

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* The lattice constant values given by Ehrlich, presumably expressed in kX units, have been changed into Å by multiplication by the factor 1.00202.

fied tellurium contained less than 0.01 % iron and only traces of aluminium, magnesium and lead.

During the first preparations of the alloys it was observed that samples with more than 45.5 atomic per cent vanadium heavily attacked the silica tubes by reducing the silicon dioxide and forming trivanadium monosilicide, V_3Si. In order to avoid this detrimental reaction, alloys with more than 45.5 atomic per cent vanadium were prepared in small crucibles of pure alumina ("Degussit" from Degussa) placed inside the silica tubes. Alloys with less than 45.5 atomic per cent vanadium could be prepared without this precaution.

A number of alloys with compositions varying from 24.81 to 71.43 atomic per cent tellurium were synthesized. The mixture of vanadium and tellurium was first heated for 2 days at 1 000°C. By this heating a sintered reaction product was obtained which could easily be changed into a powder by shaking the silica tube. The heating was continued at 1 000°C for 2 more days in the same tube. It was then quenched in ice water and small portions of each sample taken out for X-ray investigation. The rest of the sample was heated further for 20 days at 750°C and quenched from that temperature.

In this way it was only possible to obtain alloys with less than 62 atomic per cent tellurium. In alloys with higher tellurium content some tellurium was left unreacted after quenching from 1 000°C. In order to make the reaction complete above 62 atomic per cent tellurium it was necessary to cool the samples slowly down from 1 000 to 750°C. In this way alloys with up to 71.43 atomic per cent tellurium could be prepared. They were also annealed for 20 days at 750°C and quenched.

In addition to these two series of samples, one quenched from 1 000°C and the other from 750°C, small parts of some of the samples were heated further for 30 days at 550°C and cooled slowly to room temperature during 5 days. In one case a sample was also cooled slowly from 750°C. The purpose of these heat treatments was to check if the lower annealing temperature and the slower cooling rate might cause any changes of the phases and structures observed in the quenched samples. The samples slowly cooled from 550°C contained 52.38, 54.55, 64.29 and 66.67 atomic per cent tellurium and that from 750°C 63.64 atomic per cent tellurium.

The samples were all easily crushed in an agate mortar into dark gray powders. They were then subjected to an X-ray examination by the powder method.

The X-ray photographs were taken in 11.48 cm diameter cameras with asymmetric film mounting. Vanadium filtered chromium radiation was used in most cases. In a few cases nickel filtered copper radiation was also used. The lattice constants are expressed in Ångström units on the basis of $\lambda CrK\alpha_1 = 2.2896$ Å and $\lambda CuK\alpha_1 = 1.5405$ Å. The mean error in the lattice constants in judged to be less than 0.1 %.

PHASE ANALYSIS

1. Samples quenched from 1 000 °C

The most vanadium-rich sample that was prepared contained 24.81 atomic per cent tellurium, corresponding to the composition $VTe_{0.33}$. By X-ray examination this sample was found to consist of two phases: metallic vanadium — the α-phase — and an intermediate phase — the β-phase. Samples with 41.18 and 44.44 atomic per cent tellurium ($VTe_{0.70}$ and $VTe_{0.80}$, respectively) gave only reflections from the β-phase, whereas another phase — the γ_1-phase — was observed together with the β-phase at 47.37 atomic per cent tellurium ($VTe_{0.90}$). Accordingly, it is concluded that the β-phase contains about 44 atomic per cent tellurium ($VTe_{0.8}$) and thus has a composition which is markedly different from that of a monotelluride. As no displacement of the X-ray reflections on photographs of samples containing the β-phase is observed, the phase probably has a rather narrow homogeneity range.

The β-phase is observed together with the γ_1-phase in preparations with 50.00 and 52.38 atomic per cent tellurium ($VTe_{1.00}$ and $VTe_{1.10}$, respectively).

