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The Relation between The Heat of Allotropic Transitions $A_3 \rightarrow A_1$, $A_1 \rightarrow A_2$, $A_3 \rightarrow A_2$, and the Transition Temperature of Metals

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The relations between the heats of allotropic transitions $A_3 \dashrightarrow A_1$, $A_1 \dashrightarrow A_2$, $A_3 \dashrightarrow A_2$, and the transition temperatures of polymorphic metals were established. The ratios of the heats and entropies of the transitions are respectively:

$$\Delta H_{t_1}^{A3\rightarrow A1} : \Delta H_{t_2}^{A1\rightarrow A2} : \Delta H_{t_3}^{A3\rightarrow A2} = T_{t_1} : 3T_{t_2} : 4T_{t_3},$$
$$\Delta S_{t_1}^{A3\rightarrow A1} : \Delta S_{t_2}^{A1\rightarrow A2} : \Delta S_{t_2}^{A3\rightarrow A2} = 1 : 3 : 4.$$

The total difference of enthalpies and entropies between the allotropic phases is merely dependent on the structural difference of the phases across the transition points. The energy and entropy of the phases are termed the "structural energy" and the "structural entropy."

Introduction

The importance of the allotropism of metals is well known both in the field of the theory of metals and alloys as well as in the development of fabrication technology (*1–7*). The formulation of a relationship between allotropism and other physical properties would be of great help both in theory and application.

In a very recent paper (*8*), a linear relation between the temperature of allotropic transitions, $A_3 \rightarrow A_2$ and $A_1 \rightarrow A_2$, and the fusion temperature of metallic elements was established. Considering the expected uncertainty involved in the experimental data, the majority of experimental points could be fitted by the approximate equation:

$$T_t = f(T_f) \simeq 0.9T_f. \qquad (1)$$

Where T_t is the allotropic transition temperature and T_f is the fusion temperature of the elements in degrees Kelvin.

A relation between the change in energy involved with the transition and the transition temperature may be of more fundamental interest in understanding the basic phenomena of allotropism. Such relations, although not perfect, have already been established for the phase transition, solid → liquid and liquid → gas, and are widely known as Richards' rule for the former and Trouton's rule for the latter (*9*, *10*). The fundamental idea of the relations are based on the energy changes in the state of the environment of atomic coordinations and the degree of disorders between the phases (*9–11*). Based on the same reasoning it would be of value to establish a hitherto nonexisting empirical relation between the heat of allotropic transition (ΔH_t) and the allotropic transition temperature. Based on the present knowledge of allotropic transition there should be sufficient data at present date to form such a rule for allotropism relevant to that of Richard's or Trouton's, an attempt has, however, not yet been done.

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Empirical Relations

Since, thermodynamically, the change in Gibbs free energy of transition (ΔG_t) is zero at the transition temperature, the relation between the ΔH_t and T_t becomes

$$\Delta H_t = T \cdot \Delta S_t. \qquad (2)$$

Using this simple formulation, and the experimental data available one should be able to formulate simple empirical relationships for ΔH_t as a function of T_t. Relation (2) is applied to various elements. The ΔH_t values reported by various authors (*7*, *9*, *13–17*) differ by only a few percent, for some elements the reported values differ greatly. In the latter case, the ΔH_t values used are the ones that are more frequently reported and, in a few cases, the ones that provide a value closer to the empirical relations sought. The employed ΔH_t and T_t values are presented in Table I. The metals, whose phase relations are still in the state of controversy, are also listed in Table I. They are identified with references in the Table. For these metals the phase relations and values that provide proper scheme to the empirical relations sought are chosen. The plots of the data in ΔH_t vs T_t is represented in Fig. 1 along with the plots of Richards' relation of the same metals for comparison. Considering the possible errors present in the experimental data, the ΔH_t and T_t values used appear to lie along the straight lines for the allotropic transitions $A_3 \rightarrow A_1$ and $A_3 \rightarrow A_2$. By comparison with the degrees of the scattering of the data points along the Richards' line, the present data fitting is reasonable for the allotropic transitions for a large number of metallic elements from various parts of the Periodic Table and over a wide range of ΔH_t and T_t values. The experimental points for the elements of the type $A_1 \rightarrow A_2$, however, are spread widely random. These elements could not be represented by a similar form at present with the data available. Conceivable reasons

