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The order–disorder transformation in V_3Te_4

Regina Krachler and Herbert Ipser
Institut für Anorganische Chemie, Universität Wien, Währingerstr. 42, A-1090 Wien (Austria)

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Abstract

The transformation curve of V_3Te_4 (with a superstructure of the Cr_3S_4 type) into the corresponding high temperature phase (with a partially filled CdI_2-type structure) is calculated using a statistical model derived in a previous paper. A long-range order parameter η is defined and it is demonstrated that the ordered superstructure breaks down when a certain defect concentration corresponding to a critical value $\eta_c = 0.79$ is reached. It is also shown that the asymmetrical shape of the transformation curve can only be explained if an additional (5:8)-type superstructure is present within the homogeneity range of the V_3Te_4-phase. The calculated phase boundary is in good agreement with the experimentally determined phase diagram.

1. Introduction

Metallic alloys are often found to form solid solutions at high temperatures, and phases with considerable ranges of homogeneity are quite common. Such solid solutions are usually based on a statistical distribution of the atoms of the components over a common set of lattice sites. With decreasing temperatures, however, the formation of so-called superstructures is frequently observed, where this common set of lattice sites separates into different sublattices, each of which can accommodate preferentially either one certain kind of atom or vacancies.

Perfect ordering is only possible at absolute zero; at any finite temperature the thermal motion of the atoms will lead to "thermal disorder", *i.e.* a certain fraction of atoms will leave their appropriate sublattice and change into a "wrong" sublattice. In thermodynamic equilibrium the degree of disorder (or defect concentration) is a characteristic constant at a given temperature for a particular alloy system and will increase with temperature. At a certain critical temperature T_c the sublattices under consideration become indistinguishable and the ordering of the superstructure gives way to a statistical distribution of the atoms.

Such order–disorder transitions have frequently been described by means of classical statistical-thermodynamic approaches [1–7]; mostly it is assumed, in analogy to magnetic transitions, that they are second order, *i.e.* continuous, transformations [8], although Grønvold, for example, found in the course of C_p measurements on Co_3Se_4, Fe_3Se_4 and Cr_3Te_4 [9–11] that some first-

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order character seems to be involved in the corresponding order–disorder transitions.

At constant pressure and temperature the Gibbs energy of a constant amount of a crystalline substance tends towards a minimum value which will be reached if the component atoms arrange themselves on the available lattice sites in the corresponding equilibrium state of order. Assuming a long-range order parameter η, the Gibbs energy $G(\eta)$ is composed of two counteracting functions of the order parameter:

$$G(\eta)=H(\eta)-Tk\ln W=H(\eta)-TS_{\mathrm{conf}}(\eta) \qquad (1)$$

where $H(\eta)$ is the non-configurational contribution and $S_{\mathrm{conf}}(\eta)=k\ln W$ is the configurational entropy according to Boltzmann. Since both W (and with it S_{conf}) and H increase with decreasing η (*i.e.* $H(\eta)$ becomes less negative), the second term in eqn. (1) will be of particular importance at higher temperatures. At absolute zero, however, it will disappear and $H(\eta)$ alone will determine the equilibrium state. If any energetic ordering tendency exists in the system, $H(\eta)$ will have its most negative value for $\eta=1$ and therefore perfect order will be established at $T=0$ K.

Wagner and Schottky [1] treat the H term in eqn. (1) by starting from an ideally ordered lattice into which point defects are introduced in a strictly statistical manner. The energy contribution of one defect of a particular kind is assumed to be constant, *i.e.* independent of the number of defects already present. This assumption has been justified by several authors by the relatively short range of interactions in the lattice [4, 12–14]: for practical purposes, frequently only nearest-neighbour interactions are of importance, so that the linear dependence of the H term on the defect concentration is only affected if defects become nearest neighbours in the lattice, for which the probability is minute if the concentration of defects is small and their distribution is statistical. Of course, the assumption of a statistical distribution of defects also makes the calculation of W possible.

Given the restrictions discussed above, this so-called "zeroth approximation" is only applicable for not too large defect concentrations, as already pointed out by Wagner and Schottky themselves [1]. (However, the range of applicability of the models can be successfully extended to higher defect concentrations and thus to larger deviations from the stoichiometric composition by introducing "interaction energies" between defects, which consider the additional energetic effect of defect pairs on nearest-neighbour sites, as already pointed out very early by Anderson [15].)