At the latter composition the reflections from the β-phase are few and weak. The remaining reflections can all be explained in terms of the hexagonal, NiAs-like structure which Ehrlich [3] attributed to vanadium monotelluride. However, all the samples with 50 atomic per cent tellurium studied here turned out to be two-phase preparations, containing both the β-phase and the γ_1-phase. Thus, a vanadium monotelluride with the exact stoichiometric composition VTe does apparently not exist. The additional reflections which Ehrlich observed on the photograph of the sample with composition corresponding to the monotelluride, were probably due to the β-phase.

The X-ray photographs of samples with compositions in the concentration range 52.38 to 62.26 atomic per cent tellurium (VTe$_{1.10}$ to VTe$_{1.65}$, respectively) are all very similar. Some characteristic features should, however, be emphasized. First of all, no reflections from the β-phase are present for samples with 54.55 atomic per cent tellurium (VTe$_{1.20}$). Furthermore, a splitting of many of the hexagonal reflections is observed at the same composition. Finally, a marked shift in the positions of the reflections is observed as the tellurium content of the samples increases in the whole concentration range up to 60.00 atomic per cent tellurium.

These observations show that the γ_1-phase with a hexagonal, NiAs-like structure has only a narrow existence range between 52.38 and 54.55 atomic per cent tellurium (VTe$_{1.10}$ and VTe$_{1.20}$, respectively). With increasing tellurium concentration the hexagonal structure changes into one with a lower, probably monoclinic, symmetry as has earlier been found for many of the chalcogen systems of the $3d$ transition elements (see for instance Haraldsen [6]). The corresponding phase — the γ_2-*phase* — has a homogeneity range between about 54.55 and 62.26 atomic per cent tellurium, the latter composition being the highest one in tellurium which could be attained for samples quenched from 1 000°C without the tellurium phase being present.

The designations γ_1 and γ_2 are chosen to indicate that the phase γ_1 with hexagonal structure and γ_2 with monoclinic structure might constitute only one phase — the γ-*phase* — in analogy with what has been found for many related systems[6]. This further means that the hexagonal structure, present at the vanadium-rich limit of the homogeneity range, continuously changes into the monoclinic structure as the tellurium content increases.

2. S a m p l e s   q u e n c h e d   f r o m   750°C

In the series quenched from 750°C, a phase with a hexagonal structure, corresponding to that of the γ_1-phase in the series quenched from 1 000°C, could not at all be observed. Instead, large amounts of the β-phase were present in the sample with 52.38 atomic per cent tellurium, and also the γ_2-phase with its splitted reflections. A considerable change in the positions of these reflections was observed in the range from 55.56 to 62.96 atomic per cent tellurium (VTe$_{1.25}$ to VTe$_{1.70}$).

The X-ray powder photographs of the preparation with 63.64 atomic per cent tellurium (VTe$_{1.75}$) could, however, be indexed hexagonal. Consequently, the system vanadium tellurium shows the same characteristic features as has

been found in many other chalcogen systems of the $3d$ transition elements [6]. Depending upon the temperature to which the statement refers, there exists in the range between 50 and 66.7 atomic per cent chalcogen one or more phases which at concentrations low in chalcogen possess a hexagonal NiAs-like structure, at intermediate concentrations a monoclinic structure and at concentrations high in chalcogen again a hexagonal $Cd(OH)_2$-like structure, derived from the NiAs-like structure by subtraction of metal atoms. In the present case it could not be decided whether the hexagonal structures and the monoclinic structure constitute a single phase or three different phases, γ_1, γ_2 and γ_3, separated-by two-phase regions.

The hexagonal $Cd(OH)_2$-like structure was found to exist also at the composition 63.96 atomic per cent tellurium ($VTe_{1.775}$), but not at 64.29 atomic per cent tellurium ($VTe_{1.80}$), where a splitting of the X-ray reflections was again noted. The hexagonal γ_3-phase has thus only a narrow existence range, just as the hexagonal γ_1-phase which was observed in the series quenched from 1 000°C.

