

Vacancy ordering and thermodynamic properties in V_3Te_4

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(Received May 13, 1991)

Abstract

Previous isopiestic measurements of tellurium vapour pressures over solid vanadium–tellurium alloys were re-evaluated in the light of new information on the vanadium–tellurium phase diagram. From these, partial molar properties of tellurium were derived for the V_3Te_4 phase. A statistical model was derived that describes the composition dependence of the thermodynamic activities in phases with the Cr_3S_4 -type superstructure. A comparison of model curves with experimental tellurium activities indicated the existence of a (5:8)-type ordering around 61.5 at.% Te at temperatures above the previously reported transition. For stoichiometric V_3Te_4 it was found that due to thermal disorder about 3.5% of the vanadium atoms are located on positions which should be vacant in the ideal Cr_3S_4 -type structure.

1. Introduction

Many of the transition metal–chalcogen systems are characterized by the appearance of phases with a crystal structure of the NiAs-type in the composition range between 50 and 66.7 at.% of the chalcogen. In this structure type the deviation from the stoichiometric (1:1) composition to the chalcogen-rich side is achieved by removal of transition metal atoms from their regular (octahedral) lattice sites, and the resulting vacancies are frequently restricted to alternate transition metal layers; this results in a partially filled CdI_2 -type structure. In a considerable number of these chalcogen systems the vacancies which may be statistically distributed at higher temperatures start to order when the temperature is lowered, forming different kinds of superstructures [1].

One possible ordering pattern that appears frequently around 57.1 at.% of the chalcogen is the Cr_3S_4 -type structure ($C2/m$) where one-half of the transition metal sites in alternate layers are empty, as shown in Fig. 1(a). This superstructure has been observed in numerous systems, for example in Cr–S [2], Cr–Se [3], Cr–Te [4, 5], Fe–Se [6, 7], V–Te [8–10] and others. With increasing concentration of the chalcogen further vacancies are created in the partially filled transition metal layers; if three-quarters of the lattice sites in these layers are empty, and if they are arranged in an ordered way, one arrives at the V_5Se_8 type ($C2/m$) (Fig. 1(b)) as observed for example in the Cr–Te [5] or V–Te system [11].

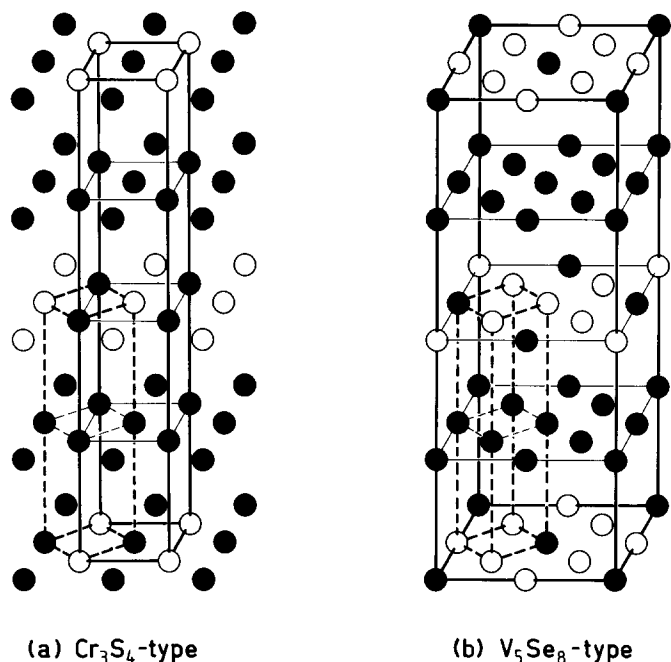


Fig. 1. Representation of the transition metal sublattice in two different NiAs-related superstructures: completely filled layers of transition metal atoms alternate with partially occupied layers (●, transition metal atom; ○, vacancy; bold lines show contours of unit cells in pseudo-orthorhombic representation; broken lines show outlines of the simple NiAs cell). (a) Cr_3S_4 type; (b) V_5Se_8 type.

