

ON A POSSIBILITY OF PREDICTING CHANGES OF THERMODYNAMICAL PROPERTIES OF METAL DURING POLYMORPHIC TRANSITIONS $A_1 \rightarrow A_2$ AND $A_3 \rightarrow A_2$

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A correlation between the ratio of the polymorphic transition temperature T_t to the Debye temperature Θ characteristic for a particular polymorph of a metal and the atomic number Z has been found.

The existence of this correlation permits the prediction of changes of some thermodynamical properties (entropy, enthalpy, specific heat) of metals during polymorphic transitions $A_3 \rightarrow A_2$ and $A_1 \rightarrow A_2$. It is also possible to predict the latent heat of polymorphic transitions. For the majority of the metals discussed the results of these predictions, which are based on the correlations found in the present work, are in good agreement with the data from literature.

1. Introduction

The problem of polymorphism of metals is recently one of the fundamental problems of the theory of metals as well as of solid state physics. There have been many efforts made by various authors to find a method which would permit the determination of thermodynamic potential of various polymorphs of the same metal as a function of temperature and pressure. These attempts were based on fundamental laws of physics, universal constants and characteristic features of their atoms [1-3]. The solution of this problem would enable the determination of the relative stability of various phases of the metal without the necessity of using experimental data on the properties of these phases. The search for such possibility involves, among others, some empirical methods in which correlation between various properties of metals (dimensions of atoms, valencies, electronegativities,

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electron configurations) and phase stability are looked for [1-3]. However the results of these studies are so far not quite satisfactory.

The present paper is another attempt of establishing some correlations between the parameters which characterize polymorphic changes in metals. It is restricted to transformations typical for metals, *i.e.*, from hexagonal structure of the type A3, or face-centred cubic structure A1 to space-centred cubic structure A2. The basis for the search for these correlations is the correlation between the temperatures of polymorphic transformations A3 → A2 and A1 → A2 and the melting temperature of the metal. The existence of this correlation has been recently reported in Ref. [4].

2. Correlations between the temperatures of polymorphic transformation A3 → A2 and A1 → A2 and the Debye temperatures of the low-and-high temperature modifications of metals

It has been shown in Ref. [4] that the A3 → A2 and A1 → A2 transformation temperatures T_t are related to the melting points T_m of these metals by a simple approximated formula

$$T_t \approx 0.9T_m. \quad (1)$$

As it can be seen from Fig. 1 the data on the transformation temperatures and melting points of metals taken from literature [5-12] are fairly well fitted by the line corresponding to Eq. (1) which confirms the validity of this approximation.

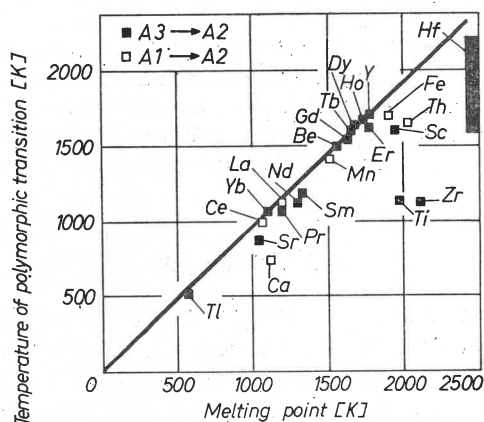


Fig. 1. Dependence of temperature of polymorphic transformation A3 → A2 and A1 → A2 on the melting point [4]

On the basis of the well known laws of the crystal lattice dynamics [13-15] and the relationship (1), one should expect the existence of a simple relation between temperatures T_t of the transitions A3 → A2 and A1 → A2 and the characteristic Debye temperatures of the particular polymorphic of metals. In order to check this conjecture the data available in literature [16] on the Debye temperatures of the low-temperature forms A3 and A1 have been compared with the transformation temperatures of these metals into the high temperature structure A2 (Table I). It was found that if one takes ratio of the polymorphic

