

Diffusion in bcc transition metals

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THE transition metals are of great importance both from industrial as well as scientific view points.

In the periodic table, the transition metals represent expansion of a group of 8 (s^2p^6) electron structures into another one of 18 ($s^2p^6d^{10}$). The ground state of free atoms, as the series progresses, also exhibits a change from 4p 3d 4s to 4p 4s 3d state. Such a transition offers excellent opportunity for sd electron hybridization somewhere in the middle of the series. The possibility of spd hybridization also increases as 4p level moves closer to 4s level. Though the exact role of s-, p- and d- electronic interactions in determining the physical stability of transition metals is a subject of discussion¹, it is conceded that the major contribution to binding energy comes from d-electrons. According to Engel² and Brewer^{3,4}, the s-, p- electrons determine the structure of the lattice. However, the strength of bonds in the lattice increases as the tendency for sd and spd hybridization increases; the maximum being expected in the middle of a period. The 'strengthening of bonds' is reflected in the nearest neighbour distances, the cohesive energy values, the melting points and self-diffusion activation energy values of the metals as one moves along K-Cr-Cu, Rb-Mo-Ag or Cs-W-Pt series. These parameters exhibit greater regularity in the first half of each period as shown in Table I.

Interatomic distances, melting points and activation energy values for self-diffusion increase from group IV B to group VI B, though cohesive energy is highest for group V B metals. Progressing along the series, one also notices a tendency for polymorphism. For example, group III B and IV B metals are close packed at low temperatures and acquire 'open' bcc structures at higher temperatures. Group V B and VI B metals are all temperature body-centered cubic. Mn, Fe, and Co exhibit phase transformation with a tendency to become close packed as seen in Ni. Similarly, after Tc, second transition period metals crystallise in hcp lattice.

Researches in the field of atom movement have well established the fact that diffusion in metals and alloys is a defect controlled process. Self- and substitutional diffusion occurs primarily by a solvent or solute-vacancy exchange. Diffusion can also occur by an interstitial mechanism e.g. C in α -Fe. Short circuiting diffusion mechanism have also been proposed in certain cases⁵,

SYNOPSIS

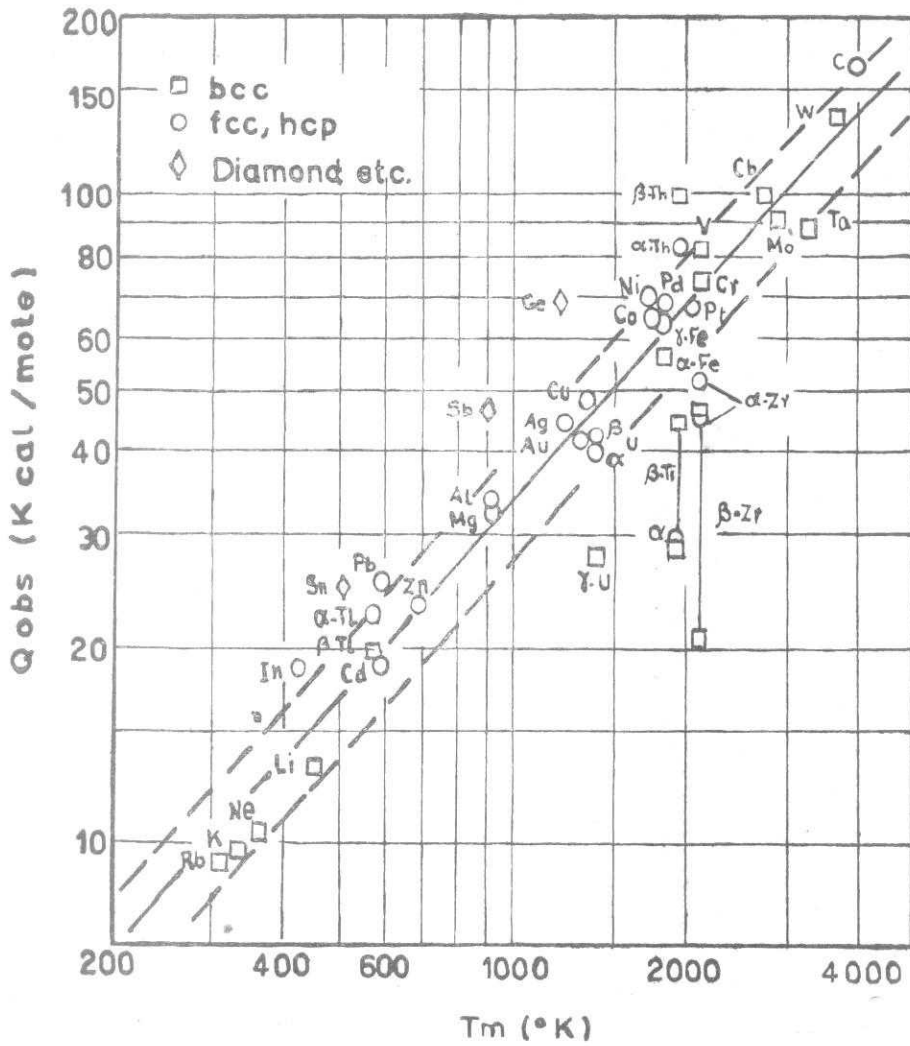
Diffusion in b. c. c. transition metals has become a subject of considerable interest in recent years. This is because some of the b.c.c. metals such as V, Ta, β -Zr and β -Ti, etc. exhibit 'anomalous' temperature dependence of the activation energy and entropy. A number of diffusion mechanism based on either oxygen-trapped extrinsic vacancies, or bimodal models such as simultaneous diffusion through dislocations and lattice, or mono- and divacancy diffusion, have been suggested as possible explanations for this anomaly. It is also probable that diffusion behaviour as observed could be an intrinsic property of the materials concerned. These various explanations have been critically reviewed in the present paper.