Thermodynamic properties of vanadium–tellurium alloys were measured by Ipsen [12] several years ago using an isopiestic vapor pressure method. At the time of that study phase relationships in the V–Te system were only partly known [8, 11, 13, 14], and there existed no complete phase diagram. Thus the thermodynamic results of ref. 12 had to be interpreted in such a way that the system of phases with NiAs-related crystal structures was assumed to be one single homogeneity region. Since then more information on the V–Te phase diagram has become available as a result of the work of Ohtani *et al.* [15] and Terzieff *et al.* [9]. In particular it was found that V_3Te_4 (with a homogeneity range between about 55.5 and 62 at.% Te at 900 K) transforms to a high-temperature phase (probably with the partially filled CdI_2 -type structure) with a maximum temperature of 1180 K at 57.1 at.% Te. Additionally there were indications that around 61.5 at.% Te the crystal lattice undergoes further ordering into the V_5Se_8 -type superstructure below 825 K [9] in accordance with the results of Brunie and Chevreton [11].

These new findings prompted us to re-evaluate the thermodynamic data of Ipsen [12] in the light of the new phase diagram, and a new set of partial molar thermodynamic data for tellurium was derived. A Wagner–Schottky-type statistical model [16] is applied to interpret the compositional variation

of the resulting activity data within the homogeneity field of the V_3Te_4 phase, and from this model the degree of disorder at the stoichiometric (3:4) composition is deduced.

2. Re-evaluation of the thermodynamic results

Figure 2 shows the data points (sample composition as a function of sample temperature T_S) for the nine isopiestic experiments with different reservoir temperatures T_R determined by Ipser [12]. The data are superimposed on the partial phase diagram determined by Terzieff *et al.* [9] and the existence of the transformation of the V_3Te_4 phase necessitates somewhat different curvatures of the so-called equilibrium curves (connecting the data points of individual runs) compared with those shown in Fig. 1 of ref. 12. It is especially striking that these curves seem to exhibit an additional inflection point around 61.5 at.% Te which might indicate the presence of a (5:8)-type ordering up to temperatures as high as 1000 K.

Only samples within the homogeneity range of V_3Te_4 were considered for the present re-evaluation. As usual, thermodynamic activities of tellurium were first calculated for all samples at the individual sample temperatures T_S , knowing the temperature dependence of the vapour pressure of pure

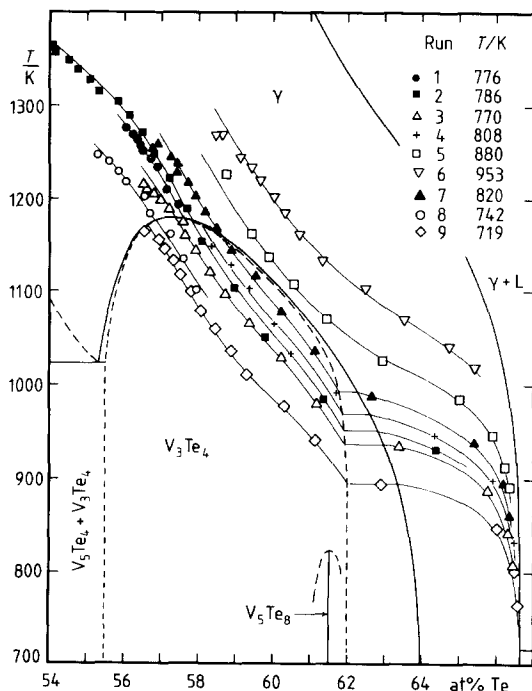


Fig. 2. Isopiestic equilibrium curves (sample temperature *vs.* sample composition) from ref. 12 superimposed on the partial V-Te phase diagram [9].

tellurium and assuming that in equilibrium the tellurium partial pressure over each sample at T_s is equal to the vapour pressure of pure tellurium at the reservoir temperature T_R [12]. For the transition metal–tellurium systems it had usually been assumed that the tellurium vapour consisted of Te_2 molecules only [12, 17–21]. In order to estimate the possible errors caused by this simplification, exact activity values were calculated considering all possible species Te_n ($1 \leq n \leq 7$). Equilibrium constants for the different dissociation reactions

$$\frac{2}{n} \text{Te}_n = \text{Te}_2 \quad (1)$$

were calculated from the compilation of Grønqvold *et al.* [22] in the form

$$\log K_n = A + B(K/T) \quad (2)$$

and the constants A and B obtained are listed in Table 1. Values for the total tellurium vapour pressure were calculated from Brooks' equation [23]

$$\ln(p/\text{Pa}) = -13723.9(K/T) + 22.3922 \quad (3)$$

It turned out that the values of $\ln a_{\text{Te}}$ calculated in this way (and used in the present re-evaluation) differ by 1% at most from those calculated under the assumption that tellurium vapour consists of Te_2 only in the temperature and pressure ranges of our experiments.