TABLE I

Metal	Atomic number A	Atomic weight M	Transition point T_t [K]	Melting point T_m [K]	Θ_I [K]	T_t/Θ_I	Density ρ_{II} [g/cc]	Atomic volume V_{II} [cc]	Θ_{II} [K]	T_t/Θ_{II}
Sr	38	88	1878	1043	148	5.93	—	—	124	7.07
Yb	70	173	1071	1097	106	10.15	6.54	26.4	94	11.39
Pr	59	141	1070	1208	74	14.31	6.64	21.2	116	9.31
Nd	60	144	1135	1297	127	8.95	6.80	21.2	112	10.13
Sm	62	150	1190	1335	130	9.19	7.40	20.3	120	9.92
Be	4	9	1500	1557	980	1.56	—	—	649	2.31
Gd	64	157	1535	1600	156	10.1	7.80	20.1	130	11.81
Tb	65	159	1590	1629	158	10.0	—	—	146	10.85
Y	39	89	1740	1770	214	8.13	4.25	20.9	179	9.72
Dy	66	162.5	1657	1680	158	10.50	—	—	151	10.99
Ho	67	165	1701	1740	174	9.79	—	—	153	11.13
Er	68	167	1643	1770	166	8.91	—	—	146	11.27
Sc	21	45	1620	1840	380	4.27	—	—	345	4.69
Hf	72	178.5	2220	2460	213	10.4	—	—	188	11.83
Zr	40	91	1135	2125	250	4.5	—	—	154	7.35
Ti	22	48	1155	1891	278	4.15	—	—	239	4.83
Ce	58	140	1000	1070	114	8.71	6.67	21.0	110	9.09
La	57	139	1140	1193	131	8.70	5.97	23.3	113	10.09
Mn	25	55	1410	1517	297	4.75	7.21	7.6	294	4.80
Fe	26	56	1700	1805	350	4.87	—	—	315	5.39
Th	90	232	1670	2023	134	12.55	—	—	116	14.35
Ca	20	40	730	1118	219	3.33	1.52	26.3	196	3.72
Pu	94	242	749	913	58	13.03	—	—	50	14.91

transformation temperature to the Debye temperature of the low-temperature form and plots it as a function of the atomic number Z , $\frac{T_t}{\Theta_1} = f(Z)$ the experimental points lie pretty well along a straight line (Fig. 2). The points have been fitted by the least squares method by the following equation

$$\frac{T_t}{\Theta_1} = 1.75 + 0.12Z. \quad (2)$$

The deviation of the experimental $\frac{T_t}{\Theta_1}$ values from those calculated from Eq. (2) amounts on the average to 13%.

On the basis of Eq. (2) it is possible to estimate the Debye temperature values for the low temperature forms of those metals for which there are no experimental data available in literature. These values are given in rectangular frames in Table I.

The main difficulty in establishing the relationship between the temperature of polymorphic transformation, atomic number and the Debye temperature of the high temperature

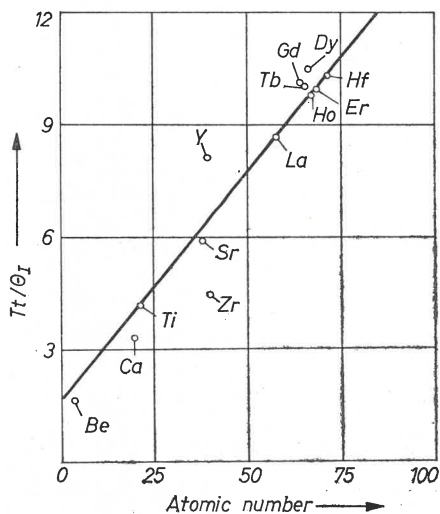


Fig. 2. Dependence of the ratio of polymorphic transformation temperature T_t to the Debye temperature Θ_1 of the low temperature form (A3 or A1) on the atomic number: $\frac{T_t}{\Theta} = f(Z)$

form (A2) was the fact that there are absolutely no data available in literature on the Debye temperature of the latter. The only possibility of overcoming this difficulty was the fact that the A2 polymorphs go over directly into liquid phase. This fact permitted the Debye temperatures to be calculated from the well-known formula of Lindemann [15]:

$$\Theta = L \sqrt{\frac{T_m}{M \cdot V^{2/3}}}, \quad (3)$$

where: Θ — is the Debye temperature, L — Lindemann constant, T_m — melting temperature, M — atomic mass, V — atomic volume.