particularly for the diffusion of insoluble tracers. It has further been observed that despite the mechanism involved the temperature dependence of diffusivity follows an Arrhenius relationship in all these cases. It is, therefore, interesting to note that self- and impurity diffusion studies in group IV B bcc transition metals like β -Ti⁶, β -Zr^{7,8} and γ -u⁹ reveal an 'anomalous' departure from the Arrhenius relationship in the diffusivity vs temperature plot. Among the group V B metals, vanadium¹⁰ shows a non-linear log D vs. 1/T plots for self-diffusion. Though the diffusion in niobium is claimed to be normal¹¹, the activation parameters for different temperature ranges, if taken in segments, exhibit considerable variation. α -Fe exhibits the effect of magnetic ordering in both self-^{12,13} and impurity diffusion.¹⁴ An unequivocal explanation for the observed diffusion 'anomaly' of bcc transition metals of group IV B and V B is not yet available.¹⁵ In the meantime it has been a subject of numerous comments.¹⁶⁻²¹ In the present paper, it is intended to review the present status of this 'anomaly' in diffusion behaviour. However, before doing so, it is necessary to discuss the laws of 'normal' diffusion in metals and alloys.

Characteristics of normal diffusion behaviour

On random walk considerations, the diffusion coefficient D is equal to $\gamma a^2 \bar{v}$ where γ , a and \bar{v} are a geometric factor, jump distance and jump probability respectively.