Partial molar enthalpies of mixing for the V_3Te_4 phase were derived from the temperature dependence of the activities in a way described previously [24, 25]; they are shown in Fig. 3 as a function of composition. The experimental data are extrapolated to both lower and higher tellurium contents in a way expected in the vicinity of so-called concentrations of order. $\Delta \bar{H}_{\text{Te}}$ values from the smoothed curve were used to convert the activities of the different samples to a common temperature of 1023 K which constitutes an average temperature for all the data points in the V_3Te_4 phase. As a final result the composition dependence of $\ln a_{\text{Te}}$ at this temperature is shown in Fig. 4.

TABLE 1

Equilibrium constants for the dissociation reactions $(2/n)\text{Te}_n = \text{Te}_2$

$\log K_n = A + B(K/T)$		
n	A	B
1	−5.5315	13237.6
3	1.5988	−1199.6
4	3.5658	−2719.5
5	3.9991	−3943.0
6	4.3431	−4104.6
7	5.4094	−4866.8

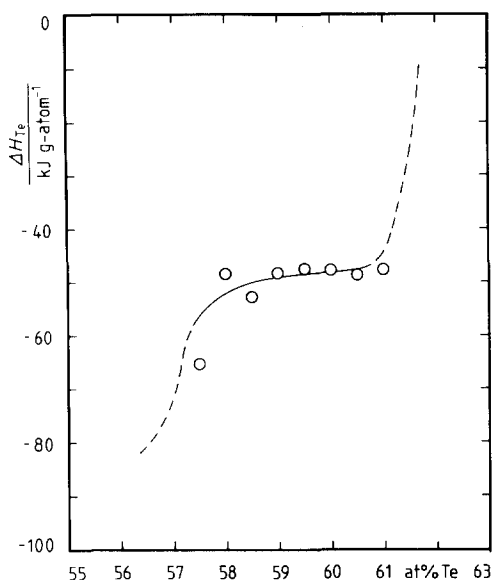


Fig. 3. Partial molar enthalpies of tellurium as a function of composition within the V_3Te_4 phase.

3. Theoretical model

For the derivation of the theoretical model following the concept of Wagner and Schottky [16] the crystal lattice is divided into the vanadium sublattice (α sublattice; for the nomenclature see ref. 26) and the tellurium sublattice (β sublattice) which is assumed to remain undisturbed. The vanadium sublattice is further divided into alternate layers being either completely filled ($\alpha 1$ sublattice; these layers are also assumed to remain undisturbed) or carrying vacancies ($\alpha 2$ sublattice). In the ideal Cr_3S_4 -type structure one-half of the vanadium sites in every other layer are empty ($\alpha 2a$, or for simplicity, a sites) and the vacancies are arranged in a regular pattern (Fig. 5). Deviations from the (3:4) stoichiometry are achieved by filling the vacant positions gradually with vanadium atoms or by creating additional vacancies on the originally occupied sites. (If all vacancies are filled with vanadium atoms we have an ideally ordered $NiAs$ structure; if alternate transition metal layers are completely empty, an ideally ordered CdI_2 structure is created.) If these additional vacancies are restricted to alternate positions ($\alpha 2b1$ or, for simplicity, $b1$ sites) one approaches a superstructure of the V_5Se_8 type (Fig. 5). (It has to be pointed out that in this way a somewhat different stacking is created than that shown in Fig. 1(b). However, it is assumed that this difference is of negligible consequence for the thermodynamic properties in particular, since several types of stacking sequences are possible for the (5:8) superstructure, as pointed out by Brunie and Chevreton [27].)

