

Densities, Lattice Parameters and Defect Chemistry of Pure Non-stoichiometric Compounds

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General relations are derived between the quantities describing the defect chemistry of pure, non-stoichiometric compounds and the experimental values of lattice parameters and densities of these materials. These relations show how to analyse the experimental data without the need for arbitrary assumptions about the defect situation. The theory is applied to published data of non-stoichiometric TiO, TiS₂, Ti₂S₃, and Bi₂Te₃. The models assumed in the literature, in order to interpret the experimental data, are shown to be only the most simple among a series of possible defect situations which are consistent with the data.

1. Introduction

The relation between density, lattice parameters, and the generalised description of defect chemistry was discussed recently for crystalline compounds M_mX_k containing an impurity L_lX_j [1]. One might expect that a corresponding approach could be made in the case of non-stoichiometric pure compounds M_mX_{k+z} (z positive or negative). A closer inspection, however, shows an essential difference between the approximate description of impure solid solutions and non-stoichiometric pure compounds. The reasonable assumption made in the description of the impure solid solution is that the defect situation is controlled by the impurity. For example: in CaF₂, the concentration of the native defects remains below 0.1% under most preparative conditions, but up to 35% of impurity, like YF₃, can be incorporated under the same conditions. The incorporated amount of impurity is known, either by the sample preparation method or by chemical analysis afterwards. Thus, one parameter controlling the defect chemistry can be treated as a known variable.

The corresponding approach in pure, non-stoichiometric compounds would mean that

the defect situation is controlled by the deviation from stoichiometry, z . Such an assumption, however, would prevent the application of the theory in the more interesting situations. These situations occur when z changes continuously from positive to negative values; for example in TiO, where equilibrating the crystals at 1000°C in different oxygen pressures causes a variation in the composition between $z = +0.20$ and $z = -0.14$ [2], while in the stoichiometric crystal ($z = 0$) itself at least 10% of the lattice sites are empty. Thus, the defect chemistry is much larger than the deviation from the stoichiometric composition would indicate. In view of the situation indicated above, it seems to be worthwhile to develop here the necessary theory for the pure binary phases. The formulae describing the relation between densities, lattice parameters, and possible defect situations are derived in section 2. Several graphical representations of the data are possible. The choice of the best representation depends somewhat upon the problem under consideration. The methods will be illustrated by using published data concerned with TiO, TiS₂, and Bi₂Te₃ (section 3).

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2. Mass-Sensitive Properties of Non-stoichiometric Pure Compounds

One way to describe the results of the measurement of the density d and the lattice parameter a (assuming a cubic lattice) of a non-stoichiometric compound M_mX_{k+z} (stoichiometric for $z = 0$) is by means of the total number of M -atoms $[M_{\text{tot}}]$ and X -atoms $[X_{\text{tot}}]$ per unit cell. This total number contains all atoms irrespective of their position in the unit cell.

Then:

$$d a^3 = \text{total mass per unit cell} \\ = \left([M_{\text{tot}}]a_M + [X_{\text{tot}}]a_X \right) N^{-1} \quad (1)$$

$$[X_{\text{tot}}] = \frac{k+z}{m} [M_{\text{tot}}] \quad (2)$$

in which a_M is the atomic weight of M , a_X the atomic weight of X , and N Avogadro's number.

The numbers $[M_{\text{tot}}]$ and $[X_{\text{tot}}]$ can be obtained immediately from equations 1 and 2:

$$[X_{\text{tot}}] = \frac{dNa^3(k+z)}{ma_M + ka_X + a_Xz} \quad (3)$$

$$[M_{\text{tot}}] = \frac{dNa^3m}{ma_M + ka_X + a_Xz} \quad (4)$$

One can proceed from this description, dealing with total numbers of atoms, to a description in terms of defects in the following way. Assuming the stoichiometric compound M_mX_k without lattice defects to be the ideal compound, and assuming the unit M_mX_k to occur χ times in each ideal unit cell, then the ideal number of M -atoms is $m\chi$, and of X -atoms, $k\chi$. Describing the deviation from the ideal number of atoms per unit cell with $[T_M]$ for the M -atoms and $[T_X]$ for the X -atoms, the following relations are obvious:

$$[T_M] = m\chi - [M_{\text{tot}}] \quad (5)$$

$$[T_X] = k\chi - [X_{\text{tot}}] \quad (6)$$

$[T_M]$ describes the number of M -atoms lacking per unit cell; when the value of $[T_M]$ is negative, an excess of M is present in comparison with the ideal structure.