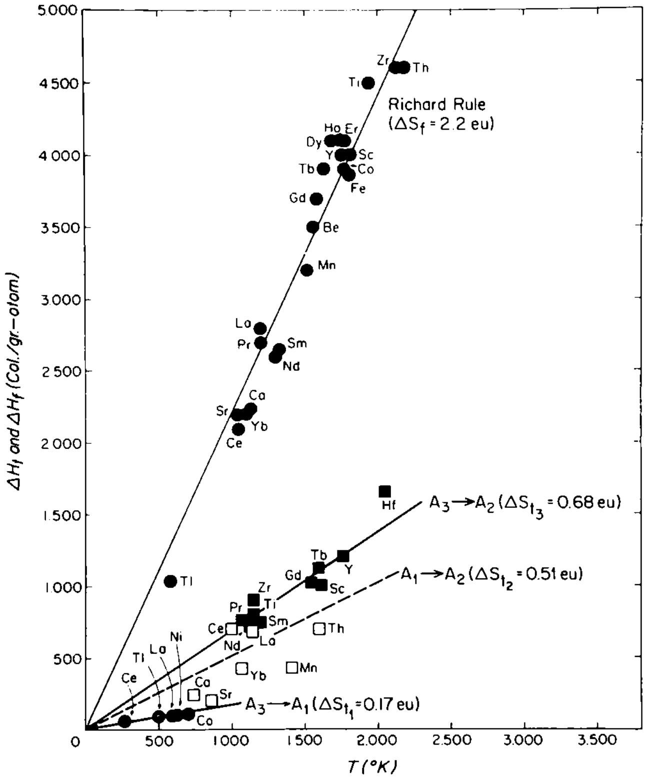

FIG. 1. The plots of the ΔH_t vs T_t. The slopes represent the entropies of transitions (ΔS_t).

TABLE I

Data on the Heat of Transitions (ΔH_t) and the Transition Temperatures (T_t)

Transition $A_3 \dashrightarrow A_1$				Transition $A_1 \dashrightarrow A_2$				Transition $A_3 \dashrightarrow A_2$			
Metal	T_t (°K)	ΔH_t (Cal)	ΔS_t (eu)	Metal	T_t (°K)	ΔH_t (Cal)	ΔS_t (eu)	Metal	T_t (°K)	ΔH_t (Cal)	ΔS_t (eu)
Co($\alpha \dashrightarrow \beta$)	700	110	0.157	Ca($\alpha \dashrightarrow \beta$)	723	240	0.332	Sc($\alpha \dashrightarrow \gamma$)	1608	958	0.60
Ni($\alpha \dashrightarrow \beta$)[a]	626	92	0.147	Mn($\gamma \dashrightarrow \delta$)	1406	432	0.307	Ti($\alpha \dashrightarrow \beta$)[d]	1155	800	0.693
La($\alpha \dashrightarrow \beta$)	583	95.5	0.164					Y($\alpha \dashrightarrow \beta$)	1758	1189	0.676
Ce($\beta \dashrightarrow \gamma$)[b]	263	65.2	0.248	Sr($\alpha \dashrightarrow \gamma$)	862	200	0.232	Zr($\alpha \dashrightarrow \beta$)	1125	900	0.800
Tl($\alpha \dashrightarrow \beta$)[c]	508	82	0.161	La($\beta \dashrightarrow \gamma$)	1141	680	0.596	Pr($\alpha \dashrightarrow \beta$)	1065	764	0.718
				Ce($\gamma \dashrightarrow \delta$)	1003	700	0.698	Nd($\alpha \dashrightarrow \beta$)	1135	713	0.628
				Yb($\alpha \dashrightarrow \beta$)	1071	425	0.397	Sm($\alpha \dashrightarrow \beta$)[e]	1190	745	0.626
				Th($\alpha \dashrightarrow \beta$)	1598	700	0.438	Gd($\alpha \dashrightarrow \beta$)[f]	1537	1032	0.671
								Tb($\alpha \dashrightarrow \beta$)[g]	1590	1063	0.668
								Hf($\alpha \dashrightarrow \beta$)	2023	(1650)	(0.816)

[a] Reference *14* and Ref. *16*, p. 115 (thin film).

[b] Reference *16*, pp. 118 and 126.

[c] Reference *14* and Ref. *16*, pp. 120 and 127.

[d] Reference *9*, p. 836; Ref. *3*, p. 316.

[e] Reference *16*, p. 127 and Ref. *19*, p. 630. Rhombohedral (pseudohexagonal) at room temperature but has *dhcp* structure at high pressure (Ref. *3*, p. 310).

[f] Reference *16*, pp. 119 and 127.

[g] Reference *3*, p. 311 and Ref. *16*, p. 127.

for the scattering of the data values may be either due to the basic nature of the metals themselves or to the experimental uncertainty involved either with the divergence in purity or with the measurement errors, or both.