In the Gorsky–Bragg–Williams approximation [2, 3, 5], critical temperatures are calculated by assuming that the energy to transfer an atom from a "right" to a "wrong" lattice site is a linear function of the degree of order. This approach is certainly an improvement over the treatment by Wagner and Schottky [1]; yet the calculated critical temperatures, where the ordering dissolves completely into a random distribution of atoms, will still be higher than the experimentally determined ones [16]. More sophisticated models for order–disorder transitions have been proposed in the past, such as the "cluster variation model" of Kikuchi [17, 18] or the approach by Gokcen [19], but they require some quite involved mathematics.

It is the object of the present study to demonstrate, using the order–disorder transition in the V_3Te_4 phase as an example, that a simple model such as the Wagner–Schottky approach, which we have already used to describe partial thermodynamic properties in this phase [20], can likewise be applied successfully to the problem of order–disorder transformations.

2. The superstructure of V_3Te_4

Figure 1 shows the partial V–Te phase diagram according to Terzieff *et al.* [21]. In the composition range between 50 and 66.7 at.% Te a series of phases exists in this system with crystal structures that can be derived from the NiAs (B8) type [21–24]. Whereas, according to experimental evidence, the high temperature γ phase crystallizes in the partially filled CdI_2 structure

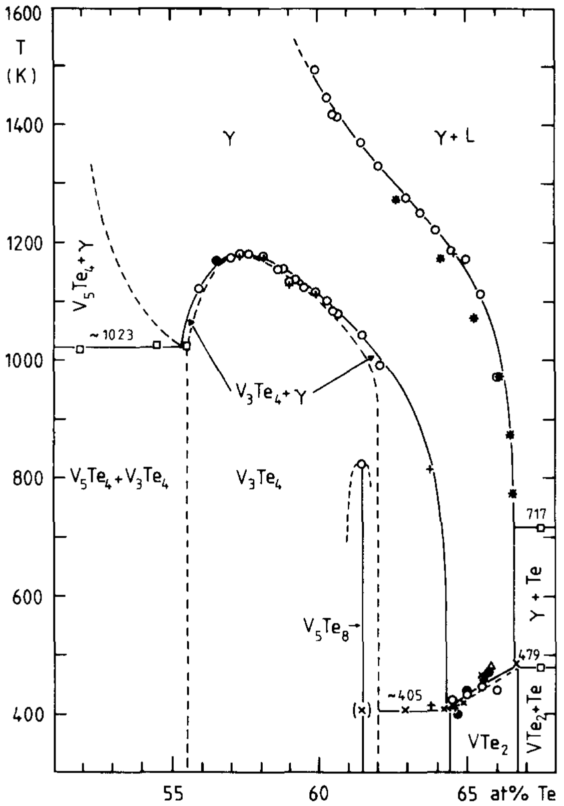

Fig. 1. Partial V–Te phase diagram according to Terzieff *et al.* [21]: ○, □, thermal effects; +, magnetic effects; *, thermodynamically deduced phase boundary; ×, ●, △, literature data from refs. 22–24.

(see below), it was found that the phases at lower temperatures are characterized by an ordered arrangement of transition metal vacancies.

The ideal NiAs structure can be envisioned as consisting of an h.c.p. arrangement of atoms of a main group element (metalloid) where all octahedral positions are filled with transition metal atoms [25]. Deviation from the 1:1 stoichiometry can occur by interstitial transition metal atoms (in the trigonal-bipyramidal or double-tetrahedral sites) towards the transition-metal-rich side or by vacancies on regular (octahedral) transition metal positions towards the other side. Since all phases with NiAs-related crystal structures in transition metal–chalcogen systems are restricted to a composition range with chalcogen contents of more than 50 at.%, only the latter case will be of interest here. It is usually assumed that the metalloid sublattice remains unaffected.

In order to understand the defect mechanism and the development of the various superstructures in these chalcogen systems, the transition metal sublattice is considered to consist of layers perpendicular to the crystallographic c axis. While it must be assumed that in the vicinity of the 1:1 stoichiometry the transition metal vacancies are statistically distributed over *all* these layers, it is a well-known fact that for larger deviations the vacancies are usually restricted to *alternate* layers and the structure should be described more appropriately as partially filled CdI_2 type (removing all transition metal atoms from alternate layers in an NiAs lattice leads to the CdI_2 structure). Further ordering phenomena are frequently observed at lower temperatures, where the vacancies tend to arrange themselves in ordered patterns within alternate transition metal layers; such superstructures have been observed, for example, for compositions M_7X_8, M_5X_6, M_3X_4, M_2X_3 and M_5X_8 (where M is a transition metal and X is a chalcogen) [25, 26].