In defect chemistry, the deviation from the ideal structure is described with vacancies (V_M, V_X), with interstitial atoms (M_i, X_i), and with atoms on wrong lattice sites (M_X, X_M) [3-5]. Although more detailed descriptions of effective charges, association of defects, etc. are being used in defect chemistry, their introduction

in the present study has no applicability. The mass in a unit cell, as calculated from experimental values of density and lattice parameter, is not influenced by these details. Therefore, concentrations $[V_M]_{\text{tot}}$, $[V_X]_{\text{tot}}$, $[M_i]_{\text{tot}}$, $[X_i]_{\text{tot}}$, $[M_X]_{\text{tot}}$, $[X_M]_{\text{tot}}$ are used, indicating the total number of each defect per unit cell, irrespective of charge and association. Obviously, $[T_M]$ summarises all possibilities for removing M from the lattice.

$$[T_M] = [V_M]_{\text{tot}} - [M_i]_{\text{tot}} + [X_M]_{\text{tot}} - [M_X]_{\text{tot}} \quad (7)$$

Here, both $[V_M]$ and $[X_M]$ mean a decrease of M -atoms: in the former case, because M -sites are empty; in the latter case, because a M -site is occupied by X and thus cannot contain M . $[M_i]$ and $[M_X]$ indicate additional M -atoms and should be counted as a negative removal.

In the same way,

$$[T_X] = [V_X]_{\text{tot}} - [X_i]_{\text{tot}} + [M_X]_{\text{tot}} - [X_M]_{\text{tot}} \quad (8)$$

One of the aspects of defect chemistry is the recognition of a common defect state in several samples. That means in the present case that a change of the composition may change the absolute values of the defect concentrations, but the ratio of these concentrations may remain constant. By expressing the concentrations of the defects relative to the total amount (ΣAll) of all defects

$$\Sigma\text{All} = [V_X]_{\text{tot}} + [V_M]_{\text{tot}} + [M_i]_{\text{tot}} \\ + [X_i]_{\text{tot}} + [X_M]_{\text{tot}} + [M_X]_{\text{tot}} \quad (9)$$

the relative quantities ρ are obtained:

$$\left. \begin{aligned} \rho_{V_M} &= \frac{[V_M]_{\text{tot}}}{\Sigma\text{All}} \\ \rho_{M_i} &= \frac{[M_i]_{\text{tot}}}{\Sigma\text{All}} \end{aligned} \right\} \quad (10)$$

etc.

Then (7) and (8) can be rewritten

$$[T_M] = (\rho_{V_M} - \rho_{M_i} + \rho_{X_M} - \rho_{M_X}) \Sigma\text{All} \quad (11)$$

$$[T_X] = (\rho_{V_X} - \rho_{X_i} + \rho_{M_X} - \rho_{X_M}) \Sigma\text{All} \quad (12)$$

or, introducing

$$R_M = \rho_{V_M} - \rho_{M_i} + \rho_{X_M} - \rho_{M_X} \quad (13)$$

$$R_X = \rho_{V_X} - \rho_{X_i} + \rho_{M_X} - \rho_{X_M} \quad (14)$$

then

$$[T_M] = R_M \Sigma\text{All} \quad (15)$$

$$[T_X] = R_X \Sigma\text{All} \quad (16)$$

Although $[T_M]$ and $[T_X]$ can be derived from the experiments by means of (3), (4), (5), and (6), there is no way to determine ΣAll from density and lattice parameter data. Thus, the individual values of R_M and R_X cannot be derived, and it is not possible to check the constancy of the defect situation along these lines. One can try to evaluate their ratio R

$$R = \frac{R_X}{R_M} = \frac{[T_X]}{[T_M]} \quad (17)$$

since constant ρ values also imply a constant ratio R . However, there are two disadvantages to this method. In some defect situations, R_M will be zero. For example, when in $TiO_{0.8}$ a pure oxygen vacancy model should predominate, then $\rho_{V_X} = \Sigma All = 1$, all other ρ 's are zero, $R_X = 1$ and $R_M = 0$. The experimental deviations will make R large and variable. Every other choice, such as R_M/R_X , or $R_M/(R_X + R_M)$, may suffer occasionally from this difficulty. The second disadvantage is that valuable information contained in $[T_M]$ and $[T_X]$ is lost if only R is calculated (see section 3.1). The best approach is to plot $[T_M]$ and $[T_X]$ in rectangular co-ordinates: points with the same defect situation will have constant R_M and R_X , and will be found on a straight line through the origin. Note that the reverse statement is not true: even when R_M and R_X are constant, the defect chemistry may change (equations 13 and 14).