The atomic volume V has been calculated on the basis of the data on the densities of high-temperature A2 forms of polymorphic metals taken from literature [7]. The value of the Lindemann constant for A2 structure has been taken as 110 [1, 13–15, 20]. These

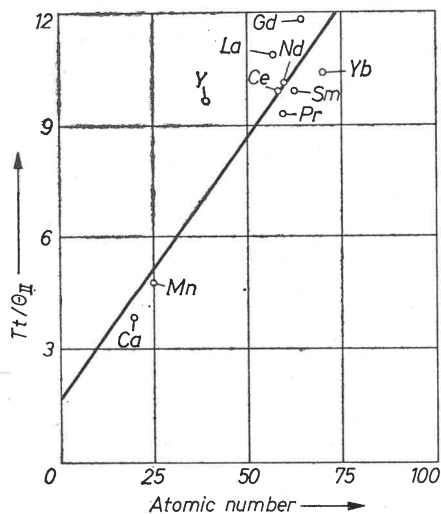


Fig. 3. Dependence of the ratio of the polymorphic transformation temperature T_t to the Debye temperature Θ_{II} of the high temperature form (A2) on the atomic number: $\frac{T_t}{\Theta_{II}} = f(Z)$

data and the calculated Debye temperatures Θ_{II} for the high-temperature A2 polymorphs are summarized in Table I.

Fig. 3 shows the ratio of the polymorphic transformation temperature to the Debye temperature Θ_{II} calculated by means of the Lindemann formula, plotted as a function of the atomic number Z of the metal. $\frac{T_t}{\Theta_{II}} = f(Z)$. It is seen that the experimental points are fairly well fitted by a straight line with the equation:

$$\frac{T_t}{\Theta_{II}} = 1.75 + 0.14Z. \quad (4)$$

The average deviation of the experimental points from the values calculated from Eq. (4) is about 8%. Eq. (4) has been used to estimate the Debye temperatures Θ_{II} for those elements for which the lack of data on the density of high temperature polymorphic forms prevented the calculation of Θ_{II} by means of the Lindemann formula (Eq. 3). These values are given in rectangular frames in Table I.

On the basis of the dependences (2) and (4) it was possible to predict the Debye

temperature ratio $\frac{\Theta_I}{\Theta_{II}}$ of the low and high temperature forms of the polymorphic metals discussed. It follows trivially from Eqs (2) and (4):

$$\frac{\Theta_I}{\Theta_{II}} = \frac{1.75 + 0.14Z}{1.75 + 0.12Z} \quad (5)$$

This ratio is plotted in Fig. 4 as function of Z .

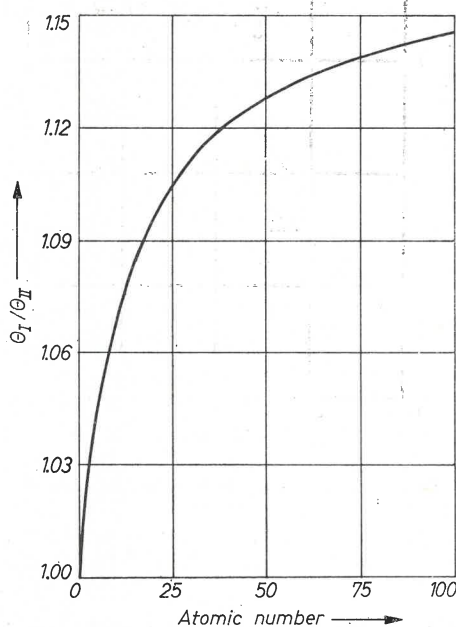


Fig. 4. Dependence of the Debye temperature ratio of the low-temperature (A3 or A1) and the high temperature (A2) form on the atomic number of the metal: $\frac{\Theta_I}{\Theta_{II}} = f(Z)$