One of the characteristic features of the V–Te phase diagram (Fig. 1) is the existence of the V_3Te_4 phase field, which transforms at higher temperatures into the γ phase. The ideal superstructure of this V_3Te_4 phase is shown in Fig. 2(a) in a pseudo-orthorhombic setting (the Te atoms are omitted for clarity) and is commonly described as Cr_3S_4 type ($C2/m$) [27]; the unit cell of the NiAs structure is indicated for comparison. One can see that half the vanadium sites in every other layer are empty and that the vacancies are arranged in "strings"; an additional shift in the relative positions of these "strings" leads to the doubling of the c parameter.

In a recent study [20] we discussed the mechanism leading to non-stoichiometry in V_3Te_4: gradual filling of the vacant positions with V atoms or removal of V atoms from the originally occupied sites in alternate layers. On the basis of this mechanism a statistical model was developed to interpret earlier thermodynamic measurements by Ipser [28]. In the course of this study [20] it was also found that the best agreement between theoretical model and experimental tellurium activities was obtained with the assumption that with increasing tellurium content the typical 3:4 superstructure changes gradually to a (5:8)-type ordering. This was taken as an indication for the V_5Te_8 superstructure to exist up to much higher temperatures than previously assumed by Terzieff *et al.* [21] (see Fig. 1).

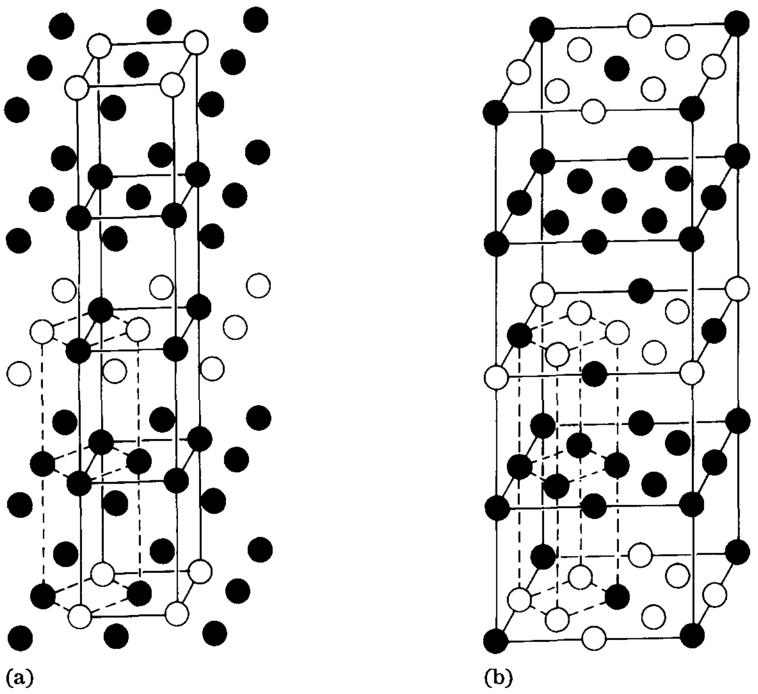

Fig. 2. Representation of the transition metal sublattice in two different NiAs-related superstructures: (a) Cr_3S_4 type; (b) V_5Se_8 type. Completely filled layers of transition metal atoms alternate with partially occupied layers: ●, transition metal atom; ○, vacancy; bold lines, contours of unit cells in pseudo-orthorhombic representation; broken lines, outlines of simple NiAs cell.

The structure reported for V_5Te_8 [29] (V_5Se_8 type, *C*2/*m* [30]) is shown in Fig. 2(b). In principle, considering only individual partially filled vanadium layers, the structure can be derived from the V_3Te_4 lattice if alternate V atoms are removed from the "strings" as discussed in ref. 20. This, however, leads to a somewhat different stacking of the partially filled layers than shown in Fig. 2(b). On the other hand, it was pointed out by Brunie and Chevreton [30] that several stacking sequences are possible. Thus it is believed, also supported by the results of ref. 20, that the stacking in V_5Te_8 is such that the structure can be directly derived from the Cr_3S_4 type.

An additional indication for the existence of the (5:8)-type ordering up to considerably higher temperatures than shown in Fig. 1 seemed to be the shape of the phase boundary of the V_3Te_4 phase. As can be seen, the boundary is markedly unsymmetrical with respect to the maximum. For the case that the (3:4)-type ordering was the only one present, one would expect a more or less perfectly symmetrical transition curve. In the following it will be demonstrated on the basis of the Wagner–Schottky type model derived in ref. 20 that this shape of the phase boundary is in perfect agreement with the assumption that the (3:4)-type ordering changes continuously to a (5:8)-type ordering within this V_3Te_4 phase.