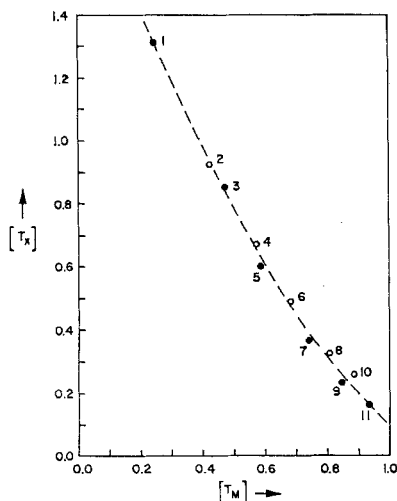


Figure 1 $[T_M]$ versus $[T_X]$ for TiO_{1+z} calculated from experimental values of d , a , and z . ○ calculated from data of Straumanis. ● calculated from data of Andersson. The numbers in the figure correspond to the experiment numbers in table I.

Finally, a few formulae are presented which may be helpful, and which can be easily derived from the foregoing equations.

Since da^3 is the mass in one unit cell, and $\chi(ma_M + ka_X)/N$ describes the mass in one unit cell in the ideal material, their ratio y

$$y = \frac{da^3 N}{\chi(ma_M + ka_X)} \quad (18)$$

indicates how much the experimentally determined mass of the unit cell deviates from the theoretical mass. When the relative atomic weight A_X of X is introduced:

$$A_X = \frac{ka_X}{ma_M + ka_X} \quad (19)$$

the following relations can be derived

$$[X_{tot}] = \frac{\chi(k+z)y}{k + A_X z} \quad (20)$$

$$[M_{tot}] = \frac{mk\chi y}{k + A_X z} \quad (21)$$

$$[T_X] = \frac{k\chi[k(1-y) + (A_X - y)z]}{k + A_X z} \quad (22)$$

$$[T_M] = \frac{m\chi[k(1-y) + (A_X z)]}{k + A_X z} \quad (23)$$

These equations relate the characteristic quantities directly to the experimental data.

Sometimes, one wants to know the densities corresponding to some special defect model. Knowledge or assumption of the defect model implies that the ρ values and thus R_M and R_X are known. When both R_M and R_X are zero, then $[T_M]$ and $[T_X]$ are zero (equations 15 and 16), and thus $[M_{tot}] = m\chi$ and $[X_{tot}] = k\chi$ (equations 5 and 6). Then da^3 will have the value of the ideal structure (equation 1). Note that this situation does not mean that the individual ρ 's are zero. The defect situation $\rho_{V_M} = \rho_{M1}$, all other ρ 's = 0, for example, may have $y = 1$.

When R_M or R_X or both are different from zero, their appropriately chosen ratio can be considered. Suppose $R_M \neq 0$, then with equations 17, 22, and 23

$$R = \frac{k[k(1-y) + (A_X - y)z]}{m[k(1-y) + (A_X z)]} \quad (24)$$

y can be solved from this equation, and after combination with equation 18 one finds

$$d = \frac{\chi(mR - k)(ma_M + ka_X + a_{Xz})}{Na^3(mR - k - z)} \quad (25)$$

A slight rearrangement of this equation permits the calculation of a^3 when d and R are known. When the individual values of R_M and R_X are preferred, the following equations can be used

$$y = \frac{(mR_X - kR_M)(k + A_{Xz})}{k(mR_X - kR_M - R_{Mz})} \quad (26)$$

$$d = \frac{\chi(mR_X - kR_M)(ma_M + ka_X + a_{Xz})}{Na^3(mR_X - kR_M - R_{Mz})} \quad (27)$$

3. Examples

3.1. Non-stoichiometric Titanium Monoxide

Experimental values of z , d , and a for TiO_{1+z} have been reported by Straumanis and Li [2] and Andersson *et al* [6]. Although the d and a values of the investigators differ somewhat, there is better agreement in the calculated mass per unit cell. Therefore, all values are reported in the sequence of increasing z , independent of their origin (see table I).

The sodium chloride structure is assumed for TiO . Thus, $\chi = 4$, $k = 1$, $m = 1$, $a_M = a_{\text{Ti}} = 47.90$, $a_X = a_{\text{O}} = 16.00$, $A_X = 0.2504$.

