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Of heat capacity at homologous temperatures for metals showing h.c.p. ⇌ b.c.c. transformation

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Abstract. Some interesting aspects of the temperature dependence of the Planck's function ϕ and heat capacities of metals exhibiting the h.c.p. ⇌ b.c.c. transformation have been brought to light by the use of reduced temperature (T^*) and Planck's function ($-\phi T^*$). It has been shown that tangents drawn to the $-\phi T^*$ vs T^* plots of these metals at any chosen value of T^* intersect at a point whose coordinates are defined by the slope and intercept of ϕ vs entropy plots at any homologous temperature and the selected T^* value. A generalized expression obtained for the temperature dependence of ϕ has been used to demonstrate that the heat capacity of these metals may be visualized to have structural and material components.

Keywords. Planck's function; h.c.p. transformation; b.c.c. transformation; homologous temperature; heat capacity.

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1. Introduction

In an earlier publication (Ramachandrarao and Lele 1980) it was shown that the Planck's function ($\phi_{T_{tr}}$) for all the eleven hexagonal close-packed (h.c.p.) metals exhibiting allotropic transformation to the body-centred cubic (b.c.c.) structure correlate linearly with the entropies of the h.c.p. modifications ($S_{T_{tr}}$) at the transformation temperature (T_{tr}). Thus

$$\phi_{T_{tr}} = -\frac{G_{T_{tr}} - G_0}{T_{tr}} = m S_{T_{tr}} - k, \tag{1a}$$

$$= 0{\cdot}881\ S_{T_{tr}} - 18{\cdot}02\ \mathrm{Jk^{-1}mol^{-1}} \tag{1b}$$

where $G_{T_{tr}}$ and G_0 are the Gibbs' free energies of a given metal at T_{tr} and absolute zero-temperature respectively. We have earlier attributed the linear relationship between $\phi_{T_{tr}}$ and $S_{T_{tr}}$ to a close similarity of the temperature dependence of isobaric heat capacity (C_p) for various metals considered. In order to explore this point further, we have now studied the temperature dependence of ϕ of all the h.c.p. metals exhibiting the h.c.p. ⇌ b.c.c. transformation using a normalized frame of reference for ϕ and T.

2. Temperature dependence of the Planck function

The T_{tr} values for the eleven metals considered vary from as low a value as 507 K to 2013 K and any comparison of ϕ needed normalizing the temperature axis with respect to T_{tr}. It was found that the most appropriate plot for any meaningful comparison of the temperature dependence of ϕ is that of $-(\phi \cdot T^*)$ versus T^* where T^* is the normalized temperature, T/T_{tr}. Such a plot retains the basic feature of a G versus T plot viz., the slope at any point is $-S$.

Consider any two curves in the normalized plot (figure 1). Tangents to these curves at any chosen value T_1^* of T^* are represented by

$$-\phi T^* + \phi_1 T_1^* = -S_1 (T^* - T_1^*), \tag{2a}$$

$$-\phi T^* + \phi_2 T_1^* = -S_2 (T^* - T_1^*), \tag{2b}$$

since their slopes are $-S_1$, $-S_2$ and they pass through the points $(T_1^*, -\phi_1 T_1^*)$ and $(T_1^*, -\phi_2 T_1^*)$ respectively. The point of intersection $(T_0^*, -\phi_0 T_0^*)$ of these two tangents is given by

$$T_0^* = T_1^* \left[1 - \frac{\phi_2 - \phi_1}{S_2 - S_1} \right], \tag{3a}$$

and

$$-\phi_0 T_0^* = -\frac{T_1^* (S_2 \phi_1 - S_1 \phi_2)}{S_2 - S_1}. \tag{3b}$$

Use of (1) in conjunction with (3) yields

$$T_0^* = T_1^* (1 - m), \tag{4a}$$

and

$$-\phi_0 T_0^* = T_1^* \cdot k. \tag{4b}$$

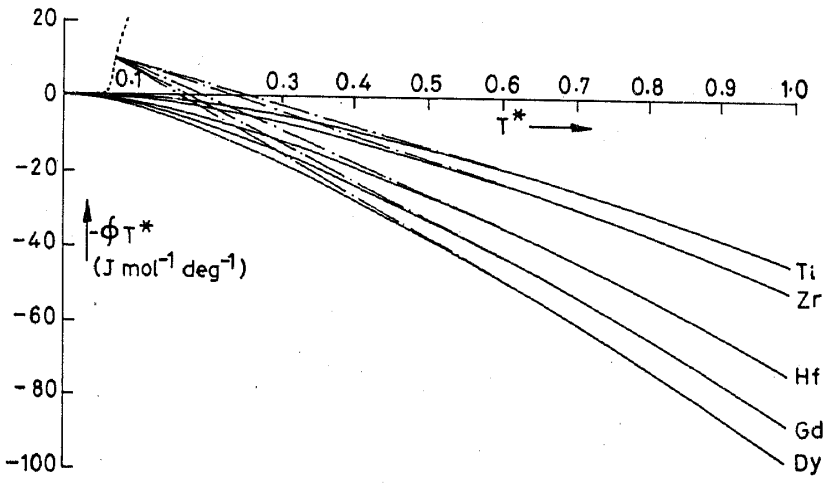

Figure 1. Variation of $-\phi T^*$ with T^* for a few of the metals undergoing the h.c.p. $\rightleftharpoons$ b.c.c. transformation. The dotted line represents the locus of the point of intersection of tangents (chain lines) drawn to the individual curves at $T^* = 0{\cdot}6$. Coordinates of the point of intersection are $(1-m)T^*$, kT^*.