In samples with 64.29 to 64.91 atomic per cent tellurium probably another phase — the γ_4-*phase* — exists. The corresponding X-ray powder photograph was tentatively indexed as orthorhombic (see Table 5). The photographs of the samples with 65.52, 66.67 and 71.43 atomic per cent tellurium ($VTe_{1.90}$, $VTe_{2.00}$, and $VTe_{2.50}$ respectively) contained also a few weak reflections which might be caused by elemental tellurium, in addition to the reflections from the γ_4-phase. No shift in the positions of the reflections from the γ_4-phase is observed on the photographs of the samples with 64.91 to 71.43 atomic per cent tellurium, and the γ_4-phase should therefore not contain more than 64.91 atomic per cent tellurium ($VTe_{1.85}$). The change from hexagonal to orthorhombic structure takes place within a narrow composition range, 63.96 to 64.29 atomic per cent tellurium, and it is very slight. It seems reasonable to suppose that the transition from the monoclinic γ_2-phase, *via* the hexagonal γ_3-phase, into the orthorhombic γ_4-phase is continuous at high temperatures and that the γ-phase has a homogeneity range between about 55.56 and 64.91 atomic per cent tellurium ($VTe_{1.25}$ and $VTe_{1.85}$) at 750°C, as far as it can be judged from the quenched samples.

3. Slowly cooled samples

The most striking feature of the slowly cooled preparations is the absence of the hexagonal structure both at low and at high tellurium concentrations. Consequently, neither the γ_1-phase, nor the γ_3-phase exists at low temperatures.

The preparation with 52.38 atomic per cent tellurium ($VTe_{1.10}$) consists also in this case of two phases, β and γ_2, whereas at 54.55 atomic per cent tellurium ($VTe_{1.30}$) only the γ_2-phase remains. With regard to the position of the X-ray reflections the photographs of these two samples are practically identical with that of $VTe_{1.30}$ quenched from 750°C, which indicates that the γ_2-phase does not contain less than 56.52 atomic per cent tellurium at room temperature. Similarly, the photograph of the slowly cooled sample with 63.64 atomic per cent tellurium indicates that the tellurium-rich limit of the γ_2-phase is close to 61.54 atomic per cent, as it is very similar to that of $VTe_{1.60}$ quenched from 750°C. The γ_4-phase was found free from other phases at 64.29 atomic

per cent tellurium ($VTe_{1.80}$) and mixed with free tellurium at 66.67 atomic per cent tellurium ($VTe_{2.00}$).

It follows from the results obtained here that a vanadium ditelluride with the exact stoichiometric composition VTe_2 does not exist, no more than a stoichiometric monotelluride VTe, at least not under the described experimental conditions. The most tellurium-rich phase obtained, the γ_4-phase, has a composition which differs markedly from the formula VTe_2, and changes in the heat-treatment apparently makes no difference as to the non-existence of the stoichiometric mono- and ditelluride.

LATTICE CONSTANT VALUES

1. The β-phase

Single crystals of the β-phase were found in the preparation with 44.44 per cent tellurium, quenched from 1 000°C. Weissenberg photographs showed that the crystals were monoclinic, and also gave approximate values for the unit cell dimensions. The powder photographs of the β-phase could then be

Table 1. Powder photograph data of the β-phase, quenched from 1 000°C, CuKα radiation.

I_{obs}	$\sin^2\Theta \times 10^4$	hkl	I_{obs}	$\sin^2\Theta \times 10^4$	hkl
m	451	$11\bar{1}$, 111	vw	1 786	604
m	499	004	vw	1 870	$51\bar{5}$
m	525	400	vw	1 918	$11\bar{7}$
m	595	$20\bar{4}$	w	1 979	117
m	615	$40\bar{2}$	st	2 054	711
m	665	204	st	2 153	$\{80\bar{2},\ 60\bar{6}$
vst	687	402, $11\bar{3}$			$22\bar{4}$
vst	727	311	vw	2 211	208, 224
m	924	$31\bar{3}$	vw	2 298	802
m	1 001	313	vw	2 458	$80\bar{4}$
st	1 201	$20\bar{6}$	vw	2 584	$51\bar{7}$
m	1 217	$51\bar{1}$	w	2 662	408
m	1 361	602	m	2 746	$22\bar{6}$
vst	1 424	$51\bar{3}$	m	2 906	622
st	1 530	315	w	3 006	$80\bar{6}$
st	1 552	020			

indexed as shown in Table 1. The lattice constants, as determined for samples of the three series, are listed in Table 2 and they are practically the same.