One result is immediately obvious from the calculations: the ratio R is not constant. Thus, there is little significance in discussing the results in terms of R . Furthermore, the calculated values of R show that information is lost when R is used instead of $[T_M]$ and $[T_X]$. For example with $z = 0.00$, the value $R = 1.00$ is obtained. Equation 24 shows that $z = 0.00$ always leads to $R = k/m$, and that no information about defect chemistry is revealed. In this situation, the use of $[M_{\text{tot}}]$ and $[X_{\text{tot}}]$ or $[T_M]$ and $[T_X]$

gives more information (fig. 1). Here, $[T_M] = [T_X] = 0.591$ for $z = 0.00$ shows that at least $(0.591/4.0) \times 100 \approx 15\%$ of either type of sites is defective at the stoichiometric composition. Individual values of ρ cannot be obtained, but the defect situations $[V_M] \approx [V_X]$, $[X_M] \approx [M_X]$, $[V_M] \approx [M_X]$ represent the simplest possibilities.

For $z \neq 0$, either $[T_M]$ ($z > 0$), or $[T_X]$ ($z < 0$) predominates. So, for $z = 0.25$, at least $(0.934/4.000) \times 100 \approx 23\%$ of the M -sites, and at least $(0.168/4.000) \times 100 = 4.2\%$ of the X -sites are defective. Suppose for a moment that this minimum possibility should represent the actual situation. Then, the defect situation could be described with $[V_M^*]$ or $[X_M^*]$ or $p \approx [V_M^*]$, etc. for 84%. One can wonder why the analysis does not show a more constant value of R . The reason is that, in terms of defect chemistry, the concentration range between $z = 0.01$ and $z = 0.25$ is quite small. The whole range belongs to the transition from $[T_M] \approx [T_X]$ to $[T_M] \gg [T_X] \approx 0$. This is demonstrated in fig. 2, where the quantity $[T_M]/([T_M] + [T_X])$ is plotted as a function of $\log z$. Then, it is obvious that the whole range between $\text{TiO}_{0.99}$ and $\text{TiO}_{1.01}$ (which is a large one in terms of defect chemistry) can be described with $[T_M] \approx [T_X] = 0.59$, or $R = 0.5$. Had measurements in this range been made, they would probably have revealed a constant R .

3.2. Non-stoichiometric Titanium Sulphide

Bernard and Jeannin have published data about non-stoichiometric titanium sulphides [7]. One series refers to TiS_2 with an excess Ti. In the terminology used in this article, that situation is described by TiS_{2+z} , $z < 0$. The hexagonal unit

TABLE I Defect chemistry of TiO_{1+z} .

	Source*	z	$d(\text{g/cm}^3)$	$a(\text{\AA})$	y	$[M_{\text{tot}}]$	$[X_{\text{tot}}]$	$[T_M]$	$[T_X]$	R
1	A	-0.284	5.01	4.196	0.8722	3.756	2.689	+0.244	+1.311	5.37
2	S	-0.140	4.998	4.1850	0.8632	3.578	3.077	+0.422	+0.923	2.19
3	A	-0.108	4.96	4.188	0.8585	3.530	3.148	+0.470	+0.852	1.81
4	S	-0.030	4.953	4.1780	0.8512	3.430	3.328	+0.570	+0.672	1.18
5	A	-0.005	4.95	4.182	0.8531	3.417	3.400	+0.583	+0.600	1.03
6	S	0.060	4.908	4.1733	0.8406	3.313	3.511	+0.687	+0.489	0.711
7	A	0.116	4.89	4.175	0.8386	3.260	3.638	+0.740	+0.362	0.489
8	S	0.150	4.854	4.1689	0.8287	3.195	3.674	+0.805	+0.326	0.405
9	A	0.195	4.83	4.172	0.8265	3.152	3.767	+0.848	+0.233	0.275
10	S	0.200	4.803	4.1661	0.8184	3.117	3.741	+0.883	+0.259	0.294
11	A	0.250	4.77	4.169	0.8145	3.066	3.832	+0.934	+0.168	0.180

* S = Straumanis; A = Andersson.