3. Theoretical calculation of the order–disorder transition in V_3Te_4

3.1. General description of the statistical model

The derivation of the statistical model for NiAs-type phases with transition metal vacancies in alternate layers in the composition range of the V_3Te_4 phase was demonstrated in full detail in ref. 20. It was shown that a continuous transition from a (3:4)-type to a (5:8)-type ordering can be accomplished if additional vacancies are created preferentially on every other vanadium position in these "strings" (see Fig. 5 of ref. 20). However, if V atoms are removed in a statistical way from the partially filled layers (the completely filled layers remain unchanged), then the (3:4)-type ordering will more or less persist beyond the M_5X_8 composition until every other layer is completely empty and we arrive at a CdI_2 lattice.

In Fig. 3 a schematic NiAs-type crystal (consisting of 32 lattice sites) with a composition M_3X_4 and the corresponding 3:4 superstructure is separated into the different sublattices, neglecting the particular spatial arrangement; the nomenclature used here follows refs. 20 and 31. The double-headed arrows symbolize the possible defect equilibria due to thermal disorder.

For the derivation of the model it was assumed that the tellurium sublattice (β sublattice; see Fig. 3) and every other layer of the vanadium sublattice (α1 sublattice) remain completely filled. The partially filled vanadium layers (α2 sublattice) are assumed to consist of α2a and α2b positions which are respectively completely empty or filled in the ideal Cr_3S_4 structure. The α2b sublattice can be further divided into the α2b1 and α2b2 positions (from now on b1 and b2 positions for simplicity) which consist of alternate sites in the transition metal "strings". For a pure 3:4 superstructure the b1 and b2 positions are indistinguishable; however, if additional (5:8)-type ordering occurs, then this can be explained by different tendencies of the b1 and b2 sublattices to carry vacancies.

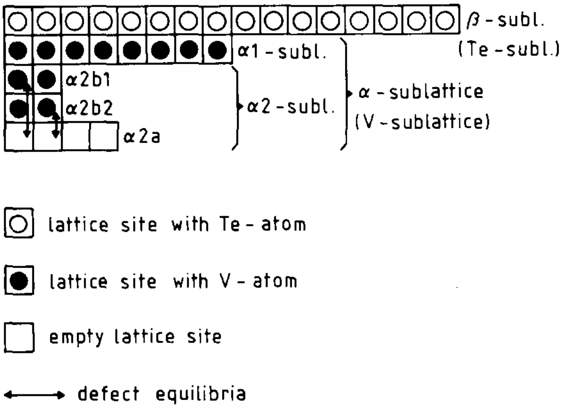

Fig. 3. Schematic representation of an NiAs-type crystal (consisting of 32 lattice sites) with a composition M_3X_4 and the corresponding 3:4 superstructure. The lattice is separated into different sublattices.

As mentioned above, there will always be a certain degree of disorder at finite temperatures, even at the exact stoichiometric composition, due to thermal motion of the atoms. For the Cr_3S_4 structure type this is assumed to be mainly due to transition metal atoms changing from filled α2b sites to empty α2a sites (for simplicity, a sites) (see Fig. 3). The resulting defect concentrations, *i.e.* V atoms on the a sublattice and vacancies on the b1 or b2 sublattice, are constant with time (dynamic equilibria) and are functions of the temperature. Two different disorder parameters were defined in ref. 20 for the "ordering concentration" M_3X_4:

$$\alpha=\left(\frac{N_{\square}^{\mathrm{b1}}}{N^{\mathrm{t}}}\right)_{3:4}, \qquad \beta=\left(\frac{N_{\square}^{\mathrm{b2}}}{N^{\mathrm{t}}}\right)_{3:4} \tag{2}$$

where $N_{\square}^{\mathrm{b1}}$ and $N_{\square}^{\mathrm{b2}}$ are the numbers of vacancies on b1 and b2 sites respectively and N^{t} is the total number of lattice sites in an NiAs lattice, *i.e.* $N^{\mathrm{t}}=N^{\alpha}+N^{\beta}=N^{\alpha 1}+N^{\mathrm{a}}+N^{\mathrm{b1}}+N^{\mathrm{b2}}+N^{\beta}$. It is clear that for the case $\alpha=\beta$ any additional vacancies will be distributed in a statistical way over all b sites; if α and β are different, then we will have a tendency to approach a (5:8)-type ordering with increasing number of vacancies on the b sites. For $\alpha=\beta=0$ the Cr_3S_4 structure would be ideal, which is possible only at 0 K; for $\alpha=\beta=1/32=0.03125$ the (3:4)-type ordering would disappear entirely and the vacancies would be statistically distributed over alternate layers (partially filled CdI_2 structure; see also ref. 20).