Discussion

The allotropic phase transition is accompanied by the change in lattice structure. The changes in atomic environment; symmetry, coordination number and coordination polyhedron of bonding atoms, and interatomic spacing as well as the state of order at the interface between the phases due to the structural modification across the transition temperature, should affect the frequency distribution of the lattice vibration, the density of states of electrons at the Fermi level, the binding energy between atoms, and the exchange energy of magnetic interaction between electron spins, etc. The allotropic phases with different structures across the transition points should thus have different energy contents, consequently different entropies, because of the different degrees of contributions of the above mentioned factors to the respective phases. For example, even in the allotropic reaction for paramagnetic titanium, α-Ti (HCP) $\rightleftarrows$ β-Ti(BCC), the difference in two important contributing factors, θ_D, the Debye-Characteristic temperature and γ, the electronic specific heat coefficient, between the phases are noticeably large (*18*): $\theta_D{}^\alpha = 365 > \theta_D{}^\beta = 300$ and $\gamma^\alpha = 8.25 > \gamma^\beta = 5.7$. In general, for an allotropism, $\alpha \rightleftarrows \beta$, the total energy contents of the phases at constant pressure and at the transition point can thus be expressed in terms of the various contributing factors associated with the transition by

$$H_t{}^\alpha = \sum_i H_{t,i} \qquad \text{and} \qquad H_t{}^\beta = \sum_j H_{t,j}. \tag{3}$$

The heat and entropy of transition are

$$\Delta H_t = H_t{}^\beta - H_t{}^\alpha = \sum_j H_{t,j} - \sum_i H_{t,i} \tag{4}$$

and

$$\Delta S_t = \frac{\Delta H_t}{T_t} = \frac{\sum_j H_{t,j} - \sum_i H_{t,i}}{T_t}. \tag{5}$$

If the absolute values of the contributing factors and their participating degrees to the energies are known for the phases, the ΔH_t and ΔS_t can readily be calculable through the Eqs. (4) and (5). Although the data presently available are not sufficient enough to test the present observation in terms of the Eqs. (4) and (5), the empirical relations shown in the Fig. 1 reveal interesting relations between the different allotrops as:

$$A_3\,(\mathrm{HCP}) \rightarrow A_2(\mathrm{BCC}), \qquad \Delta S_{t_3}{}^{A_3\rightarrow A_2} = 0.68, \tag{6}$$

$$A_3(\mathrm{HCP}) \rightarrow A_1(\mathrm{FCC}), \qquad \Delta S_{t_1}{}^{A_3\rightarrow A_1} = 0.17. \tag{7}$$

Upon subtraction of the entropy changes one obtains

$$A_1\,(\mathrm{FCC}) \rightarrow A_2(\mathrm{BCC}), \qquad \Delta S_{t_2}{}^{A_1\rightarrow A_2} = 0.51. \tag{8}$$

As stated before, because of the wide spread of the data points for the transition $A_1 \rightarrow A_2$, a tentative broken line is drawn for the transition in Fig. 1. If one takes account of this line, the ratios of the energies and entropies of the transitions

$$(A_3 \rightarrow A_1) \;:\; (A_1 \rightarrow A_2) \;:\; (A_3 \rightarrow A_2)$$

are, respectively,

$$\Delta H_{t_1}{}^{A_3\rightarrow A_1} \;:\; \Delta H_{t_2}{}^{A_1\rightarrow A_2} \;:\; \Delta H_{t_3}{}^{A_3\rightarrow A_2} = T_{t_1} \;:\; 3T_{t_2} \;:\; 4T_{t_3}$$

$$\Delta S_{t_1}{}^{A_3\rightarrow A_1} \;:\; \Delta S_{t_2}{}^{A_1\rightarrow A_2} \;:\; \Delta S_{t_3}{}^{A_3\rightarrow A_2} = 1 \;:\; 3 \;:\; 4.$$

Since the total difference of enthalpies between the phases appears to be merely dependent on the structural difference of the phases across the transition point the energy and entropy of the phases concerned may be termed "structural energy" and the "structural entropy."

Klement and Jayaraman (*3*) state that the order of increasing entropy is HCP < Sm < DHCP < FCC < BCC or in terms of the Strukterbericht symbols used in this paper, $A_3 < A_1 < A_2$, where the present paper lumps HCP, double HCP (DHCP) and Samarium (Sm) structures together under A_3. The greater lattice vibration of the BCC (A_2) structure with lower coordination number produces a higher entropy when two structures have comparable energies (*4*). The exception to this general behavior of Fe due to its great ferro ⇄ para magnetic contribution to the specific heat, consequently entropy, has been extensively analyzed and discussed in detail in the Refs. *1*, *5*, and *12*. Because of this anomalous behavior of Fe, the iron is eliminated from the present discussion.

Although the consequences of the relations given in the present paper are the subject of further studies, it is hoped that the implication of the present study could lead to a better understanding of the physical nature of matter and allotropism.

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