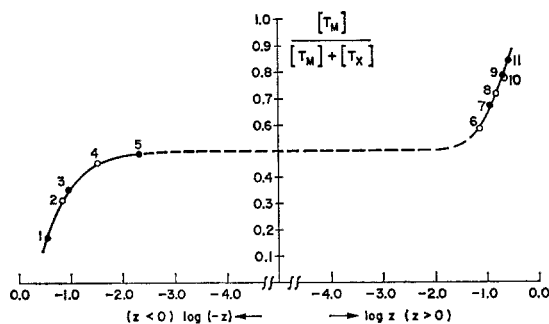


Figure 2 Defect chemistry of TiO_{1+z} as a function of $\log z$. Compare subscript of fig. 1.

cell of the ideal compound TiS_2 is supposed to have 1 molecule per unit cell. Thus, $m = 1$, $k = 2$, $\chi = 1$, $a_M = a_{\text{Ti}} = 47.90$, $a_X = a_S = 32.064$, $A_X = 0.5724$. The second series can be referred to Ti_2S_3 as the ideal structure. The hexagonal unit cell contains 4 sulphur atoms

and $8/3$ titanium atoms (statistical distribution). Thus, the description is done with $\text{Ti}_2\text{S}_{3+z}$ (here z can be both positive and negative), $m = 2$, $k = 3$, $\chi = 1.3333$, $a_M = a_{\text{Ti}} = 47.90$, $a_X = a_S = 32.064$, $A_X = 0.5010$.

In table II, the calculated values of the volume of the unit cell V , $[T_M]$, $[T_X]$, $[M_{\text{tot}}]$, $[X_{\text{tot}}]$, and R are reported in addition to the experimental values of a , c , and d (a and c refer to the hexagonal unit cell).

The results of the calculations show that the description given by Bernard and Jeannin is only approximate. They have concluded that the sulphur lattice is largely intact. The deviation from stoichiometry is explained by an excess of interstitial titanium or by titanium vacancies. This situation should correspond with $[T_X] = 0.00$, $[X_{\text{tot}}] = 2.00$, $R = 0.00$ for " TiS_2 ", and with $[T_X] = 0.00$, $[X_{\text{tot}}] = 4.00$, $R = 0.00$ for " Ti_2S_3 ". It is true that generally $|[T_M]|$ is

TABLE II Defect chemistry of titanium sulphides.

Compound	z	d	a	c	V	$[T_M]$	$[T_X]$	$[M_{\text{tot}}]$	$[X_{\text{tot}}]$	R
" TiS_2 "	-0.081	3.294	3.4085	5.7028	57.376	-0.0402	0.0038	1.040	1.996	-0.094
	-0.081	3.293	3.4091	5.7019	57.388	-0.0401	0.0040	1.040	1.996	-0.100
	-0.096	3.306	3.4089	5.7060	57.422	-0.0495	0.0018	1.050	1.998	-0.037
	-0.097	3.298	3.4095	5.7040	57.422	-0.0472	0.0071	1.047	1.993	-0.151
	-0.125	3.296	3.4109	5.7077	57.507	-0.0568	0.0184	1.057	1.982	-0.324
	-0.131	3.313	3.4109	5.7089	57.519	-0.0644	0.0106	1.064	1.989	-0.165
	-0.144	3.326	3.4123	5.7119	57.596	-0.0742	0.0063	1.074	1.994	-0.085
	-0.159	3.328	3.4125	5.7138	57.622	-0.0802	0.0114	1.080	1.989	-0.143
	-0.175	3.357	3.4132	5.7153	57.661	-0.0956	0.0006	1.096	1.999	-0.006
	-0.184	3.344	3.4134	5.7166		not calculated				
	-0.181	3.345	3.4123	5.7166	57.644	-0.0933	0.0113	1.093	1.989	-0.121
	-0.184	3.358	3.4131	5.7176	57.681	-0.0992	0.0038	1.099	1.996	-0.038
	-0.177	3.355	3.4138	5.7170	57.698	-0.0963	0.0015	1.096	1.999	-0.016
" Ti_2S_3 "	0.190	3.532	3.4213	11.4400	115.965	0.1758	0.0271	2.491	3.973	0.154
	0.186	3.538	3.4219	11.4419	116.025	0.1687	0.0207	2.498	3.979	0.123
	0.174	3.529	3.4218	11.4418	116.017	0.1703	0.0383	2.496	3.962	0.225
	0.170	3.537	3.4222	11.4422	116.048	0.1624	0.0307	2.504	3.969	0.189
	0.146	3.532	3.4226	11.4402	116.055	0.1560	0.0507	2.511	3.949	0.325
	0.098	3.585	3.4243	11.4368	116.136	0.0964	0.0187	2.570	3.981	0.194
	0.096	3.587	3.4244	11.4383	116.158	0.0936	0.0170	2.573	3.983	0.181
	0.084	3.528	3.4245	11.4352	116.133	0.1315	0.0908	2.535	3.909	0.690
	0.066	3.600	3.4249	11.4334	116.142	0.0719	0.0222	2.595	3.978	0.309
	0.040	3.602	3.4245	11.4338	116.119	0.0598	0.0375	2.607	3.962	0.628
	-0.018	3.622	3.4272	11.4320	116.284	0.0161	0.0479	2.651	3.952	2.986
	-0.028	3.640	3.4279	11.4318	116.329	0.0026	0.0334	2.669	3.967	-12.722
	-0.068	3.676	3.4310	11.4339	116.561	-0.0527	0.0135	2.719	3.986	-0.256
	-0.100	3.673	3.4335	11.4333	116.725	-0.0690	0.0332	2.736	3.967	-0.481
	-0.162	3.701	3.4388	11.4327	117.080	-0.1277	0.0348	2.794	3.965	-0.273
	-0.214	3.718	3.4405	11.4322	117.190	-0.1685	0.0506	2.835	3.949	-0.301
	-0.242	3.747	3.4417	11.4310	117.260	-0.2062	0.0383	2.873	3.962	-0.186
	-0.244	3.737	3.4416	11.4314	117.257	-0.1995	0.0504	2.866	3.950	-0.253
-0.246	3.743	3.4422	11.4298	117.281	-0.2057	0.0448	2.872	3.955	-0.218	