Missing reflections on the photographs are of the type:

hkl when $h + k = 2n + 1$, $k + l = 2n + 1$, $(l + h = 2n + 1)$

$h0l$ when $l = 2n + 1$, $(h = 2n + 1)$

$0k0$ when $(k = 2n + 1)$

Table 2. Lattice constants of the β-phase.

Annealing temperature °C	a in Å	b in Å	c in Å	β	Volume of the unit cell in Å³
1 000	13.48	3.91_3	13.82	$93.5_8°$	727.1
750	13.47	3.92_7	13.86	93.66°	731.6
550	13.47	3.92_0	13.85	93.6°	729.9

They are characteristic of the space groups C_s^4 and C_{2h}^6. The observed density, 6.73_7 g cm^{-3}, corresponds to 19.3 vanadium and 15.4 tellurium atoms in the unit cell. The true content is probably 20 vanadium and 16 tellurium atoms, which corresponds to the formula V_5Te_4 or $VTe_{0.80}$. The determination of the structure is under way.

2. The γ-phase

The lattice constants of the γ-phase determined for the three series of samples at different compositions are given in Table 3. Weak additional lines on the photographs of the monoclinic samples, both when quenched from 750°C and when slowly cooled, require for their explanation a doubling of the c-axis, and this is indicated in the table.

The values determined for the hexagonal $γ_1$-phase at the composition 52.38 atomic per cent tellurium and 1 000°C agree fairly well with the values found by Ehrlich [3] as far as the c-axis is concerned ($a = 3.81_3$ Å, $c = 6.13_2$ Å). The a-axis is, however, considerably larger.
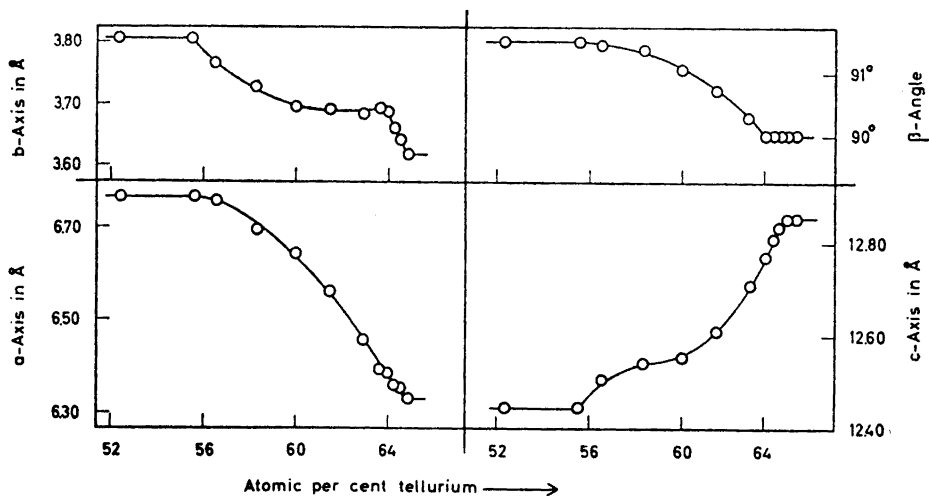

Fig. 1. Lattice constants of the γ-phase after quenching from 750°C.

Table 3. Lattice constants of the γ-phase.