3. Changes in the entropy of metals during polymorphic transformation A3→A2 and A1→A2

It follows from the values given in Table I that the Debye temperatures of the low- and-high temperature forms of the polymorphic metals as well as the transformation temperatures T_t satisfy fairly well the condition $T_t \gg \frac{\Theta}{4}$ on both sides of the transformation point. The Debye theory of crystal lattice vibrations predicts in such a case that the entropy can be expressed as

$$S = 4R - 3R \ln \left(\frac{\Theta}{T} \right) \quad (6)$$

where R is the gas constant.

In this situation the change in the entropy during the polymorphic transformation can be presented by the formula:

$$\Delta S = S_{II} - S_I = 3R \ln \left(\frac{\Theta_I}{\Theta_{II}} \right) \quad (7)$$

where Θ_I is the Debye temperature of the low- and Θ_{II} that of the high temperature form.

Substituting into Eq. (7) the $\frac{\Theta_I}{\Theta_{II}}$ ratio given by Eq. (5) we obtain:

$$\Delta S = 3R \ln \frac{1.75 + 0.14Z}{1.75 + 0.12Z} \quad (8)$$

Eq. (8) permits the calculation of the entropy changes during the transformations A3 \rightarrow A2 and A1 \rightarrow A2 of polymorphic metals from the knowledge of the atomic number Z only. Fig. 5 shows the graph of the dependence (8) while the comparison of the entropy changes

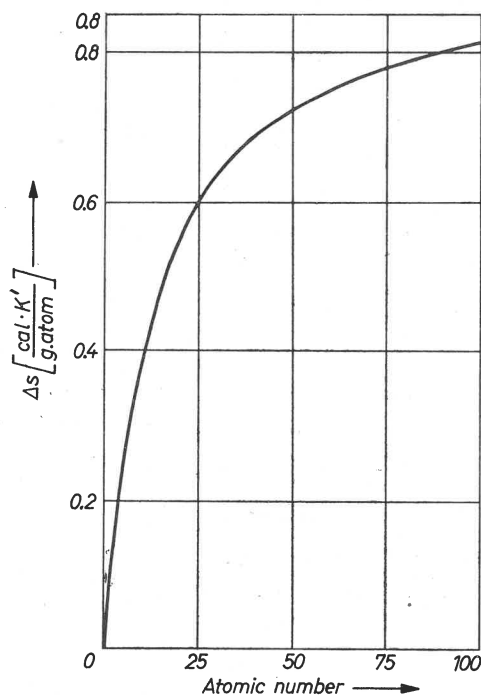


Fig. 5. Dependence of the entropy change ΔS during polymorphic transformations A3 \rightarrow A2 or A1 \rightarrow A2 on the atomic number of the polymorphic metal: $\Delta S = f(Z)$

predicted by this relationship with the experimental data available in literature [9, 10, 23, 18] is made in Table II. It is seen that the majority of experimental data is in agreement with the values predicted on the basis of Eq. (8).