Using these disorder parameters, theoretical equations were derived in ref. 20 which describe the composition dependence of the thermodynamic activities of vanadium and tellurium in the range including the compositions M_3X_4 and M_5X_8. Applying the model to the experimental tellurium activities (from ref. 28) at 1023 K, the best agreement was obtained with the parameters $\alpha=0.00039$, $\beta=0.004$ and $\ln a_{\mathrm{Te}(3:4)}=-4.35$ (where $a_{\mathrm{Te}(3:4)}$ is the tellurium activity at the exact 3:4 stoichiometry). From the considerable difference between α and β it was concluded that the (5:8)-type ordering must still exist at 1023 K.

3.2. Temperature dependence of the disorder parameter

At the stoichiometric 3:4 composition we can write for constant pressure and for constant numbers of moles, n_{V} and n_{Te},

$$G=G(\alpha,\beta,T) \tag{3}$$

and in thermodynamic equilibrium the Gibbs energy must be a minimum with respect to α and β:

$$\left(\frac{\partial G}{\partial \alpha}\right)_{T,\beta}=0 \tag{4a}$$

$$\left(\frac{\partial G}{\partial \beta}\right)_{T,\alpha}=0 \tag{4b}$$

If G is separated into configurational and non-configurational terms, eqn. (3) can be expanded (for T=constant) as

$$G = H(\alpha,\beta) - TS_{\mathrm{th}}(\alpha,\beta) - TS_{\mathrm{conf}}(\alpha,\beta) \tag{5}$$

where S_{th} is the thermal, *i.e.* non-configurational, entropy contribution. Combining eqns. (4) and (5), one obtains

$$\left(\frac{\partial H}{\partial \alpha}\right)_{T,\beta} - T\left(\frac{\partial S_{\mathrm{th}}}{\partial \alpha}\right)_{T,\beta} - T\left(\frac{\partial S_{\mathrm{conf}}}{\alpha}\right)_{T,\beta} = 0 \tag{6a}$$

$$\left(\frac{\partial H}{\partial \beta}\right)_{T,\alpha} - T\left(\frac{\partial S_{\mathrm{th}}}{\partial \beta}\right)_{T,\alpha} - T\left(\frac{\partial S_{\mathrm{conf}}}{\partial \beta}\right)_{T,\alpha} = 0 \tag{6b}$$

According to Wagner and Schottky [1], S_{th} and H are linear functions of the defect concentrations and therefore also of α and β, *i.e.* the derivatives of the non-configurational terms must be constants (C_1–C_4):

$$\left(\frac{\partial H}{\partial \alpha}\right)_{T,\beta} = C_1, \quad \left(\frac{\partial S_{\mathrm{th}}}{\partial \alpha}\right)_{T,\beta} = C_2, \quad \left(\frac{\partial H}{\partial \beta}\right)_{T,\alpha} = C_3, \quad \left(\frac{\partial S_{\mathrm{th}}}{\partial \beta}\right)_{T,\alpha} = C_4$$

Any possible temperature dependence of these constants is neglected. From this follows

$$\left(\frac{\partial S_{\mathrm{conf}}}{\partial \alpha}\right)_{T,\beta} = \frac{C_1}{T} - C_2 \tag{7a}$$

$$\left(\frac{\partial S_{\mathrm{conf}}}{\partial \beta}\right)_{T,\alpha} = \frac{C_3}{T} - C_4 \tag{7b}$$

These derivatives can be calculated using Boltzmann's formula and Stirling's approximation as shown in ref. 20; for the exact stoichiometric 3:4 composition one obtains

$$\left(\frac{\partial S_{\mathrm{conf}}}{\partial \alpha}\right)_{T,\beta} = R\frac{N^{\mathrm{t}}}{N_{\mathrm{L}}}\ln\left(\frac{16\alpha}{1-16\alpha}\,\frac{8(\alpha+\beta)}{1-8(\alpha+\beta)}\right) \tag{8a}$$

$$\left(\frac{\partial S_{\mathrm{conf}}}{\partial \beta}\right)_{T,\alpha} = R\frac{N^{\mathrm{t}}}{N_{\mathrm{L}}}\ln\left(\frac{16\beta}{1-16\beta}\,\frac{8(\alpha+\beta)}{1-8(\alpha+\beta)}\right) \tag{8b}$$

(N_{L} is Avogadro's number), which yield after division by the constant term $RN^{\mathrm{t}}/N_{\mathrm{L}}$ the relationships

$$\ln\left(\frac{16\alpha}{1-16\alpha}\,\frac{8(\alpha+\beta)}{1-8(\alpha+\beta)}\right) = \frac{c_1}{T} - c_2 \tag{9a}$$

$$\ln\left(\frac{16\beta}{1-16\beta}\,\frac{8(\alpha+\beta)}{1-8(\alpha+\beta)}\right) = \frac{c_3}{T} - c_4 \tag{9b}$$

where c_1–c_4 are constants. If we know α and β at two different temperatures, we have four equations to solve for the four constants and we can calculate the temperature dependences $\alpha=\alpha(T)$ and $\beta=\beta(T)$.