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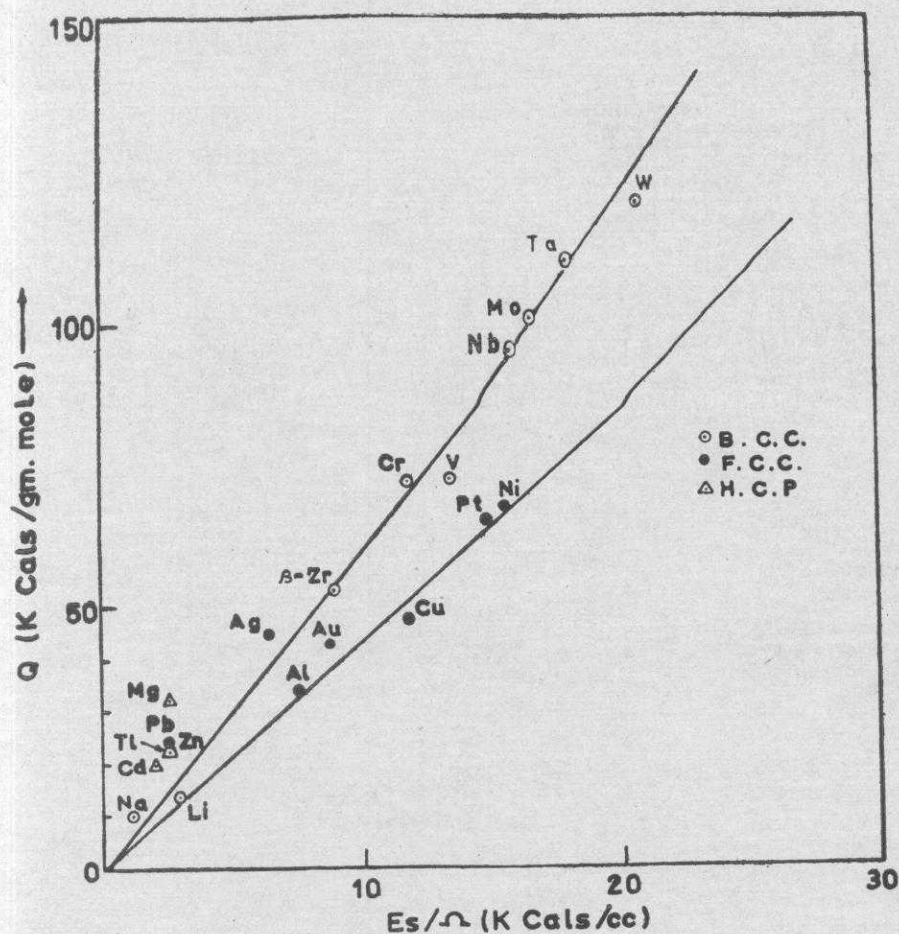


1 Q vs absolute melting point $Q=34T_m$

TABLE I Physical parameters of some first, second and third period transition metals

	Metal	Interatomic distance, Å	E_s Kcal/gm mol	T_m °C	Q_s Kcal/gm mol
First period	β -Ti	2.863 (extrapolated)	95.5	1720	60*
	V	2.622	198.5	1900	72
	Cr	2.498	86.0	1880	73
Second period	β -Zr	3.125 (extrapolated)	124.0	1860	47*
	Nb	2.858	173.0	2500	92
	Mo	2.725	155.0	2625	100.3
Third period	β -Hf	3.03	—	2230	—*
	Ta	2.86	20.0	3000	98-110
	W	2.76	20.0	3400	120-150

*Anomalous diffusion data.


 2 Showing the plot of Q vs E_s/Ω for bcc, fcc and hcp metals

For diffusion to occur by vacancy, the probability of elementary jump would be a product of the probability of the existence of a vacancy at a site adjacent to the moving atom and the probability of diffusing atom moving into the vacancy. Thus, diffusion co-efficient is written as

$$D = \gamma f a^2 \bar{v} \exp \left[-\frac{(\Delta G_r + \Delta G_m)}{RT} \right] \quad (i)$$

where ΔG_r and ΔG_m are free energy values per gm mol for vacancy formation and migration and f is vacancy diffusion correlation factor. Eqn. (i) can be expanded as

$$D = \gamma f a^2 \bar{v} \exp(\Delta S_r + \Delta S_m/R) \exp \left(-\frac{\Delta H_r + \Delta H_m}{RT} \right) \quad (ii)$$

