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S. Tiwari

## Interrelationship between the Diffusion Behaviour and the Phase Transformation Characteristics

By G. P. Tiwari\* and Ken-ichi Hirano\*\*

It has been observed that the metals which exhibit anomalous diffusion behaviour are all allotropic in nature. A hypothesis to rationalise this interrelationship between the diffusion behaviour and the phase transformation characteristics is discussed here. This relationship arises from the correspondence between the saddle-point configuration of the diffusing atom and the structure of an allotrope of the matrix. Thus, in the embryonic form, the saddle-point configuration represents the structure of the matrix after the phase transformation. Several characteristics of the anomalous diffusion behaviour can be explained with the help of the present suggestion. Further, an estimate of the diffusion rates for several metals made on the basis yields satisfactory agreement with the experimental results.

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### I. Introduction

Several transition<sup>(1)~(3)</sup>, lanthanide<sup>(4)(5)</sup> and actinide<sup>(6)~(8)</sup> elements exhibit anomalies in their diffusion behaviour. These anomalies comprise the small values of the activation energies as well as the frequency factors<sup>(1)(9)</sup>. In some cases, a curved Arrhenius plot for diffusivity is also seen<sup>(2)(3)</sup>. The anomalous metals also have significantly higher diffusion rates at the corresponding fractions of the melting temperatures<sup>(9)</sup>. An important additional characteristic of the metals showing anomalous diffusion behaviour is that they are all allotropic in nature<sup>(10)~(12)</sup>. This relationship between the diffusion behaviour and the phase transition characteristics is underscored by the correlations of the entropy of fusion with either of these properties<sup>(13)~(15)</sup>. It has been shown that the metals having the entropy of fusion less than  $6.7 \text{ Jmol}^{-1}\text{K}^{-1}$  are allotropic in nature<sup>(13)</sup>. Again, the metals having the entropy of fusion less than  $6.7 \text{ Jmol}^{-1}\text{K}^{-1}$  are found to exhibit anomalous diffusion characteristics<sup>(14)</sup>. Through their identical dependence upon the entropy of fusion, the diffusion behaviour and the phase transformation characteristics are intimately related to

each other.

The object of the present paper is to discuss a hypothesis to rationalise the interrelationship between the diffusion behaviour and the phase transformation characteristics. This rationalization is achieved by assuming that the configuration of the diffusing atom at the saddle-point corresponds to the structure of an allotrope of the matrix. On this basis, the diffusion characteristics such as the violation of the correlation between the diffusion and the melting parameters, small activation energies and relatively higher diffusion rates at the corresponding fractions of the melting-point can be explained. A calculation of the diffusion rates is also made on the basis of the present suggestion and a satisfactory agreement with the experimental data is obtained.

The model for diffusion discussed here is somewhat similar to the one proposed by Sanchez and DeFontaine<sup>(11)(12)</sup>. It was suggested by these authors that in the case of anomalous diffusion, the saddle-point atoms form an embryo of some phase ( $\omega$ -phase in the case of  $\beta$ -Zr and Ti-Mn alloys). The diffusion jump is postulated to occur through the atomic exchange within this embryo. A generalisation of the same view-point is presented here. Specifically, it is suggested that the saddle-point configuration for normal as well as anomalous metals adopts the configuration of the phase which the matrix acquires after phase transition. In this way, it is possible to discuss the diffusion process in normal as well as

Cu → Cu  
Al → Al  
Pu → Pu  
U → U  
YMo → YMo  
Fe → Fe  
Zr → Zr  
Ti → Ti

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anomalous metals with the help of a single hypothesis.

## II. Relationship between the Diffusion Behaviour and the Phase Transition Characteristics

The parameters of the diffusion process in metals follow the simple relationships with the melting parameters. The activation energy for vacancy diffusion,  $Q$  ( $\text{Jmol}^{-1}$ ), is related to the melting-point and the latent heat of fusion<sup>(16)</sup> as follows:

$$Q = 159 T_m, \quad (1)$$

$$Q = 16.5 L_m, \quad (2)$$

where  $T_m(\text{K})$  and  $L_m(\text{Jmol}^{-1})$  represent the melting temperature and the latent heat of fusion respectively.  $T_m$  and  $L_m$  are similarly related to the formation energy of the vacancy also<sup>(17)(18)</sup>. Further, the activation volume for diffusion bears the same relation to the activation energy as that exists between the volume change associated with melting and the latent heat of fusion<sup>(19)</sup>. However, these relationships embodying the correlations between the process of diffusion and melting breakdown for metals exhibiting the anomalies in their diffusion behaviour<sup>(1)(9)</sup>. As mentioned in the previous section, the anomalous metals are allotropic. Melting as well as the solid-state transformations occurring in metals belong to the category of the first order transformations. In either case, the transformation is accompanied by a fixed entropy change. In the case of metals showing normal diffusion behaviour and obeying the correlations between the diffusion parameters and melting mentioned above, it has been proposed that the region around the vacancy structurally resembles a liquid and the process of diffusion involves the atomic exchange or shuffling of atoms in this liquid-like region<sup>(16)(20)</sup>. An analogous statement for the anomalous metals can be made by stating that the region around the vacancy, during the process of diffusion, acquires the structure adopted by the matrix after the phase transformation and the process of diffusion is equivalent to the atomic exchange in this region. Thus during the diffusion in an anomalous metal,

the saddle-point configuration is structurally related to an allotrope of the matrix. In case there are several allotropic modifications of the matrix, the saddle-point configuration will be based on the phase requiring the least amount of excess free energy.

It is important to emphasize here that the presence of a vacancy itself does not lead to the formation of a saddle-point configuration related to either a liquid phase or an allotrope of the matrix. A definite amount of the thermal fluctuation is necessary before the region around the vacancy can acquire diffusive configuration.

On the basis of the preceding discussion, a diffusive jump is postulated to occur through the following steps:

- (a) The formation of a vacancy in one of the nearest neighbour positions.
- (b) The formation of a saddle-point configuration structurally related to either the liquid phase or an allotrope of the matrix.
- (c) Vacancy migration within the saddle-point configuration to affect the positional change of the diffusing atom.
- (d) The disintegration of the saddle-point complex through thermal fluctuation.

## III. Estimation of the Diffusion Rates

According to the model outlined above, the diffusion rates will be controlled by the energy required to carry out the steps (a) through (c). The expression for the diffusion coefficient derived on the basis of the absolute reaction rate theory<sup>(21)</sup> can be easily adopted here. The diffusion coefficient is expressed as

$$D = fa^2v \exp(-\Delta G/RT), \quad (3)$$

where  $D$  is the diffusion coefficient,  $f$  the correlation factor,  $a$  the lattice parameter,  $v$  the Debye frequency, and  $\Delta G$  the energy required to carry out the steps (a) to (c).

### Evaluation of $\Delta G$

$G$  can be expressed as the sum of the three contributions mentioned above; namely the energy required for vacancy formation ( $\Delta G_f$ ), the energy required for the formation of the saddle-point configuration ( $\Delta G_v$ ) and the

anomalous metals with the help of a single hypothesis.

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### Evaluation of $\Delta G$

$G$  can be expressed as the sum of the three

energy required for the atomic exchange within the embryo formed at the saddle-point ( $\Delta G_m$ ). Hence

$$\Delta G = \Delta G_f + \Delta G_v + \Delta G_m, \quad (4)$$

(a)  $\Delta G_f$  can be expressed as

$$\Delta G_f = \Delta H_f - T\Delta S_f, \quad (5)$$

$\Delta H_f$  and  $\Delta S_f$  being the enthalpy and the entropy of vacancy formation respectively. The experimental values of  $\Delta S_f$  for a few *fcc* metals have been determined by Simmons and Balluffi<sup>(22)~(25)</sup>. These values lie in the range of  $\Delta S_f/R = 1 \sim 2.4$ . Theoretical estimates of  $\Delta S_f/R$  for *fcc* as well as *bcc* metals yield a value of nearly 1.5<sup>(26)(27)</sup>. Hence, for common *fcc* as well as *bcc* metals,  $\Delta S_f/R = 1.5$  is taken here. In the case of anomalous metals, neither experimental nor theoretical values are available. However, in these cases, very low values of diffusional entropy—which are sometimes even negative—are obtained. Hence for these cases, it seems reasonable to take  $\Delta S_f/R = 0$ . The effect of  $\Delta S_f/R$  on the calculated values of the diffusion coefficient is discussed later.

(b) The energy required for the formation of an embryo of the phase formed as a result of the transformation,  $\Delta G_v$ , is taken equal to the difference in the free energy of the matrix and the phase resulting after the transformation. This is schematically shown in Fig. 1 depicting a hypothetical two phase system ( $\alpha$  and  $\beta$ ). At any temperature  $T$ , the excess free energy for the formation of  $\beta$ -structure is obtained by extrapolation and is equal to  $PQ$ . Hence  $\Delta G_v = PQ$  (Fig. 1). The values of this parameter have been graphically evaluated from the published data on the thermodynamic properties<sup>(28)</sup>.