larger than $|[T_X]|$, but deviations of 20 to 30% from this proposed defect situation are not uncommon, as can be seen from the R values. The very large values of R found in the neighbourhood of stoichiometric Ti_2S_3 do not make much sense, since all experimental errors are accumulated here, and appear greatly exaggerated.

It is, of course, possible to interpret the calculated values of R in exact ρ values. For example, $R = -0.15$ in the case of " TiS_2 " means:

$$\begin{aligned} & \rho_{V_X} - \rho_{X_1} + \rho_{M_X} - \rho_{X_M} = \\ & -0.15(\rho_{V_M} - \rho_{M_1} + \rho_{X_M} - \rho_{M_X}) \\ \text{or} \\ & \rho_{V_X} - \rho_{X_1} + 0.15 \rho_{V_M} - 0.15 \rho_{M_1} \\ & + 0.85 \rho_{M_X} - 0.85 \rho_{X_M} = 0 \quad (28) \end{aligned}$$

This represents the maximum information obtainable from the experiments. All other interpretations are assumptions. Thus, assuming absence of antistructural defects, for example, means $\rho_{X_M} = \rho_{M_X} = 0$. When the further assumption is made of an excess of interstitial cations, and cation vacancies are assumed to be absent ($\rho_{V_M} = 0$), equation 28 becomes

$$\rho_{V_X} - \rho_{X_1} - 0.15 \rho_{M_1} = 0 \quad (29)$$

The simplest defect situation corresponding to this equation is found for $\rho_{V_X} = 0.15 \rho_{M_1}$ and $\rho_{X_1} = 0$, showing that a certain amount of empty anion sites must be present. It seems doubtful, however, that the pursuit of the interpretation along these lines will lead to definitive results. All deviations from the assumed defect situation may be due to experimental uncertainties. This may be regretted in regard to the very careful experimental work of Bernard and Jeannin, but it simply represents the limits of the information obtainable from density and lattice parameter data.

The examples of the titanium sulphides are illustrative in another way, too. According to the theory developed in this article, all defect situations with the same $[T_M]$ and $[T_X]$ are reconcilable with one set of experimental data. That means, for example, in the case of TiS_2 , that in addition to the minimum number of interstitial cations ($[T_M] = [M_1]$) more cations may be shifted from lattice sites to interstitial sites ($[T_M] = [V_M] - [M_1]$). In some defect situations, such an additional shift is improbable, since the increase of entropy does not compensate for the increase in energy. In the case of TiS_2 ,