Even at the exact stoichiometric composition V_3Te_4 (57.14 at.% Te) there will be a certain disorder at finite temperatures as a result of thermal

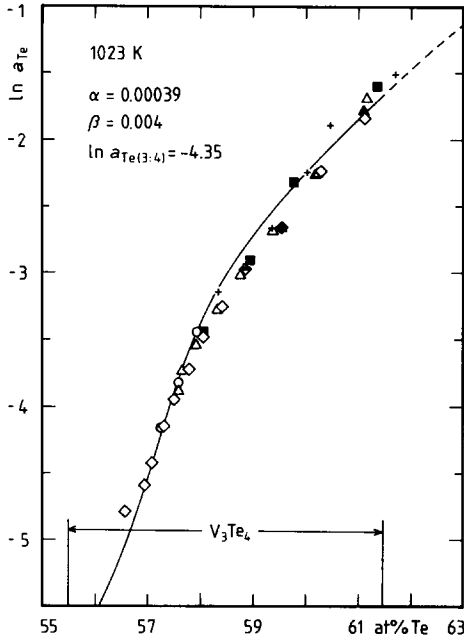


Fig. 4. Natural logarithm of tellurium activity at 1023 K as a function of composition within the V_3Te_4 phase; the full line shows the theoretical curve calculated with $\alpha = 0.00039$, $\beta = 0.004$, and $\ln a_{Te(3:4)} = -4.35$.

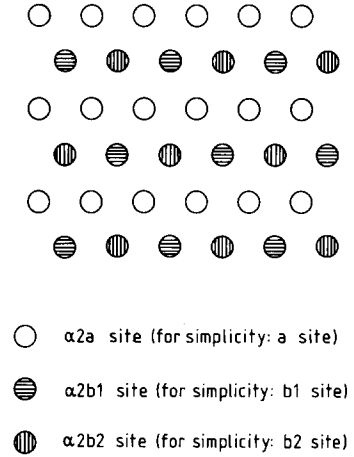


Fig. 5. Partially occupied transition metal layer in NiAs-derivative superstructures. In the perfectly ordered Cr_3S_4 -type structure, all a sites are completely empty, all b sites are completely filled. In the perfectly ordered V_5Se_8 -type structure, all a and b1 sites are completely empty, all b2 sites are completely filled.

agitation (so-called thermal or intrinsic defects), *i.e.* within the partially filled layers a certain number of vanadium atoms will change place vacancies. To account for the possibility that a V_5Te_8 superstructure develops with increasing tellurium content, the probabilities for such an exchange are assumed to be different for alternate vanadium sites (b1 and b2 sites; cf. Fig. 5). Consequently we define two different disorder parameters describing the degree of disorder for a given temperature at the stoichiometric (3:4) composition:

$$\alpha = \left(\frac{N_{\square}^{b1}}{N^t} \right)_{(3:4)} \quad \beta = \left(\frac{N_{\square}^{b2}}{N^t} \right)_{(3:4)} \quad (4)$$

where N_{\square}^{b1} and N_{\square}^{b2} are the number of vacancies on b1 or b2 sites, respectively (cf. Fig. 5), and N^t is the total number of lattice sites in an NiAs lattice, *i.e.* $N^t = N^a + N^b = N^{a1} + N^a + N^{b1} + N^{b2} + N^b$ (generally, the subscript specifies the species and the superscript specifies the type of lattice site). For the case $\alpha = \beta$, any additional vacancies will be distributed statistically over all b sites; if α and β are different, then there will be a tendency to approach a (5:8)-type ordering with increasing number of vacancies on the b sites.

Thus there are basically two different and independent equilibria describing the exchange of vanadium atoms between b1 or b2 sites and empty a sites:



(where V_i is a vanadium atom on an i site); in thermodynamic equilibrium (with p and T constant) we have the following equilibrium conditions:

$$\left(\frac{\partial G}{\partial N_{\square}^{b1}} \right) + \left(\frac{\partial G}{\partial N_V^a} \right) = 0 \quad (6a)$$

$$\left(\frac{\partial G}{\partial N_{\square}^{b2}} \right) + \left(\frac{\partial G}{\partial N_V^a} \right) = 0 \quad (6b)$$

(where N_V^a is the number of vanadium atoms on a sites). This implies a third condition:

$$\left(\frac{\partial G}{\partial N_{\square}^{b1}} \right) - \left(\frac{\partial G}{\partial N_{\square}^{b2}} \right) = 0 \quad (6c)$$

The total Gibbs energy of the crystal is given by

$$G = (1/N_L)(N^t \mu_{(3:4)}^* + N_V^a \mu_V^a + N_{\square}^{b1} \mu_{\square}^{b1} + N_{\square}^{b2} \mu_{\square}^{b2}) - TS_{\text{conf}} \quad (7)$$

where N_L is Avogadro's number; $\mu_{(3:4)}^*$ is the Gibbs energy of an ideally ordered crystal of 1 mole (V+Te) with stoichiometric (3:4) composition; μ_V^a is the change of Gibbs energy, referred to 1 mole, for the occupation of a sites by vanadium atoms; μ_{\square}^{b1} and μ_{\square}^{b2} are the changes of Gibbs energy for the removal of 1 mole of vanadium atoms from the b1 or b2 sublattice respectively. All these Gibbs energy terms are assumed to be composition independent.