(c) With reference to the Fig. 1, if  $\beta$  is a liquid phase, the diffusion jump will be affected by the atomic movement within a liquid-like region constituted by the saddle-point configuration. This step is equivalent to the process of diffusion in a liquid phase. According to Sherby and Simnad<sup>(29)</sup> the

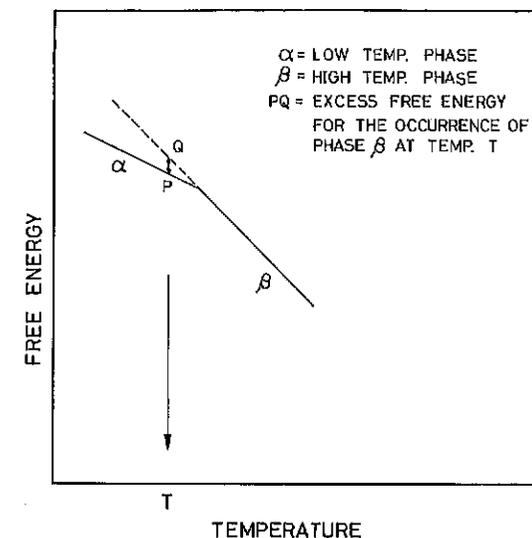


Fig. 1 Schematic variation of free energy with temperature for the polymorphic phases  $\alpha$  and  $\beta$ . The figure shows excess free energy required for the occurrence of  $\beta$  in temperature region where  $\alpha$  is stable.

phase, we may write

$$\Delta G_m = RKT_m. \quad (6)$$

Thus from (a), (b) and (c) above,  $\Delta G$  can be written as

$$\Delta G = \Delta H_f + \Delta G_v + RKT_m. \quad (7)$$

In case  $\beta$  is not a liquid phase, such as will be the case for diffusion in  $\alpha$ -Zr,  $\alpha$ -Ti etc., the diffusive step will be accomplished within an embryo of  $\beta$ -Zr,  $\beta$ -Ti etc. A calculation of the energy required for atomic exchange within such a configuration has been made by Sanchez and [DeFontaine<sup>(12)</sup> for diffusion in  $\beta$ -Zr. This has not been attempted here. The quantitative estimate of the diffusion rates is, therefore, limited to the cases where the saddle-point configuration adopts the structure of a liquid phase.

## IV. Comparison with the Experimental Results

Table 1 Comparison of the calculated and experimental values of the diffusion coefficient.