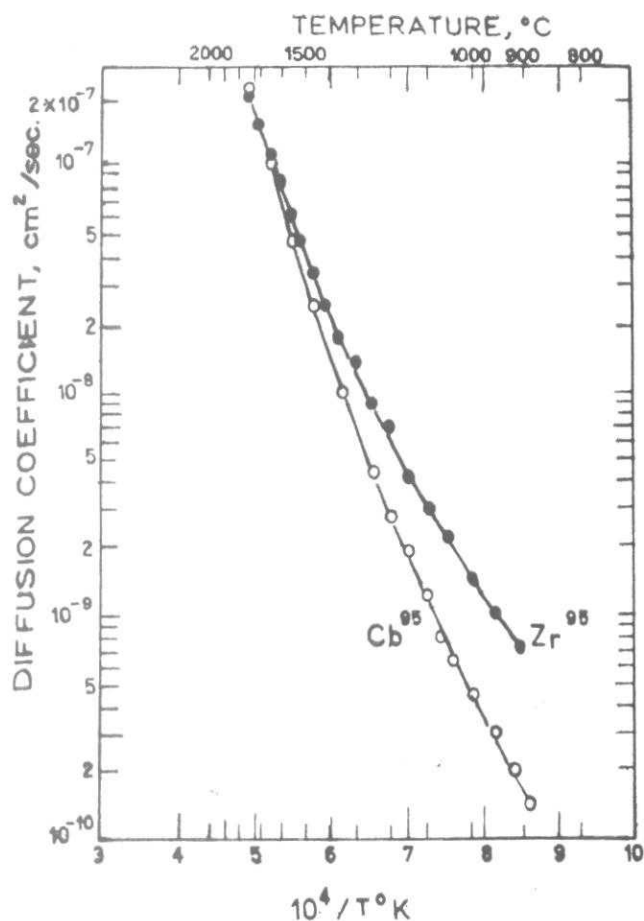
where ΔS_r , ΔS_m , ΔH_r and ΔH_m are the entropy and enthalpy terms corresponding to the subscript indicated. Writing the pre-exponential factor as D_0 , and putting $\Delta H_r + \Delta H_m = Q$, eqn. (ii) reduces to

$$D = D_0 \exp(-Q/RT) \quad (iii)$$

Thus a plot of logarithm of diffusion co-efficients versus reciprocal of absolute temperature should give a straight line. It is possible to draw some inference regarding diffusion mechanism from the magnitude of Q and D_0 . The characteristics of vacancy diffusion parameters are as follows:

1. The activation energy for self-diffusion can be evaluated on the basis of an energy bond calculation or elastic continuum model.²² Some rigorous calculations based on quantum mechanical treatment are also available.²³ The activation energy for vacancy diffusion is, however, more conveniently obtained by empirical relations such as $Q=34 T_m$ rule²⁴ or Sherby-Simnad's modification²⁵ of it i.e. $Q=RT_m(K+1.5V)$ where K is a lattice structure dependent constant, and V is the normal chemical valency. Recently Ray *et al.*²⁶ have shown that the activation energy for self-diffusion can also be correlated with cohesive energy density by writing $Q=K(E_s/\Omega)$ where E_s is the cohesive energy and Ω the atomic volume. K is found to be structure dependent constant. $Q = 34 T_m$ rule and Ray *et al.*'s, $Q = K(E_s/\Omega)$ relationships are shown in Figs. 1 and 2.

2. Assuming that entire energy during diffusion jump is expended in straining the lattice, Zener²⁷ has shown that


 3 Log D vs $1/T$ for self- and Nb diffusion in β -Zr

$$\Delta S = -\frac{\lambda Q}{T_m} \cdot \left(\frac{\partial(\mu/\mu_0)}{\partial(T/T_m)} \right) \quad (\text{iv})$$

where μ and μ_0 are rigidity modulus at temperatures T and 0°K respectively and λ is a constant. Since most of the metals exhibit negative values for $\frac{\partial(\mu/\mu_0)}{\partial(T/T_m)}$, ΔS is positive. Generally equation (iv) gives a satisfactory interpretation of diffusion data in fcc metals and alloys. For ΔS to be positive, D_0 should be within an order magnitude of 0.5.

3. Besides enthalpy and entropy, activation volume is another important parameter in any activated process. It is defined as the change in the volume of the crystal associated with diffusion jump. According to Lawson²⁸ the entropy and activation volume for diffusion are related and can be expressed by eqn. (v)

$$\Delta S/\Delta v = \alpha/\beta \quad (\text{v})$$

where α and β are the coefficients of thermal expansion and compressibility respectively. It has been suggested by Ray et al.²⁶ that the value of 'K' in the cohesive energy density correlation for self-diffusion activation energy is equivalent to activation volume. The value of K has been found to match well with the activation volumes estimated from Nachtrieb et al.²⁹ and Keyes³⁰ correlations.