The above equations clearly show that for a chosen value of T_1^*, the point of intersection is independent of the pair of metals chosen, as m and k are equally valid for all metal pairs. Hence, we expect that tangents to the normalized plots at fixed T^* intersect at a point if the ϕ versus S plot for the given set of metals is linear. Such a linearity has been already established at $T^* = 1$ (Ramachandrarao and Lele 1980). It is worthwhile to explore if a relationship similar to (1) exists at other homologous temperatures.

In order to obtain ϕ and S values at various homologous temperatures a simple computer program was used. The C_p of each metal was represented as a function of temperature using the expressions and data given by Barin *et al* (1973). Where necessary the temperature regime was suitably divided so that the given set of constants in the C_p expression are applicable. It may, however, be remarked that the expressions provided by Barin *et al* (1973) do not reproduce the tabulated C_p near the transformation temperature and underestimate C_p by 0·05 in a few cases.

3. Results and discussion

Straight lines of the type of (1) were fitted at T^* values in the range 0·25–1·0 at small intervals by the least square procedure. Slope and intercept of the straight line and the correlation coefficient were obtained in each case. The results at a few T^* values are shown in table 1. The high values of the correlation coefficients for the $\phi - S$ plots indicate, as already discussed, that the tangents to the $-\phi T^*$ versus T^* plots at any given T^* value intersect at a well-defined point. We thus establish an interesting feature of the $-\phi T^*$ versus T^* plots for metals exhibiting the h.c.p. $\rightleftharpoons$ b.c.c. allotropic transformation.

Recognizing that

$$y' = \left.\frac{\partial(-\phi T^*)}{\partial T^*}\right|_P = \left.\frac{\partial(G_T - G_0)}{\partial T}\right|_P = -S,$$

(1) can be expressed as

$$y' - \frac{y}{mT^*} + \frac{k}{m} = 0, \tag{5}$$

Table 1. Slope, intercept and correlation of the ϕ versus S plots at various values of T^*.

T^*	Slope	Intercept (J deg.$^{-1}$ mol.$^{-1}$)	Correlation coefficient
0·3	0·7832	9·9655	0·9979
0·4	0·8334	12·9640	0·9990
0·5	0·8623	15·1723	0·9994
0·6	0·8804	16·9150	0·9995
0·7	0·8924	18·3546	0·9994
0·8	0·9005	19·5802	0·9993
0·9	0·9061	20·6475	0·9992
1·0	0·9098	21·5921	0·9990

where $y = -\phi T^*$ and k as well as m are functions of T^*. This general first order differential equation has a solution of the form

$$y = u(T^*) \cdot [v(T^*) + A], \tag{6a}$$

where

$$u(T^*) = \exp \int \frac{1}{mT^*} dT^*, \tag{6b}$$

and

$$v(T^*) = -\int \frac{k}{m \cdot u(T^*)} \cdot dT^*, \tag{6c}$$

where A is a constant.

Solutions to (5) can be obtained to yield $-\phi T^*$ versus T^* plots for each metal with appropriately chosen values of A. However, as seen from (6), the functional dependence of m and k on T^* is essential for obtaining an explicit solution for (5). Since no such relationship could be arrived at *a priori* no specific solutions are being presented. The observation that (5) defines the family of $-\phi T^*$ versus T^* curves for all metals exhibiting h.c.p. $\rightleftharpoons$ b.c.c. transformation is significant and some of its implications will now be discussed.

Noting that y'' corresponds to $-(C_p/T^*)$ we can show, from (5), that

$$C_p = -T^* \{[v(T^*) + A] u''(T^*) + 2v'(T^*) u'(T^*) + v''(T^*) \cdot u(T^*)\}. \tag{7}$$

The material dependence of C_p arises only through the term containing A in (7) above. The rest of the terms are common to all metals exhibiting the h.c.p. $\rightleftharpoons$ b.c.c. transformation and can thus be visualized as contributing to a 'structural' component of C_p. Since the C_p values for the individual metals are different and characteristic of each, $u''(T^*)$ must be finite. By virtue of (k/m) being finite, $v(T^*)$ becomes finite as well. Consequently, the C_p of any metal being considered should have two components viz 'structural' and 'material'. The former is common to the entire family.

The 'structural' part of C_p is in itself a function of only T^*. Since the transformation occurs at $T^* = 1$, the h.c.p. structure can be considered to be destabilized when the 'structural' component of C_p attains a critical value. In the present study we have used thermodynamic data of only the h.c.p. phase. Identical arguments apply to the b.c.c. phase with different sets of m and k values.

4. Conclusions

It has been demonstrated that choosing homologous temperatures and plotting the temperature dependence of the Planck's function in the $-\phi T^*$ versus T^* frame of reference brings out some interesting features common to all metals exhibiting the h.c.p. $\rightleftharpoons$ b.c.c. transformation. Tangents drawn to these plots at a chosen T^* value for these metals intersect at a well-defined point whose coordinates are fixed by the conventional ϕ versus S plot and T^* value chosen. The temperature dependence of ϕ of each metal in the new frame of reference can be obtained as a solution to a first-order differential equation defined by (5). A perusal of the solution to (5) suggests that the isobaric heat capacity has two components viz the structural and material parts.

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