Element	Temp. (K)	$\Delta H_f$ (kJ/mol)	$\Delta G_v$ (kJ/mol)	$\Delta G_m$ (kJ/mol)	$f\bar{a}^2$ (m <sup>2</sup> /s)	$D$ (cal) (m <sup>2</sup> /s)	$D$ (exp) (m <sup>2</sup> /s)	Ref.* for $D$ value
Al	600	74.48 <sup>(1)*</sup>	8.41	23.28	$1 \times 10^{-6}$	$5.7 \times 10^{-16}$	$7.0 \times 10^{-17}$	(4)
	700		5.79			$1.8 \times 10^{-14}$	$4.1 \times 10^{-15}$	
	800		3.18			$2.6 \times 10^{-13}$	$8.8 \times 10^{-14}$	
	900		0.56			$2.0 \times 10^{-12}$	$9.5 \times 10^{-13}$	
Cu	900	112.97 <sup>(1)</sup>	10.57	33.84	$7.3 \times 10^{-7}$	$5.4 \times 10^{-16}$	$4.5 \times 10^{-17}$	(5)
	1000		8.02			$5.9 \times 10^{-15}$	$7.5 \times 10^{-16}$	
	1100		5.46			$4.1 \times 10^{-14}$	$7.5 \times 10^{-15}$	
$\epsilon$ -Pu	800	38.70 <sup>(2)</sup>	2.51	23.19	$2.0 \times 10^{-7}$	$1.2 \times 10^{-11}$	$5.2 \times 10^{-11}$	(6)
	850		1.88			$2.4 \times 10^{-11}$	$1.0 \times 10^{-10}$	
	900		1.25			$4.3 \times 10^{-11}$	$1.9 \times 10^{-10}$	
$\gamma$ -U	1100	59.62 <sup>(2)</sup>	10.88	35.04	$3.7 \times 10^{-7}$	$3.6 \times 10^{-12}$	$2.6 \times 10^{-13}$	(7)
	1200		8.37			$1.2 \times 10^{-11}$	$7.7 \times 10^{-13}$	
	1300		5.86			$3.4 \times 10^{-11}$	$1.9 \times 10^{-12}$	
Mo	1200	228.45 <sup>(1)</sup>	51.44	788.9	$1.2 \times 10^{-7}$	$3.0 \times 10^{-23}$	$1.6 \times 10^{-22}$	(8)
	1400		45.00			$8.8 \times 10^{-21}$	$4.0 \times 10^{-20}$	
	1600		38.56			$6.3 \times 10^{-19}$	$2.5 \times 10^{-18}$	
	1800		32.12			$1.7 \times 10^{-17}$	$6.4 \times 10^{-17}$	
	2000		15.69			$2.5 \times 10^{-16}$	$8.4 \times 10^{-16}$	
	2200		19.25			$2.2 \times 10^{-15}$	$6.9 \times 10^{-15}$	
2400	12.81	$1.3 \times 10^{-14}$	$4.0 \times 10^{-14}$					
$\delta$ -Fe	1700	124.78 <sup>(1)</sup>	2.51	45.12	$6.5 \times 10^{-7}$	$3.3 \times 10^{-12}$	$8.0 \times 10^{-12}$	(9)
	1750		1.88			$4.9 \times 10^{-12}$	$1.3 \times 10^{-11}$	
	1800		1.05			$7.1 \times 10^{-12}$	$2.2 \times 10^{-11}$	
$\beta$ -Zr	1400	105.02 <sup>(3)</sup>	14.84	53.00	$6.2 \times 10^{-7}$	$4.0 \times 10^{-11}$	$3.6 \times 10^{-13}$	(10)
	1600		10.70			$2.1 \times 10^{-11}$	$1.4 \times 10^{-12}$	
	1800		6.56			$1.0 \times 10^{-11}$	$5.2 \times 10^{-12}$	
	1900		4.49			$1.9 \times 10^{-12}$	$9.6 \times 10^{-12}$	
	2000		2.42			$2.2 \times 10^{-13}$	$1.8 \times 10^{-11}$	
$\beta$ -Ti	1200	88.02 <sup>(3)</sup>	16.74	48.46	$7.0 \times 10^{-7}$	$1.5 \times 10^{-13}$	$7.6 \times 10^{-14}$	(11)
	1300		14.65			$5.9 \times 10^{-13}$	$2.1 \times 10^{-13}$	
	1400		12.97			$1.9 \times 10^{-12}$	$5.3 \times 10^{-13}$	
	1600		8.37			$1.3 \times 10^{-11}$	$2.7 \times 10^{-12}$	
	1800		4.60			$5.5 \times 10^{-11}$	$1.2 \times 10^{-11}$	
	1900		2.51			$1.1 \times 10^{-10}$	$2.3 \times 10^{-11}$	

(1) G. P. Tiwari and R. V. Patil: Scripta Met., 9 (1975), 833.

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(8) J. Askill and D. H. Tomlin: Phil. Mag., 8 (1963), 997.

(9) D. Graham and D. H. Tomlin: Phil. Mag., 8 (1963), 1581.

(10) J. L. Federer and T. S. Lundy: Trans. Met. Soc. AIME, 227 (1963), 592.