Atomic per cent tellurium	Annealing Temperatur °C	a $(b\sqrt{3})$ in Å	b in Å	c in Å	β	Volume of the unit cell in Å³
52.38	1 000	(6.828)	3.942	6.126	(90°)	82.44
	750	6.763	3.807	2 × 6.225	91.52°	4 × 80.10
	550 *	6.760	3.770	2 × 6.25	91.5°	4 × 79.62
54.55	1 000	6.788	3.828	6.221	91.15°	2 × 80.81
	750	6.763	3.807	2 × 6.225	91.52°	4 × 80.10
	550 *	6.759	3.767	2 × 6.254	91.46°	4 × 79.59
55.56	750	6.763	3.807	2 × 6.225	91.52°	4 × 80.10
56.52	1 000	6.761	3.767	2 × 6.240	91.58°	4 × 79.43
	750	6.759	3.767	2 × 6.254	91.46°	4 × 79.59
58.33	750	6.692	3.728	2 × 6.273	91.40°	4 × 78.23
60.00	1 000	6.637	3.693	2 × 6.276	91.00°	4 × 76.90
	750	6.642	3.696	2 × 6.279	91.07°	4 × 77.06
61.17	1 000	6.598	3.680	2 × 6.26	90.9°	4 × 76.0
61.54	750	6.563	3.693	2 × 6.306	90.72°	4 × 76.41
62.26	1 000	6.541	3.677	2 × 6.255	90.73°	4 × 75.25
62.96	750	6.460	3.685	2 × 6.355	90.3°	4 × 75.64
63.64	750	(6.398)	3.695	6.385	(90°)	75.50
	750 *	6.550	3.664	2 × 6.295	90.67°	4 × 75.53
63.96	750	(6.390)	3.689	6.405	(90°)	75.49
64.29	750	6.362	3.661	2 × 6.412	(90°)	4 × 74.66
64.60	750	6.356	3.642	2 × 6.427	(90°)	4 × 74.39
64.91	1 000	6.541	3.677	2 × 6.255	90.73°	4 × 75.25
	750	6.333	3.618	2 × 6.427	(90°)	4 × 73.62

* slowly cooled.

The variations in lattice constants with composition are seen from Fig. 1, where the lattice constants of the γ-phase for the 750°C series are plotted against the composition. The *a*-axis decreases smoothly with increasing tellurium content in the whole concentration range, while the *b*-axis shows an abrupt decrease at about 64 atomic per cent tellurium as the structure changes

Table 4. Powder photograph data of the γ_4-phase, $VTe_{1.85}$ quenched from 750°C, $CuK\alpha$ radiation.

I_{obs}	$\sin^2\Theta \times 10^4$ obs.	hkl	$\sin^2\Theta \times 10^4$ calc.	I_{obs}	$\sin^2\Theta \times 10^4$ obs.	hkl	$\sin^2\Theta \times 10^4$ calc.
w	143	002	144	vw	1 520	—	—
vw	448	010	453	vw	1 657	—	—
vw	466	—	—	m	1 780	310	1 785
m	575	004	575	w	1 813	020	1 813
w	594	200	592	st	1 894	116	1 894
w	604	110	601	w	2 001	—	—
m	730	202	735	vw	2 068	—	—
vst	751	112	745	m	2 303	008	2 298
vw	845	—	—	w	2 336	314	2 359
vw	870	—	—	w	2 399	024	2 388
vw	967	—	—	w	2 504	402	2 510
vw	1 120	—	—	m	2 545	222	2 548
st	1 176	204	1 166	w	2 906	118	2 900
		114	1 176	m	2 982	224	2 980
vw	1 255	—	—	m	3 697	226	3 698
vw	1 296	006	1 293				
vw	1 452	103	1 441				

from hexagonal to orthorhombic. Even though the c-axis increases, the volume of the unit cell decreases as well, see Table 3.

It is furthermore apparent from Fig. 1 that the vanadium rich limit of the homogeneity range of the γ-phase for the 750°C series is at about 55.5 atomic per cent tellurium. This is somewhat higher than found on basis of the 1 000°C series, where the limit lies between 52.38 and 54.55 atomic per cent tellurium if the hexagonal range is included.

The lattice constant values for the hexagonal structures fall nicely on the curves drawn through the values for the monoclinic structure. This is also the case with the hexagonal lattice constants of the 1 000°C series (not shown in the figure). This might indicate that the transition from one structure into the other is continuous under the experimental conditions used here. The observations are, however, too few for deciding this question with certainty.

As already stated, the X-ray powder photograph of the γ_4-phase was indexed orthorhombic. This gave a satisfactory agreement between observed and calculated $\sin^2\Theta$-values for most of the reflections, as can be seen from Table 4 where the values are listed. There remain, however, a few, very weak reflections which cannot be accounted for in this way. They might be due to a superstructure, indicating that the true unit cell is larger.*

The lattice constants calculated for the orthorhombic unit cell are:

$$a = 6.333 \text{ Å}, \quad b = 3.618 \text{ Å}, \quad c = 2 \times 6.427 \text{ Å}$$

at 64.91 atomic per cent tellurium.