Keeping in mind that the β and the $\alpha 1$ sublattice (tellurium sublattice and alternate layers of the vanadium sublattice) remain undisturbed, the configurational entropy can be obtained in the following way:

$$S_{\text{conf}} = k \ln \frac{N^a !}{N_V^a ! (N^a - N_V^a) !} \frac{N^{b1} !}{N_{\square}^{b1} ! (N^{b1} - N_{\square}^{b1}) !} \frac{N^{b2} !}{N_{\square}^{b2} ! (N^{b2} - N_{\square}^{b2}) !} \quad (8)$$

With the aid of eqns. (7) and (8) (and using Stirling's approximation) the partial derivatives in eqns. (6) can be evaluated, yielding

$$\frac{1}{N_L} (\mu_V^a - \mu_{\square}^{b1}) + \frac{RT}{N_L} \ln \frac{N_V^a N_{\square}^{b1}}{(N^a - N_V^a)(N^{b1} - N_{\square}^{b1})} = 0 \quad (9)$$

$$\frac{1}{N_L} (\mu_V^a - \mu_{\square}^{b2}) + \frac{RT}{N_L} \ln \frac{N_V^a N_{\square}^{b2}}{(N^a - N_V^a)(N^{b2} - N_{\square}^{b2})} = 0 \quad (10)$$

It is obvious that the second terms in both equations must be constants since μ_V^a , μ_{\square}^{b1} and μ_{\square}^{b2} were assumed to be composition independent.

From the definitions of the disorder parameters in eqn. (4) the number of defects at the exact stoichiometric composition can be expressed as

$$N_{\square}^{b1} = \alpha N^t; N_{\square}^{b2} = \beta N^t; N_v^a = (\alpha + \beta) N^t$$

If eqns. (9) and (10) are now calculated for the stoichiometric (3:4) composition itself, and if it is remembered that the Gibbs energy terms in these equations are constants, then one obtains the following relationships:

$$\frac{N_v^a N_{\square}^{b1}}{[(N^t/8) - N_v^a][(N^t/16) - N_{\square}^{b1}]} = \frac{\alpha(\alpha + \beta)}{[(1/8) - (\alpha + \beta)][(1/16) - \alpha]} \quad (11)$$

$$\frac{N_v^a N_{\square}^{b2}}{[(N^t/8) - N_v^a][(N^t/16) - N_{\square}^{b2}]} = \frac{\beta(\alpha + \beta)}{[(1/8) - (\alpha + \beta)][(1/16) - \beta]} \quad (12)$$

where the numbers of the different sublattice sites have been expressed in terms of N^t ; *i.e.* $N^a = (N^t/8)$ and $N^{b1} = N^{b2} = (N^t/16)$.

For one mole of alloy the total number of atoms and the number of vanadium atoms are given by

$$N_L = N^t - N^a - N_{\square}^{b1} - N_{\square}^{b2} + N_v^a = (7/8)N^t - N_{\square}^{b1} - N_{\square}^{b2} + N_v^a \quad (13)$$

$$N_v = (1 - x_{Te})N_L = (3/8)N^t - N_{\square}^{b1} - N_{\square}^{b2} + N_v^a \quad (14)$$

This now yields a system of four independent equations (eqns. (11)–(14)) which can be solved for the four unknowns N^t , N_{\square}^{b1} , N_{\square}^{b2} , N_v^a . With the well-known thermodynamic relationships

$$\mu_v = RT \ln a_v = N_L \left(\frac{\partial G}{\partial N_v} \right)_{N_{Te}, p, T} \quad (15a)$$

$$\mu_{Te} = RT \ln a_{Te} = N_L \left(\frac{\partial G}{\partial N_{Te}} \right)_{N_v, p, T} \quad (15b)$$

one can derive expressions for the thermodynamic activities of vanadium and tellurium relative to their values at the stoichiometric (3:4) composition ($a_{v(3:4)}$ and $a_{Te(3:4)}$). Since we are interested in a comparison of theoretical tellurium activities with the experimentally obtained values, the derivation of the corresponding expression is shown below.