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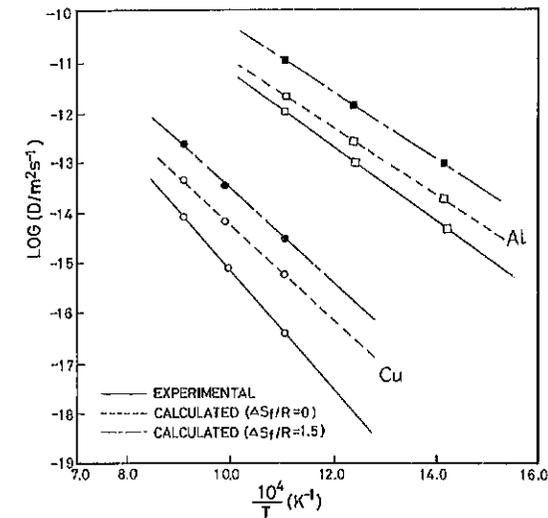
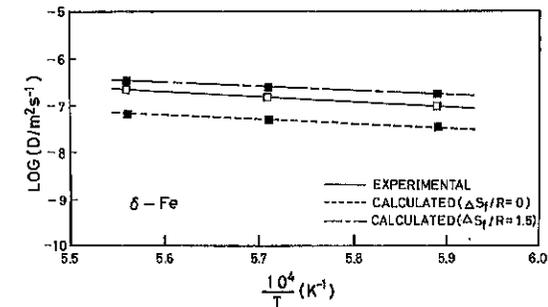
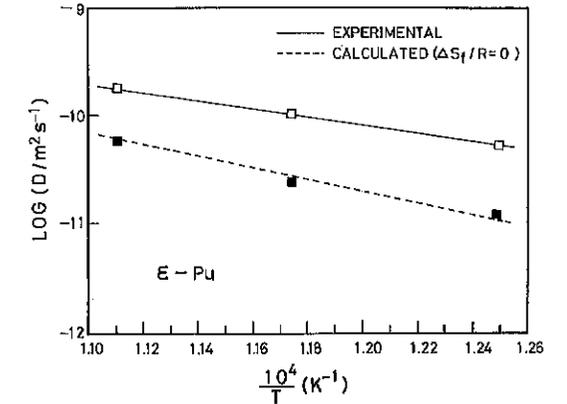
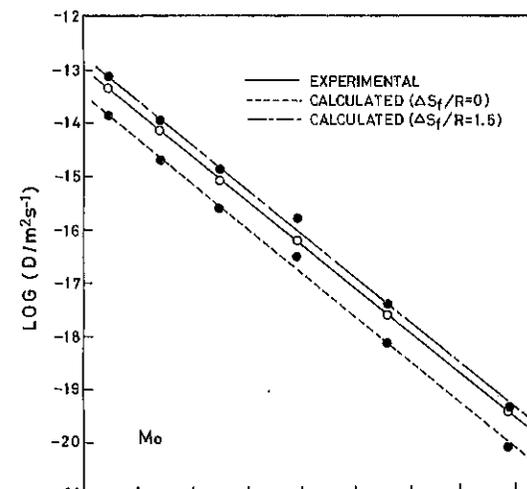
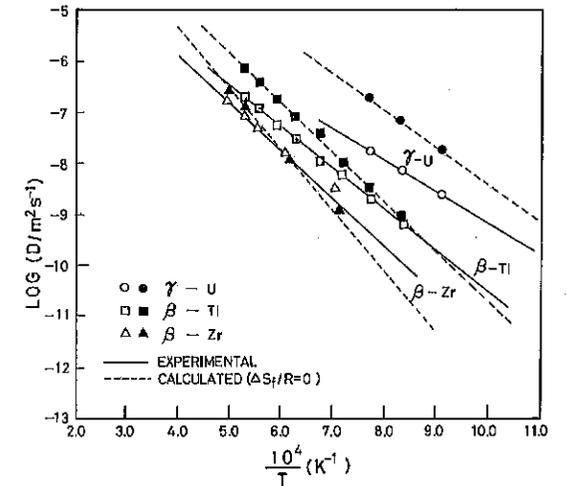
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Fig. 2 Log  $D$  vs  $1/T$  plots for self-diffusion in aluminium and copper.Fig. 3 Log  $D$  vs  $1/T$  plot for self-diffusion in  $\delta$ -iron.Fig. 5 Log  $D$  vs  $1/T$  plot for self-diffusion in  $\epsilon$ -plutonium.Fig. 6 Log  $D$  vs  $1/T$  plots for self-diffusion in  $\beta$ -zirconium,  $\gamma$ -uranium and  $\beta$ -titanium.

measured values are usually accurate to within 10–15% whereas the precision of the calculated values depends on the uncertainty in the knowledge of  $\Delta G$ . It is estimated that the uncertainty in  $\Delta G$  does not exceed 20%. This will give rise to the uncertainty of nearly one order of magnitude in the calculated values of the diffusion coefficient. Except for copper, the discrepancies between the calculated and the experimental values lie within this limit. Hence we conclude that the degree

The effect of the variation in  $\Delta S_f$  on the calculated values of the diffusion coefficient is shown in Fig. 2-4 for Cu, Al,  $\delta$ -Fe and Mo. The diffusion coefficients are calculated for  $\Delta S_f/R=0$  and 1.5. In the case of Cu and Al, the agreement is worsened by taking  $\Delta S_f/R=1.5$  whereas it improves in the case of  $\delta$ -Fe and Mo. The statistical nature of agreement will, therefore, be perhaps not significantly influenced by the neglect of  $\Delta S_f$  for anomalous metals.