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* Note added in proof: Weissenberg photographs of a crystal of $VTe_{1.85}$ has confirmed the correctness of the orthorhombic interpretation and shown that the b-axis must be tripled.

Table 5. Interatomic distances in the hexagonal γ_1 and γ_3 structures.

Atomic per cent tellurium	V — Te	V — V	Te — Te within the layers	Te — Te between the layers
52.38	2.74 Å	3.06 Å	3.94 Å	3.82 Å
63.64	2.67 Å	3.20 Å	3.69 Å	3.85 Å

The structure bears a close relationship to that of the hexagonal γ_3-phase, but it has so far no parallel among the other sulfides, selenides and tellurides of the $3d$ transition elements. It is especially worth mentioning that the structure is not of the marcasite type as one might have thought on basis of its orthorhombic structure and its composition.

In the hexagonal γ-phase, each vanadium atom is surrounded by six tellurium atoms at the corners of a deformed octahedron (trigonal antiprism) and two vanadium atoms at the distance $c/2$. The tellurium atoms form an approximately hexagonal closepacking. The distances vanadium-tellurium, vanadium-vanadium and tellurium-tellurium found in the two preparations with 52.38 and 63.96 atomic per cent tellurium are listed in Table 5.

The distances vanadium-tellurium are distinctly shorter than the sum of the ionic radii: 0.74 Å + 2.11 Å = 2.85 Å. They agree, however, very well with the sum of the metallic radii as given by Pauling [7]. With an average coordination number of 7.6 for vanadium and 5.5 for tellurium in the vanadium rich preparation and 6.4 for vanadium and 3.5 for tellurium in the tellurium rich preparation, the sum of the metallic radii is:
1.27 Å + 1.50 Å = 2.77 Å and 1.26 Å + 1.44 Å = 2.70 Å, respectively, *i.e.* only 0.03 Å higher than the experimental values.

The distance tellurium-tellurium between the layers remains almost unchanged from 52.38 to 63.96 atomic per cent tellurium, whereas the distance within

Table 6. The distance metal-tellurium in tellurides with NiAs-like, respectively $Cd(OH)_2$-like structure.

Composition $MeTe_n$	Distance Me-Te in Å	Sum of ionic radii r(Me) + r(Te) in Å	Sum of metallic radii r(Me) + r(Te) in Å
TiTe	2.736		1.41 + 1.51 = 2.92
TiTe₂	2.717	0.64 + 2.11 = 2.75	1.38 + 1.42 = 2.80
VTe₁.₁	2.74	0.74 + 2.11 = 2.85	1.27 + 1.50 = 2.77
VTe₁.₇	2.67		1.26 + 1.44 = 2.70
CrTe₁.₅	2.726	0.65 + 2.11 = 2.76	1.28 + 1.46 = 2.74
MnTe	2.923	0.91 + 2.11 = 3.02	1.21 + 1.51 = 2.72
FeTe₁.₅	2.62	0.67 + 2.11 = 2.78	1.18 + 1.46 = 2.64
CoTe₁.₂	2.62	0.82 + 2.11 = 2.93	1.19 + 1.49 = 2.68
CoTe₁.₈	2.58		1.17 + 1.43 = 2.60
NiTe₁.₁	2.654	0.78 + 2.11 = 2.89	1.18 + 1.50 = 2.68
NiTe₂	2.584		1.15 + 1.42 = 2.57

Table 7. Pycnometric densities of vanadium-tellurium preparations.

Atomic per cent tellurium	Density in g cm⁻³	Atomic per cent tellurium	Density in g cm⁻³
41.18	6.682	60.00	6.876
44.44	6.737	61.54	6.855
47.37	6.775	62.96	6.844
50.00	6.770	63.64	6.840
54.54	6.830	64.29	6.850
55.56	6.850	65.52	6.854
56.52	6.860	66.67	6.841
58.33	6.869		

the layers changes from 3.94 Å to 3.69 Å. This great change brings about that the distance within the layers, which is the larger one at 52.38 atomic per cent tellurium, is the smaller one at the tellurium rich composition.