The values of α and β for the V_3Te_4 phase are known at 1023 K from ref. 20; to obtain values at a second temperature, the tellurium activities were converted to 1073 K using the corresponding partial molar enthalpies $\Delta\bar{H}_{Te}$ and the resulting curve was evaluated in terms of the theoretical model (Fig. 4). This resulted in $\alpha=0.00093$ and $\beta=0.0062$ at 1073 K and together with the values $\alpha=0.00039$ and $\beta=0.0040$ at 1023 K from ref. 20 it was possible to compute the constants c_1–c_4.

Furthermore, as discussed above, the (3:4)-type superstructure gives way to a statistical vacancy distribution in alternate transition metal layers (partially filled CdI_2 type) if $\alpha=\beta=1/32=0.03125$. From this condition the ideal critical temperature can be derived using eqns. (9), yielding

$$T_{c,id}=\frac{c_1}{c_2}=\frac{c_3}{c_4} \tag{10}$$

and with the values of c_1–c_4 calculated above one obtains $T_{c,id}=1423$ K. The variation in the disorder parameters α and β with temperature for the

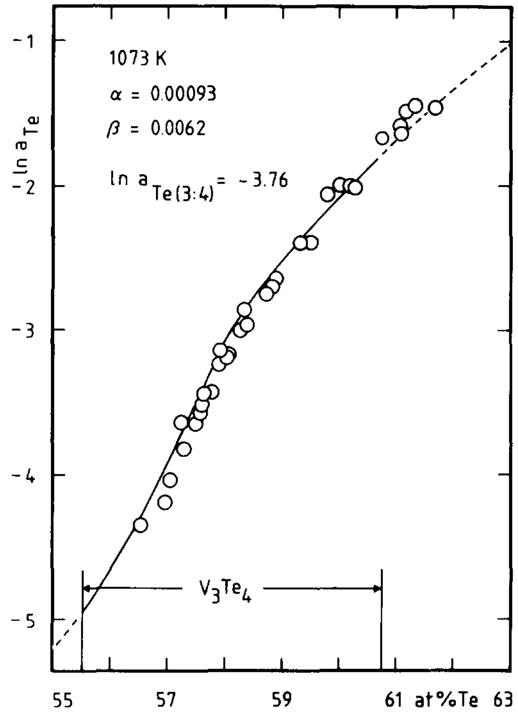

Fig. 4. Natural logarithm of tellurium activity at 1073 K as a function of composition within the V_3Te_4 phase. The full line shows the theoretical curve calculated with $\alpha=0.00093$, $\beta=0.0062$ and $\ln a_{Te(3:4)}=-3.76$.

V_3Te_4 phase is shown in Fig. 5. It can be seen that the two parameters become equal at 1423 K, where they reach the critical value $1/32 = 0.03125$; any larger value would be physically meaningless.

It has to be pointed out here that the assumptions of the present model result in the fact that if α and β are different, they will remain so below the ideal critical temperature, although their temperature variations may differ considerably. This means that the tendency to form a (5:8)-type ordering does not disappear before the (3:4)-type superstructure disappears. Furthermore, it can be shown that the ideal critical temperature calculated according to the Wagner–Schottky-type model (without considering interaction energies between like defects) turns out to be composition independent.

From Fig. 1 it can be seen that the experimentally determined transition temperature, $T_c = 1180$ K at about 57.1 at.% Te, is far below the ideal critical temperature of 1423 K. Therefore we must conclude that the ordering breaks down at a certain limiting defect concentration in the lattice. A possible way to calculate the transition temperatures on the basis of this assumption will be presented below.