### V. Characteristics of the Anomalous Diffusion Behaviour

In the present section, the diffusion model discussed here will be used to explain certain observed characteristics of the diffusion behaviour in anomalous metals. Referring to the Fig. 1 and considering the diffusion in the  $\alpha$ -phase at any temperature,  $T$ , the saddle-point configuration will be akin to the structure of the  $\beta$ -phase. In the case of normal metals,  $\beta$  is a liquid phase and the diffusion parameters will bear correlations to the parameters of the liquid phase. For an anomalous metal like  $\alpha$ -Zr or  $\alpha$ -Ti,  $\beta$  is a crystalline phase. Hence the diffusion parameters will not be related to the parameters of the liquid phase and will show deviations from the correlations followed by the normal metals.

In Fig. 7, a free energy vs temperature plot similar to the Fig. 1 is shown. Here  $\alpha$  and  $\beta$  represent crystalline phases and  $L$  is a liquid phase. Considering again diffusion in the  $\alpha$ -phase, the excess free energies required for the formation of the saddle-point configuration related structurally to either  $\beta$  or  $L$  are  $PQ$  and  $PR$  respectively. As  $PQ < PR$ , the structure of the  $\beta$ -phase will be adopted. Consequently, the free energy associated with the diffusion process ( $PQ$ ) will be smaller than expected on the basis of melting-point correlations ( $PR$ ).

The diffusion in the high temperature phase of a polymorphic metal is different from the low temperature phase in the sense that the saddle-point configuration is related to the liquid phase. However, even in this case, the deviations from the correlations referred to earlier are observed and the relative diffusion

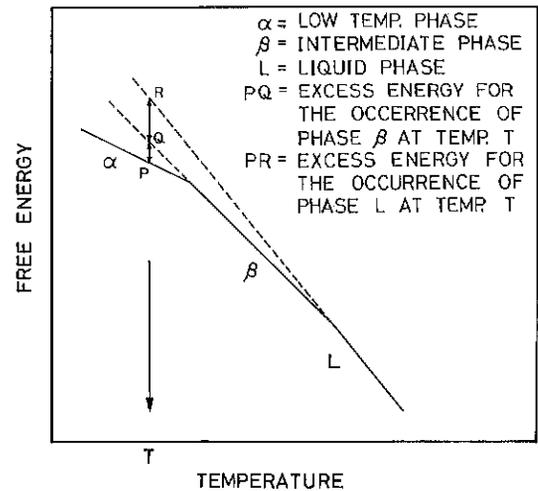


Fig. 7 Schematic variation of free energy with temperature for the polymorphic phases  $\alpha$ ,  $\beta$  and  $L$ . The figure shows the excess free energy required for the occurrence of phases  $\beta$  and  $L$  in the temperature where  $\alpha$  is stable.

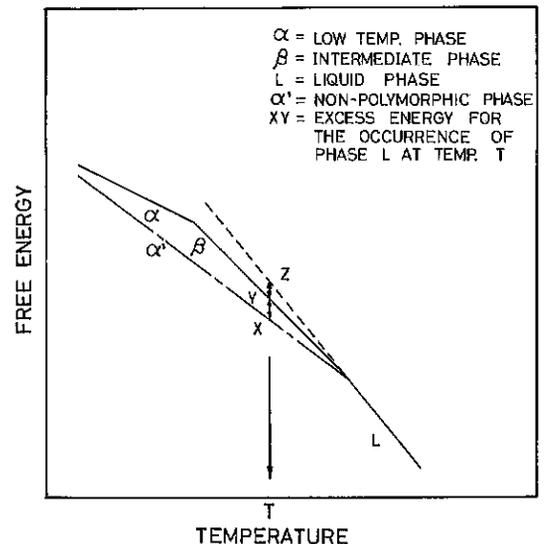


Fig. 8 Schematic comparison of free energies for the occurrence of liquid phase in polymorphic and non-polymorphic systems. The figure shows that the occurrence of the liquid phase in  $\alpha'$  (non-polymorphic system having same melting point as the polymorphic system formed by the phases  $\alpha$  and  $\beta$ ) will always require higher energy as compared to the  $\beta$ -phase.

rates at the corresponding fractions of the melting-point are higher. This can be explained with the help of Fig. 8 where  $\alpha$  and  $\beta$  have the same meaning as in Fig. 7 and  $\alpha'$  represents

The effect of the variation in  $\Delta S_f$  on the calculated values of the diffusion coefficient is shown in Fig. 2-4 for Cu, Al,  $\delta$ -Fe and Mo. The diffusion coefficients are calculated for  $\Delta S_f/R=0$  and 1.5. In the case of Cu and Al, the agreement is worsened by taking  $\Delta S_f/R=1.5$  whereas it improves in the case of  $\delta$ -Fe and Mo. The statistical nature of agreement will, therefore, be perhaps not significantly influenced by the neglect of  $\Delta S_f$  for anomalous metals.