Considering that the total Gibbs energy G is a function of the variables N^t , N_v^a , N_{\square}^{b1} , N_{\square}^{b2} , one can write the total differential dG , and from this one obtains (for constant p and T)

$$\begin{aligned} \left(\frac{\partial G}{\partial N_{Te}} \right)_{N_v} &= \left(\frac{\partial G}{\partial N_v^a} \right) \left(\frac{\partial N_v^a}{\partial N_{Te}} \right)_{N_v} + \left(\frac{\partial G}{\partial N_{\square}^{b1}} \right) \left(\frac{\partial N_{\square}^{b1}}{\partial N_{Te}} \right)_{N_v} + \left(\frac{\partial G}{\partial N_{\square}^{b2}} \right) \left(\frac{\partial N_{\square}^{b2}}{\partial N_{Te}} \right)_{N_v} \\ &\quad + \left(\frac{\partial G}{\partial N^t} \right) \left(\frac{\partial N^t}{\partial N_{Te}} \right)_{N_v} \end{aligned} \quad (16)$$

Since the total number of lattice sites is twice the number of tellurium atoms (the tellurium sublattice remains undisturbed), we have

$$\left(\frac{\partial N^t}{\partial N_{\text{Te}}}\right)_{N_V} = 2 \quad (17)$$

Differentiation of eqn. (14) with respect to N_{Te} yields the following expression:

$$\left(\frac{\partial N_{\square}^{b1}}{\partial N_{\text{Te}}}\right)_{N_V} = \frac{3}{4} - \left(\frac{\partial N_{\square}^{b2}}{\partial N_{\text{Te}}}\right)_{N_V} + \left(\frac{\partial N_V^a}{\partial N_{\text{Te}}}\right)_{N_V} \quad (18)$$

and inserting eqns. (17) and (18) into eqn. (16) results after some rearrangement in

$$\begin{aligned} \left(\frac{\partial G}{\partial N_{\text{Te}}}\right)_{N_V} &= \left(\frac{\partial N_V^a}{\partial N_{\text{Te}}}\right)_{N_V} \left[\left(\frac{\partial G}{\partial N_V^a}\right) + \left(\frac{\partial G}{\partial N_{\square}^{b1}}\right) \right] + \left(\frac{\partial N_{\square}^{b2}}{\partial N_{\text{Te}}}\right)_{N_V} \\ &\quad \times \left[\left(\frac{\partial G}{\partial N_{\square}^{b1}}\right) - \left(\frac{\partial G}{\partial N_{\square}^{b2}}\right) \right] + \frac{3}{4} \left(\frac{\partial G}{\partial N_{\square}^{b1}}\right) + 2 \left(\frac{\partial G}{\partial N^t}\right) \end{aligned} \quad (19)$$

However, according to the equilibrium conditions defined in eqns. (6a) and (6b) the terms in the square brackets must be zero in thermodynamic equilibrium, and eqn. (19) reduces to

$$\left(\frac{\partial G}{\partial N_{\text{Te}}}\right)_{N_V} = \frac{3}{4} \left(\frac{\partial G}{\partial N_{\square}^{b1}}\right) + 2 \left(\frac{\partial G}{\partial N^t}\right) \quad (20)$$

The necessary differentials can easily be computed from eqns. (7) and (8) to give an expression for μ_{Te} . If $\mu_{\text{Te}(3:4)}$, *i.e.* its value at the stoichiometric (3:4) composition, is subtracted one obtains

$$\begin{aligned} \ln \frac{a_{\text{Te}}}{a_{\text{Te}(3:4)}} &= \frac{3}{4} \ln \frac{16n_{\square}^{b1}}{1-16n_{\square}^{b1}} + \frac{1}{8} \ln(1-16n_{\square}^{b1})(1-16n_{\square}^{b2})(1-8n_V^a)^2 \\ &\quad - \frac{3}{4} \ln \frac{16\alpha}{1-16\alpha} - \frac{1}{8} \ln(1-16\alpha)(1-16\beta)[1-8(\alpha+\beta)]^2 \end{aligned} \quad (21)$$