however, the excess titanium cations are supposed to be present between two adjacent sulphur layers (TiS_2 as a pure material should have a layer structure). Additional shifts of lattice cations to interstitial layers cause the difference between a "lattice layer of cations" and an "interstitial layer of cations" to disappear. This may mean that the free energy becomes more favourable for larger disorder. This particular behaviour can occur in certain lattice types with rather extensive disorder situations (for example, in spinels, fluorites, CdI_2 structures). It stresses the danger of using only the most simple defect situations early in the analysis of the density data. Also interesting in this respect is " Ti_2S_3 ". Here, the titanium cations occupy statistically only a fraction of the available sites. This complication has been avoided in the calculations represented in table II, by assuming that there are 2.67 cation sites in a unit cell. This number corresponds to the number of cations in a unit cell with the composition $Ti_{2.67}S_{4.00}$. The calculations can, of course, also be made with a larger number of cation sites. Then the same values of $[M_{tot}]$, $[X_{tot}]$, and $[T_X]$ will be found as with the calculations represented. $[T_M]$, however, will be larger. This example shows that the calculations can be adapted easily to different descriptions of the defect structure.

3.3. Non-stoichiometric Bismuth Telluride

Recently, density measurements of Bi_2Te_{3+z} (z positive and negative) were reported [8]. The density data were combined with electrical data from the literature, and theoretical values of the densities were calculated for two defect situations. While the abstract of the article states that "precision density measurements reveal the existence of antistructure defects", the calculations show that antistructural disorder does not lead to agreement between the experimental and theoretical values of the densities. The authors mention some factors that may explain the disagreement, and thus retain the possibility that an antistructural defect situation still exists.

According to the theory in section 2, the quantities characteristic for the defect situation cannot be calculated when the lattice parameters are unknown. It is possible, however, to make some reasonable assumptions about the possible changes of the lattice parameters when the stoichiometry is changed, and to see if, in

addition to the antistructural disorder, other defect situations are possible.

Fig. 3 shows the assumptions made in the calculations. Assumption 1 (constant lattice parameter) should correspond to the assumption used by Miller and Li [8]. Assumptions 2, 3, 4, and 5 correspond to a change of 0.1% in the lattice parameters for each change of 1 at.% tellurium in the composition. A much larger change of lattice parameter cannot be excluded. The materials with excess tellurium, for example, can be described as a crystalline solid solution of Bi_2Te_3 (60 at.% tellurium) and Bi_2Te_4 (67.5 at.% tellurium), each having a corresponding structure and space group. If changes of 10% of the lattice parameters are acceptable between these structures, a 1.3% change should occur for each 1% change in tellurium. Assumptions 6 and 7 are based upon this larger

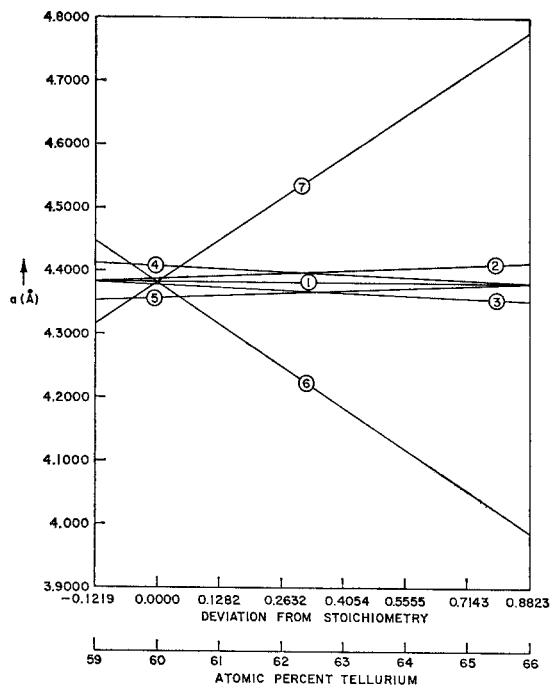


Figure 3 Assumptions made about the lattice parameter a as a function of the composition in $\text{Bi}_2\text{Te}_{3+x}$.

change of lattice parameters. Other assumptions than those in fig. 3 can be made, but the purpose of the calculations is only to obtain some idea about which of all defect situations are reconcilable with the observed densities. The material has a hexagonal structure. Thus, in addition to the lattice parameter a , the parameter c must be specified. Since the changes in c were

assumed to be proportional to a , fig. 3 also represents c (then the scale must be multiplied by 30.487/4.3835). Using the assumed values of the lattice parameters and the densities and compositions reported in reference 8, the characteristic quantities $[T_M]$ and $[T_X]$ were calculated. The results are shown in fig. 4.

Also shown are the lines representing some simple defect situations, that are summarised in table III.

TABLE III Some simple defect situations.