### V. Characteristics of the Anomalous Diffusion Behaviour

In the present section, the diffusion model discussed here will be used to explain certain observed characteristics of the diffusion behaviour in anomalous metals. Referring to the Fig. 1 and considering the diffusion in the  $\alpha$ -phase at any temperature,  $T$ , the saddle-point configuration will be akin to the structure of the  $\beta$ -phase. In the case of normal metals,  $\beta$  is a liquid phase and the diffusion parameters will bear correlations to the parameters of the liquid phase. For an anomalous metal like  $\alpha$ -Zr or  $\alpha$ -Ti,  $\beta$  is a crystalline phase. Hence the diffusion parameters will not be related to the parameters of the liquid phase and will show deviations from the correlations followed by the normal metals.

In Fig. 7, a free energy vs temperature plot similar to the Fig. 1 is shown. Here  $\alpha$  and  $\beta$  represent crystalline phases and  $L$  is a liquid phase. Considering again diffusion in the  $\alpha$ -phase, the excess free energies required for the formation of the saddle-point configuration related structurally to either  $\beta$  or  $L$  are  $PQ$  and  $PR$  respectively. As  $PQ < PR$ , the structure of the  $\beta$ -phase will be adopted. Consequently, the free energy associated with the diffusion process ( $PQ$ ) will be smaller than expected on the basis of melting-point correlations ( $PR$ ).

The diffusion in the high temperature phase of a polymorphic metal is different from the low temperature phase in the sense that the

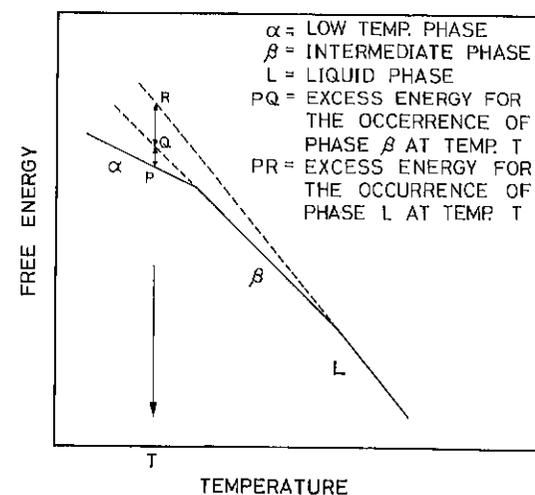


Fig. 7 Schematic variation of free energy with temperature for the polymorphic phases  $\alpha$ ,  $\beta$  and  $L$ . The figure shows the excess free energy required for the occurrence of phases  $\beta$  and  $L$  in the temperature where  $\alpha$  is stable.

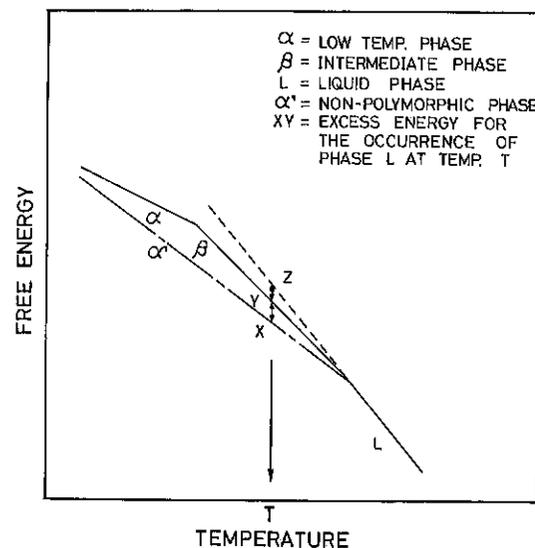


Fig. 8 Schematic comparison of free energies for the occurrence of liquid phase in polymorphic and non-polymorphic systems. The figure shows that the occurrence of the liquid phase in  $\alpha'$  (non-polymorphic system having same melting point as the polymorphic system formed by the phases  $\alpha$  and  $\beta$ ) will always require higher energy as compared to the  $\beta$ -phase.

a single phase system having the same melting-point as the system consisting of  $\alpha$  and  $\beta$ . If we now consider diffusion at any temperature  $T$ , the saddle-point configuration will be based on the liquid phase for  $\alpha'$  as well as  $\beta$ . The excess free energies for diffusion are  $XZ$  and  $YZ$  respectively. Since  $YZ < XZ$ , it follows that the free energy of diffusion in the  $\beta$ -phase will be smaller than that in the  $\alpha'$ -phase despite the fact that both have the identical melting-point. Thus the effect of phase transformation is to reduce the energy required for diffusion in the low- as well as the high temperature phases of a polymorphic system. Further, as the energy associated with the diffusion process is smaller than the value derived from the correlations with the liquid phase parameters, the allotropic metal will, therefore, exhibit higher diffusion rates at the corresponding fractions of the melting-point.