3.3. The long-range order parameter η

In order to define the degree of disorder in the entire V_3Te_4 phase in a mathematical way, we will introduce the composition-dependent long-range order parameter η according to Bragg and Williams [2, 3]:

$$\eta = \frac{8}{N^t}\left(|N_\square^{b1} - N_\square^{b2}| + |N_\square^{b1} + N_\square^{b2} - N_\square^{a}|\right) \tag{11}$$

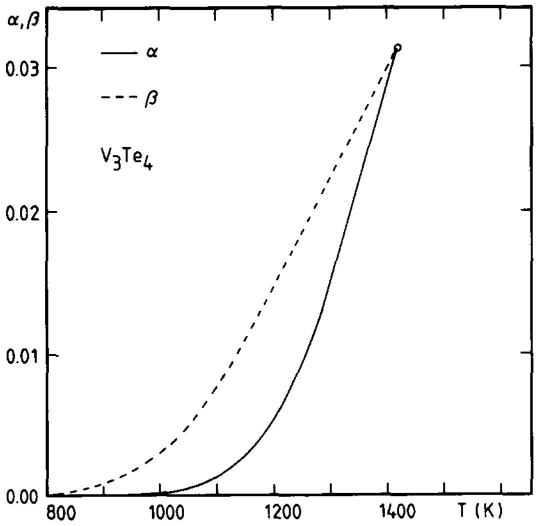

Fig. 5. Disorder parameters α and β for the V_3Te_4 phase as a function of temperature. $T_{c,id} = 1423$ K for $\alpha = \beta = 1/32 = 0.03125$.

It can be shown (see Fig. 3) that $\eta = 1$ for ideal (3:4)-type and (5:8)-type ordering and that $\eta = 0$ if the 3:4 superstructure disappears completely, *i.e.* for a partially filled CdI_2 type.

Figure 6 shows the variation in η with temperature for stoichiometric V_3Te_4 obtained with eqn. (11) and using the relationships between the defect concentrations and the parameters α and β as given in the definitions in eqns. (2).

Let us define η_c as the critical value of the long-range order parameter where the superstructure breaks down, *i.e.* for $\eta > \eta_c$ the ordered vacancy arrangement will be stable, while for $\eta < \eta_c$ we will have a statistical distribution of the vanadium vacancies in alternate layers. It is further assumed that η_c is a constant for the entire homogeneity range of the V_3Te_4 phase and that the ordering breaks down if η becomes smaller than η_c at any composition within the phase.

The experimentally determined transition temperature for stoichiometric V_3Te_4 is $T_c = 1180$ K [21] and this temperature is marked in Fig. 6, resulting in a value of $\eta_c = 0.79$. From this it is concluded that long-range order can only exist for larger values of η, whereas for $\eta \leq 0.79$ a random vacancy distribution over the α2b sublattice will be stable. This was assumed to be valid for the entire homogeneity range, as discussed above.

If the long-range order parameter η is calculated as a function of composition for different temperatures, using the model equations of ref. 20 and the temperature dependence of α and β derived here, one obtains the diagram in Fig. 7. It is interesting to observe that the maximum in the curve of η *vs.* T shifts gradually to higher tellurium contents with increasing temperature or decreasing order. The value $\eta_c = 0.79$ is indicated as a horizontal line in this figure; from the intersections of this line with the η curves it is possible to determine the phase boundaries at different temperatures. It has to be noted that according to the simple model presented here, the transformation would be of first order, since η changes abruptly from 0.79 to zero.

The final result is given in Fig. 8, where the calculated phase boundary is compared with the experimental phase diagram according to Terzieff

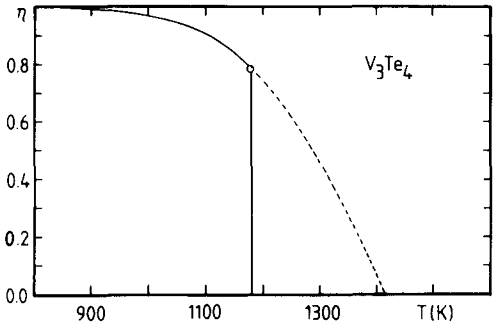

Fig. 6. Long-range order parameter η for stoichiometric V_3Te_4 as a function of temperature. The critical value $\eta_c = 0.79$ is reached at $T_c = 1180$ K.