Anomalous diffusion results

It has been pointed out earlier that the anomaly in diffusion behaviour of bcc transition metals lies in the nature of curved diffusivity plots. Fig. 3 shows such a plot for self- and impurity (Nb) diffusion in β -zirconium from $\alpha \rightarrow \beta$ transformation temperature to the melting point. The characteristic diffusion parameters, D_0 and Q , (eqn. iii) vary with temperature. Similar deviations from an Arrhenius relationship have been observed in the case of β -titanium and γ -uranium. Further in these cases, Q is $< 34 T_m$ and ΔS is found to be negative at lower temperatures. Similar data have been reported for β -hafnium and δ -Pu.³¹ Table II gives the diffusion parameters in some anomalous cases.

 TABLE II D_0 and Q values for self-diffusion in β -Zr and β -Ti, β -Hf, V and γ -U

Metal	D_0 , cm ² /sec	Q Kcal/gm mol	$Q_{\text{kcal}} = 34T_m$
β -Zr (low temp.)	8.5×10^{-5}	27.7	
do (high temp.)		46.0	71.5
β -Ti (low temp.)	3.50×10^{-5}	31.2	
do (high temp.)	1.09	60.0	67.8
β -Hf	1.2×10^{-8}	38.70	85.0
γ -U	2.33×10^{-8}	28.5	47.8
V (low temp.)	0.36	73.6	
do (high temp.)	214.0	94.1	73.88

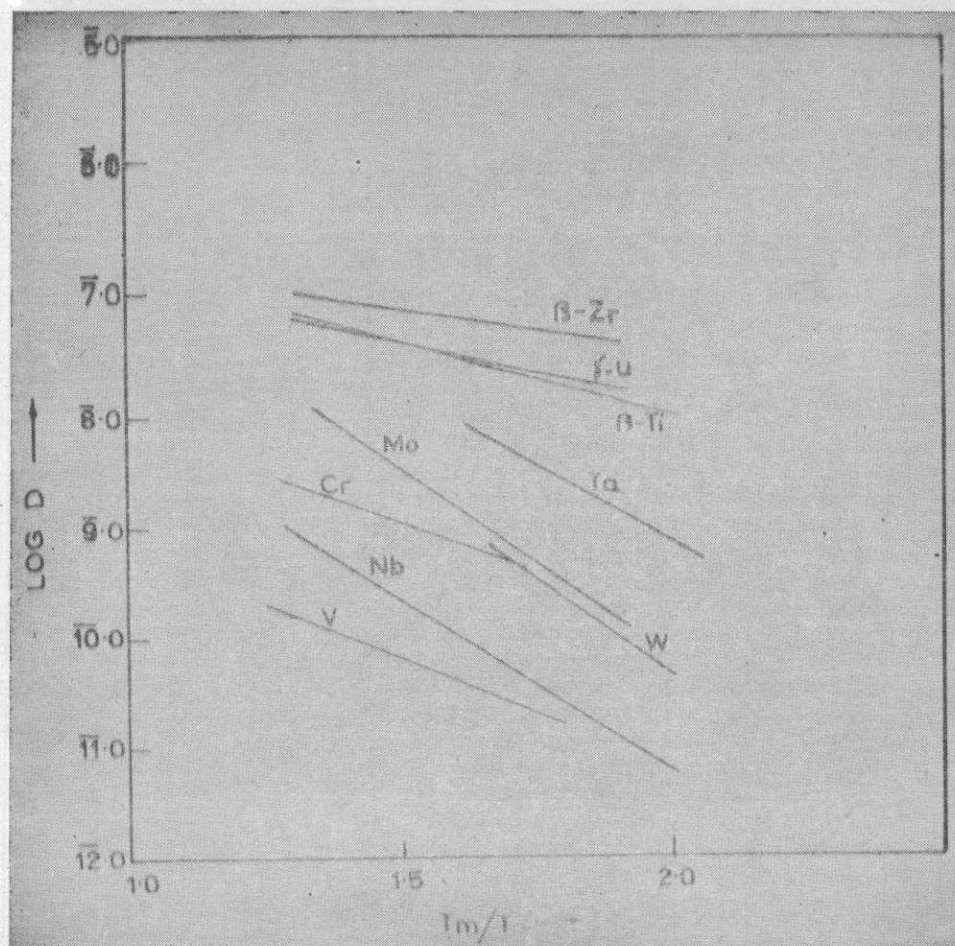
A comparison of self-diffusivity in β -Zr, β -Ti and γ -U with other bcc transition metals is shown in Fig. 4 by plotting log D vs (T_m/T) relationship. It can be seen that as compared to Mo, Cr, W and Nb, etc. the diffusivity values for the anomalous metals are greater by about two orders of magnitude.