where the numbers of defects are now expressed as defect concentrations, *i.e.* $n_{\square}^{b1} = N_{\square}^{b1}/N^t$, $n_{\square}^{b2} = N_{\square}^{b2}/N^t$ and $n_V^a = N_V^a/N^t$. A similar procedure yields the expression for the vanadium activity

$$\ln \frac{a_V}{a_{V(3:4)}} = \ln \frac{1-16n_{\square}^{b1}}{16n_{\square}^{b1}} - \ln \frac{1-16\alpha}{16\alpha} \quad (22)$$

The influence of the variation in the parameters α and β on the possible shape of the $\ln a_{\text{Te}}$ curve is shown in Fig. 6. Curve 1 is obtained for the limiting value of $\alpha = \beta = 0.03125 = (1/32)$ which means a strictly statistical distribution of the vacancies on alternate layers (partially filled CdI_2 type) and no additional ordering tendency. Curve 2 for $\alpha = \beta = 0.001$ shows the typical inflection point at 57.14 at.% Te, indicating the appearance of Cr_3S_4 -type ordering, but no V_5Se_8 -type superstructure. With $\alpha = 0.00001$ and $\beta = 0.005$, Curve 3 is obtained, and the significant difference between α and

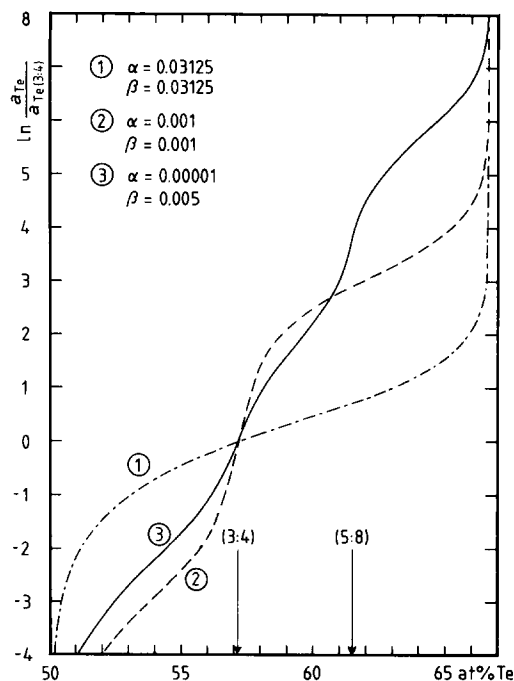


Fig. 6. Theoretical activity curves for different parameter combinations: Curve 1 shows no additional ordering tendency between 50 and 66.7 at.% Te, Curve 2 shows (3:4)-type ordering, and Curve 3 shows both (3:4)- and (5:8)-type ordering.

β is reflected by the additional inflection point at 61.5 at.% Te. This is equivalent to a different probability for the creation of vacancies on b1 and b2 sites (cf. Fig. 5) and will result in the appearance of V_5Se_8 -type ordering on the vanadium sublattice.

Equation (21) was used to describe the composition dependence of the tellurium activities in V_3Te_4 at 1023 K, and the best fit was obtained with $\alpha = 0.00039$, $\beta = 0.004$, and $\ln a_{Te(3:4)} = -4.35$, as shown in Fig. 4. According to the definition of α and β it turns out that at the stoichiometric (3:4) composition about 3.5% of the vanadium atoms in the half-filled layers are on "wrong" lattice sites (a sites) leaving the corresponding number of b sites vacant. From the difference in the values of α and β which is responsible for the flattening of the activity curve around 61.5 at.% Te we must conclude that the typical (5:8)-type ordering still exists at 1023 K in the " V_3Te_4 -phase", *i.e.* it extends to much higher temperatures than previously thought [9, 11]. This is also indicated by the asymmetric shape of the transformation of this phase (see Fig. 2), and model calculations [28] have shown that the inclusion of V_5Se_8 -type ordering is perfectly compatible with this shape. Of course, it would be desirable to test the present results by an independent crystallographic investigation or by heat capacity measurements at the composition V_5Te_8 .

Acknowledgments

The authors want to thank Dr. T. Gnanasekaran for a thorough review of this manuscript and Prof. K. L. Komarek for his permanent interest in this work.

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