TABLE II

Metal	Entropy change ΔS [cal/g.atom·K]					Thermal effect of the transition ΔH [kcal/g.atom]				
	Predicted	[18]	[9]	[10]	[7]	Predicted	[18]	[9]	[10]	[7]
Sr	0.63	0.23	—	—	—	0.56	0.20	—	—	—
Yb	0.78	—	—	—	—	0.84	—	—	—	—
Pr	0.75	—	—	—	—	0.80	—	—	—	—
Nd	0.75	0.63	—	—	—	0.85	0.71	—	—	—
Sm	0.75	0.62	0.62	—	—	0.89	0.76	0.74	—	—
Be	0.21	—	—	—	—	0.32	—	—	—	—
Gd	0.76	—	—	—	—	1.17	—	—	—	—
Tb	0.76	—	—	—	—	1.21	—	—	—	—
Y	0.69	0.68	—	—	—	1.20	1.19	—	—	—
Dy	0.76	—	—	—	—	1.26	—	—	—	—
Ho	0.77	—	—	—	—	1.31	—	—	—	—
Er	0.77	—	—	—	—	1.27	—	—	—	—
Sc	0.56	—	—	—	—	0.91	—	—	—	—
Hf	0.78	0.70	0.74	—	—	1.73	1.13	1.65	—	—
Zr	0.69	0.91	0.81	0.62	—	0.78	1.04	0.92	0.70	—
Ti	0.58	0.88	0.72	—	0.91	0.67	1.01	0.83	—	1.05
Ce	0.75	0.70	0.70	—	—	0.75	0.70	0.70	—	—
La	0.74	0.75	0.61	—	—	0.84	0.85	0.70	—	—
Mn	0.61	0.30	0.30	0.30	—	0.86	0.43	0.43	0.43	—
Fe	0.61	0.16	0.09	0.07	—	1.04	0.26	0.16	0.15	—
Th	0.80	0.40	—	—	—	1.33	0.67	—	—	—
Ca	0.55	0.08	—	0.27	0.16	0.40	0.06	—	0.20	0.12
Pu	0.80	0.63	0.59	—	0.63	0.60	0.47	0.44	—	0.47

4. Latent heat of $A3 \rightarrow A2$ and $A1 \rightarrow A2$ transformations of polymorphic metals

The knowledge of the change in the entropy of the phase transformation of the I-st order (at a given known phase transformation temperature T_i) permits the calculation of the change in the enthalpy ΔH , i.e., the so-called latent heat of phase transformation:

$$\Delta H = \Delta S \cdot T_i \quad (9)$$

After substituting Eq. (8) for ΔS we obtain for the transformation $A3 \rightarrow A2$ and $A1 \rightarrow A2$ of polymorphic metals the following formula:

$$\Delta H = 3RT_i \ln \frac{1.75 + 0.14Z}{1.75 + 0.12Z} \quad (10)$$

This equation permits the calculation of the latent heat of the transformation $A3 \rightarrow A2$ or $A1 \rightarrow A2$ in the case when the transformation temperature T_i is known.

Table II contains the comparison of the values of latent heat known from literature [23, 9, 10, 18] with the values predicted on the basis of Eq. (10). It can be seen that the agreement is satisfactory.

5. Discussion

The correlation dependences presented in this paper permit fairly accurate predictions of changes in entropy and enthalpy which occur during polymorphic transformations of metals from hexagonal (A3) and face-centred cubic structure (A1) into space-centred cubic structure (A2). The differences between the experimental values and those calculated on the basis of the above correlations which are observed in case of metals with small atomic numbers (Ca, Sr, Th, Fe, Mn) result either from the fact that the condition $T_i \gg \frac{\Theta}{4}$ is not fulfilled, or from possible experimental errors. In such cases it is necessary to calculate the entropy and enthalpy directly from the Debye function (without approximate assumptions). It is also necessary to determine precisely the transition temperature and latent heat of the transformation.

It is also interesting to measure the changes in entropy and enthalpy in polymorphic transformations of those elements for which there are no experimental data available (Yb, Pr, Gd, Tb, Dy, Ho, Er, Sc) and to compare them with the predicted values.

The correlation dependences given in the present work offer also a possibility of predicting other physical properties of metals during polymorphic transitions (specific heat C_V , density, atomic volume, Debye temperature). This encourages us to look for analogous correlations in other polymorphic transformations of metals and chemical compounds, however, it requires more experimental information on the polymorphism of such substances.

The appearance of dependences on the atomic number of the metal can be regarded as another proof of the connection between the polymorphism of metals and the electron structure of their atoms [2, 21, 22].

Further studies are in progress.

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