Table II and Fig. 5 also show that anomaly of diffusion in vanadium differs from that in β -Zr and β -Ti. Whereas the latter metals deviate, vanadium conforms to the $Q = 34 T_m$ rule in low temperature range. The anomaly in vanadium lies in the activation energy being higher than $34 T_m$ at elevated temperatures. Similar results have been reported for tantalum³³ also.

Discussion

The 'anomalous' curvature in the diffusivity plots of bcc transition metals have been attributed to one or more of the following:

1. Presence of excess 'extrinsic' vacancies due to impurity vacancy interaction.
2. Diffusion through dislocations in lower β -ranges
3. Diffusion involving monovacancies at lower temperatures and divacancies at higher temperatures.



4 Showing the plot of $\log D$ vs T_m/T for b.c.c. metals

4. Variation of enthalpy and entropy due to 'anomalous' temperatures dependence of elastic constants.
5. Na-type self-diffusion β -Zr and β -Ti through relaxed vacancies.

Conclusive experimental evidence to support any single mechanism is not yet available. A greater difficulty lies in the fact that each possible explanation has its own inner contradictions. Hence, a clear understanding of 'anomalous' diffusion behaviour of these metals has not yet been achieved. The various possibilities have been reviewed in the following discussion.

Bimodal diffusion

The concept of bimodal diffusion through 'extrinsic' vacancies, dislocations or divacancies has been developed since it appears improbable that such a wide range of entropy and enthalpy should be applicable for any one process in the same material. The total diffusivity can be expressed as the sum of diffusion due to two competing processes. For example, the temperature dependence of self-diffusivity of β -Zr can be

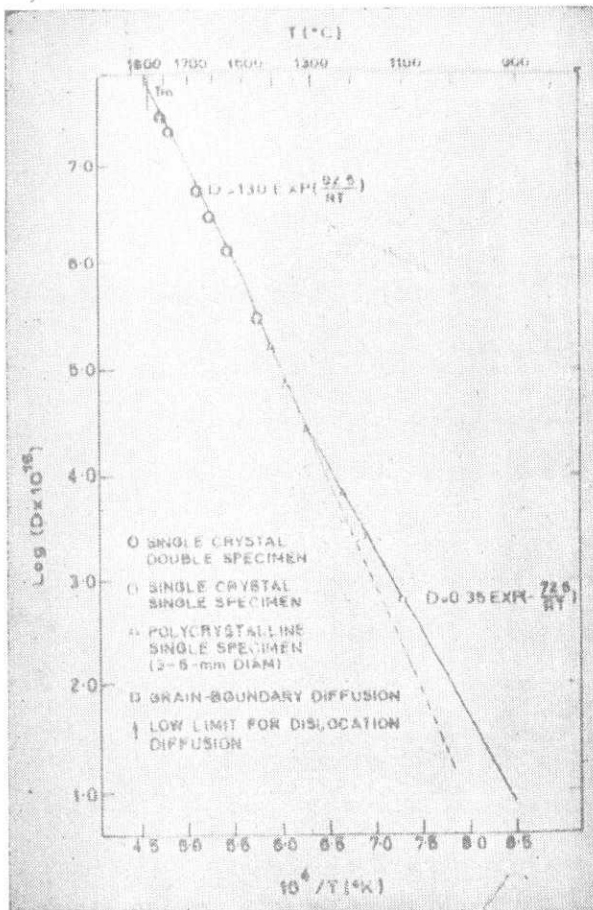
expressed by $D_2 = 8.5 \times 10^{-5} \exp(-27700/RT)$ in 865°-1400°C range and $D_1 = 1.34 \exp(-65,200/RT)$ in 1400 m. p. range. Diffusivity at any temperature can be written as

$$D = 1.34 \exp(-65200/RT) + 8.5 \times 10^{-5} \exp(-27700/RT) \quad \dots \text{(vi)}$$

Fig. 6 shows the application of eqn. (vi) to β -Zr. The various types of bimodal diffusion suggested depend upon the different interpretations to the parameters in equation (vi).