Situation	Defect	Characterisation	Name of model
Excess Bi	V_{Te}	$[T_X]$ positive, $[T_M] = 0$	Vacancy
	Bi_i	$[T_M]$ negative, $[T_X] = 0$	Interstitial
	Bi_{Te}	$[T_M]$ negative, $[T_X]$ positive, $[T_M]/[T_X] = -1$	Antistructural
Excess Te	V_{Bi}	$[T_M]$ positive, $[T_X] = 0$	Vacancy
	Te_i	$[T_X]$ negative, $[T_M] = 0$	Antistructural
	Te_{Bi}	$[T_M]$ positive, $[T_X]$ negative, $[T_M]/[T_X] = -1$	Antistructural

It is obvious that each of the simple defect situations is reconciled with the experimental density data, even when the lattice parameter varies only within the limits assumed in the calculations.

Another interesting point is that assumption 1 (constant lattice parameter) leads to a defect situation that can be characterised with $[T_M]/[T_X] = [R_M]/[R_X] = -0.63$; whereas a ratio -1.00 would be required for a pure antistructural model. Thus, it is clear that assumption 1 excludes the possibility of a pure antistructural model. This assumption was also used in reference 8. It is also remarkable that a calculation of V , using the theoretical density lines in reference 8 and the corresponding values of $[T_M]$ and $[T_X]$, does not lead to a constant value of V , as should be expected. Furthermore, the statement in that article that bismuth telluride is stoichiometric at the composition where p-type conductivity changes into a n-type conductivity is incomprehensible. Bi_2Te_3 is stoichiometric when it contains 60.0% tellurium. The fact, that there is some change in conductivity at 62.8% tellurium, indicates that

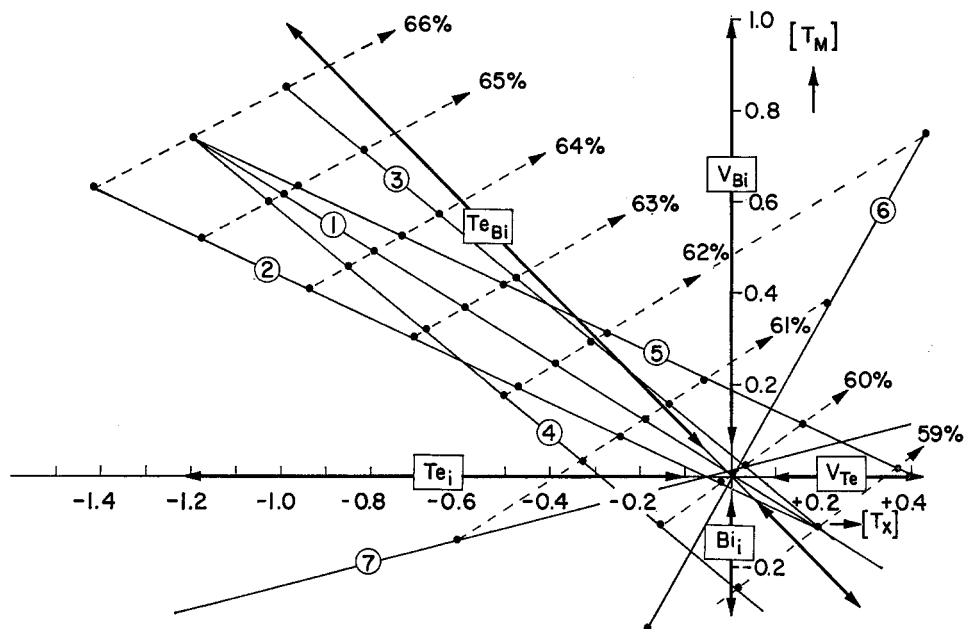


Figure 4 Calculated defect chemistry of Bi_2Te_3 , lines 1 to 7 correspond to the assumptions 1 to 7 in fig. 3. The lines labelled V_{Bi} , Te_{Bi} , etc. represent the simple defect situations described in table III. The percentages refer to the composition of bismuth telluride.

there must be some major change in defect chemistry at this composition. But, meaningful terminology requires that we describe bismuth telluride with 62.8% tellurium as non-stoichiometric and defective.

To summarise—the inconsistencies of the reported calculations together with the lack of lattice parameter data leave the defect chemistry of Bi_2Te_3 uncertain. Nevertheless, the anti-structure model is not impossible and to a certain extent even plausible. It would be interesting to have available accurate lattice parameters in addition to the accurate values of the densities. A check of the model is possible, at least within the limits stressed earlier in this article.

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