The diffusion in  $\beta$ -Zr and  $\beta$ -Ti presents a special case because the temperature range of diffusion measurements is rather large. It extends over nearly 1170 K. As a result, for diffusion in the low  $\beta$ -range, it perhaps energetically more favourable for saddle-point atoms to adopt a configuration similar to the  $\alpha$ -phase instead of the liquid phase. This is because the large extrapolation required in the latter case makes it energetically less favourable. In the high  $\beta$ -range, the saddle-point configuration will adopt the structure of the liquid phase as an atomic arrangement similar to the  $\alpha$ -phase will become less favourable for an identical reason (Fig. 8). Hence, in  $\beta$ -Zr and  $\beta$ -Ti, we have a situation where the nature of saddle-point configuration changes with the temperature. The origin of curvature in the Arrhenius plots for these cases may be attributed to this feature.

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### REFERENCES

- (1) A. D. LeClaire: *Diffusion in Body-Centered Cubic Metals*, ASM (1965), p. 4.
- (2) J. I. Federer and T. S. Lundy: *Trans. Met. Soc. AIME*, **227** (1963), 592.
- (3) J. F. Murdock, T. S. Lundy and E. E. Stanbury: *Acta Met.*, **12** (1964), 1033.
- (4) M. P. Dariel, D. Dayan and A. Languille: *Phys. Rev.*, **B4** (1971), 4348.
- (5) M. P. Dariel, G. Erez and G. M. J. Schmidt: *Phil. Mag.*, **19** (1969), 1045.
- (6) N. L. Peterson and S. J. Rothman: *Phys. Rev.*, **3A** (1964), A842.
- (7) M. Dupuy and D. Calais: *Trans. Met. Soc. AIME*, **242** (1968), 1679.
- (8) A. J. Cornet: *J. Phys. Chem. Solids*, **32** (1971), 1489.
- (9) D. Lazarus: *Diffusion in Body-Centered Cubic Metals*, ASM (1965), p. 155.
- (10) N. L. Peterson: *J. Nucl. Mat.*, **69 & 70** (1978), 3.
- (11) J. M. Sanchez and D. DeFontaine: *Phys. Rev. Letters*, **35** (1975), 227.
- (12) J. M. Sanchez and D. DeFontaine: *Acta Met.*, **26** (1978), 1083.
- (13) G. P. Tiwari: *Metal Science*, **12** (1978), 317.
- (14) G. P. Tiwari: *Trans. Japan Inst. Metals*, **19** (1978), 125.
- (15) G. V. Kidson and R. Ross: *Radioisotope in Scientific Research*, Pergamon Press, (1958), p. 185.
- (16) G. S. Handler and N. H. Nachtrieb: *Acta Met.*, **2** (1964), 797.
- (17) T. Gorecki: *Z. Metallk.*, **65** (1974), 426.
- (18) J. A. Kraftmaker and P. G. Strelkov: *Fiz. Tverd. Tela.*, **8** (1966), 1049.
- (19) T. Gorecki: *Z. Metallk.*, **68** (1977), 231.
- (20) G. J. Dienes: *J. Appl. Phys.*, **21** (1950), 1189.
- (21) C. Zener: *Imperfections in Nearly Perfect Crystals*, Eds. W. Shockley *et al.*, John Wiley and Sons, (1952), p. 289.
- (22) R. O. Simmons and R. W. Balluffi: *Phys. Rev.*, **117** (1960), 52.
- (23) R. O. Simmons and R. W. Balluffi: *Phys. Rev.*, **119** (1960), 600.
- (24) R. O. Simmons and R. W. Balluffi: *Phys. Rev.*, **125** (1962), 862.
- (25) R. O. Simmons and R. W. Balluffi: *Phys. Rev.*, **129** (1963), 1533.
- (26) H. B. Huntington, G. A. Shirn and E. S. Wajda: *Phys. Rev.*, **99** (1955), 1085.
- (27) L. Dobrzynski: *J. Phys. Chem. Solids*, **30** (1969), 2395.
- (28) B. Hultgren *et al.*: *Selected Values of Thermody-*