The system vanadium-tellurium was the only tellurium system of the $3d$ transition elements from titanium to nickel for which data about the distance metal-tellurium still lacked. A compilation of the values found for this distance in the phases with NiAs-like, respectively $Cd(OH)_2$-like structure, is presented in Table 6 and compared with distances calculated on the basis of the ionic radii of Goldschmidt, and the metallic radii of Pauling. The metallic radii have been corrected for the coordination number valid for the compositions given in the table.

It can be seen from Table 6 that the observed distance metal-tellurium for the titanium tellurides TiTe and $TiTe_2$ and for manganese monotelluride MnTe is best in accordance with the sum of the ionic radii, whereas the metallic radii lead to the most satisfactory agreement for the vanadium, iron, cobalt and nickel tellurides. The chromium telluride $CrTe_{1.5}$ represents an intermediate case in so far as the distance chromium-tellurium agrees equally well with the sum of the ionic radii as that of the metallic radii.
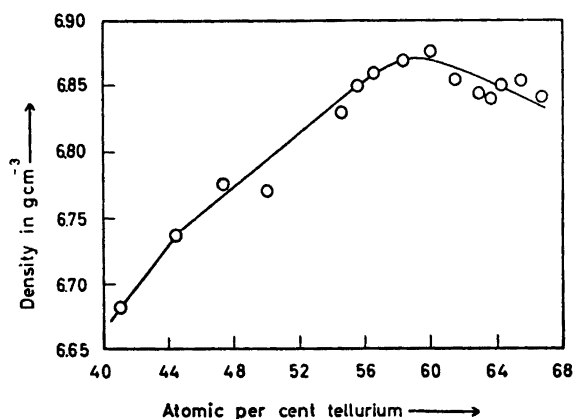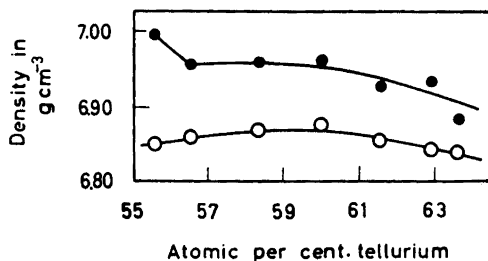

Fig. 2. Densities of the vanadium tellurides.

Fig. 3. Observed density ○ and calculated density ● of the γ-phase.

DENSITY MEASUREMENTS

Density measurements of the 750°C series were carried out at 25°C by the vacuum pycnometric method and with kerosene as displacement liquid. The results are listed in Table 7, and plotted against the composition of the samples in Fig. 2. There is a break in the curve at about 44.4 atomic per cent tellurium, coinciding with the composition of the β-phase, and a maximum at about 60 atomic per cent tellurium, i.e. within the homogeneity range of the γ-phase.

The densities which are found within the homogeneity range of the γ-phase confirm, furthermore, that the solid solubility in this concentration range is due to a subtraction of vanadium atoms. This appears from Fig. 3 where the densities, calculated on the basis of this hypothesis, are compared with the observed values. The agreement between the calculated and observed values in the concentration range 56.5 to about 64 atomic per cent tellurium leaves no doubt that a subtraction of vanadium atoms occurs in this region. An addition of tellurium atoms to the lattice or substitution of vanadium atoms by tellurium atoms would lead to an increase in the values of the calculated densities, and is not at all consistent with the observations. The subtraction of the vanadium atoms does, however, not go so far that a complete transition into a structure of the $Cd(OH)_2$-type is reached. The subtraction comes to an end at the tellurium rich limit of the γ_4-phase, i.e. at about 64 atomic per cent tellurium.

Certain changes which are observed in the relative intensities of the X-ray reflections, are also in favour of the hypothesis that the solid solution is of the subtractive type. The reflection (001) for example, which is forbidden in a structure of the NiAs-type, is distinctly seen on the photograph of the preparation with 62.96 atomic per cent tellurium.

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