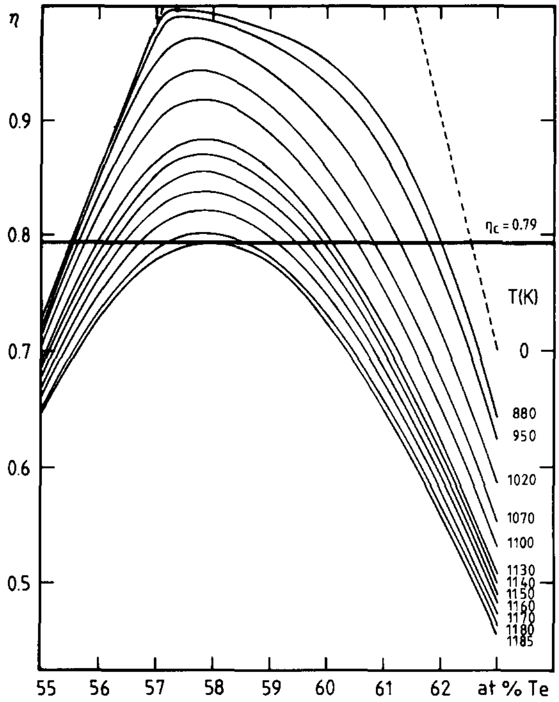

Fig. 7. Long-range order parameter η as a function of composition for different temperatures. The hypothetical isotherm at $T=0$ K is included as a broken line.

et al. [21]. It can be seen that the agreement is very good and that the width of the phase field is correctly obtained. However, owing to the presence of (5:8)-type ordering in the V_3Te_4 phase, the maximum in the theoretical curve is shifted slightly away from the stoichiometric composition to about 57.8 at.% Te (see Fig. 7) and the temperature of the maximum is calculated as 1185 K, which is still within experimental error.

A comparison with data for the Cu_3Au phase shows that a similar critical long-range order parameter was found in this case. As discussed by Guttman [32], several authors observed a gradual diminishing of the long-range order parameter with temperature in Cu_3Au down to about 0.8, which is followed by a sudden drop to zero at the critical temperature where the superstructure disappears [33–35]. The coincidence with the present value $\eta_c=0.79$ for V_3Te_4 is quite remarkable.

4. Conclusions

The good agreement between theoretical and experimental phase boundaries shows that the approximations of the Wagner–Schottky model yield in principle a correct description of the order–disorder transition. Likewise it proves that the assumption of a composition-independent critical long-range

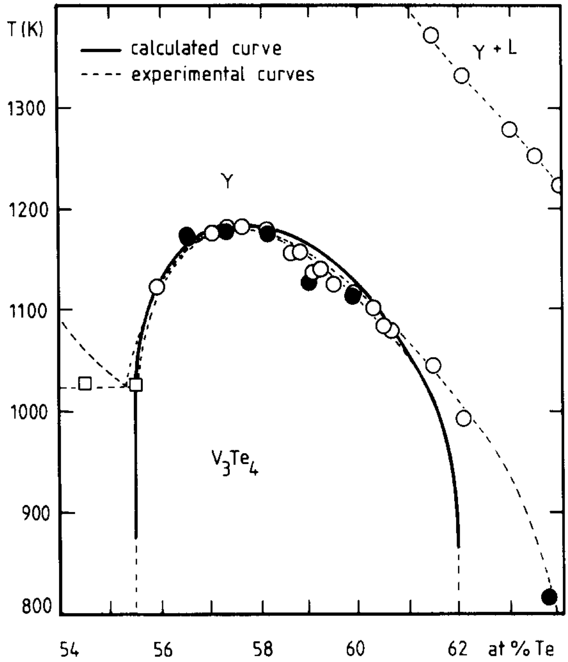

Fig. 8. Comparison of the calculated phase boundary (full curve) with the experimental phase diagram (broken curve): ○, thermal effects; ●, magnetic effects.

order parameter η_c for the V_3Te_4 phase is a good and useful approach. On the other hand, the good agreement confirms also the consistency of the thermodynamic data of Ipser [28] (from which the parameters α and β were deduced) with the differential thermal analysis measurements of Terzieff *et al.* [21].

It can be shown with the present model that a (3:4)-type ordering alone would result in a symmetrical transformation curve for the V_3Te_4 phase. Only the inclusion of an additional (5:8)-type ordering tendency within the homogeneity range of this phase yields this unsymmetrical phase boundary. Thus the shape of the experimentally determined boundary confirms the conclusion drawn from the activity curves [20] that an additional (5:8)-type ordering tendency exists in the V_3Te_4 phase up to the temperature where the order–disorder transformation occurs.

Brunie and Chevreton [29] found this V_5Te_8 superstructure only in slowly cooled samples, whereas they reported that the additional ordering had disappeared for samples quenched from 1073 K which showed the Cr_3S_4 type superstructure only. This, of course, would not quite agree with our results. A possible explanation could be that with increasing disorder (and thus with increasing temperature) the 5:8 superstructure would be more and more difficult to distinguish. However, we hope that it will be possible to clarify this question in the near future by high temperature X-ray and C_p measurements.

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