Extrinsic-vacancy model

It is well known that the vacancy concentration in alloys is related to the impurity-vacancy binding energy. Kidson⁷ has explained the enhanced self-diffusivity in β -Zr due to excess 'extrinsic vacancies' associated with interstitially dissolved oxygen. α -zirconium dissolves about 30 at % oxygen in octahedral interstitial positions. On transformation to β -phase, this large oxygen content causes lattice strain as octahedral positions are constricted. The lattice strain can be relieved if each oxygen interstitial is associated



5 Log D vs 1/T for self-diffusion in V

with a vacancy. Thus total vacancy concentration can be written as sum of thermal (C_{th}) and 'extrinsic' components (C_e).

$$C = C_{th} + C_e$$

and the corresponding diffusion co-efficient is given by

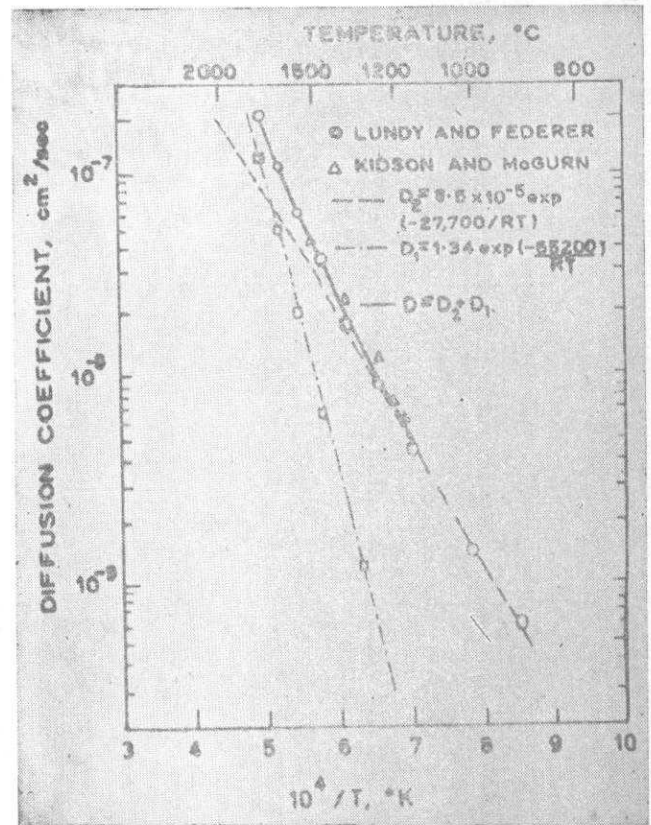
$$D = \gamma f a^2 \bar{v} (C_{th} + C_e) \quad (vii)$$

Substituting for vacancy concentration parameters in equation (vii) it can be re-written as

$$D = \gamma f a^2 \bar{v} \exp(\Delta S/R) \exp(-Q/RT) + \gamma f a^2 \bar{v} C_e \exp(\Delta S_m/R) \exp(-\Delta H_m/RT) \quad (viii)$$

If second term of equation (viii) corresponds with the same of equation (vi), then $\Delta H_m = 27\,700$ cal/gm mol and $Q = 65\,000$ cal/gm mol. The concentration of extrinsic vacancy is estimated to be 0.038%. Activation energy of self-diffusion, $Q = 65\,200$ cal/gm. mol and vacancy migration energy, $\Delta H_m = 27\,700$ cal/gm ml. for β -Zr are quite reasonable from empirical considerations.

This model which could be extended to β -Ti also, has received strong support from Lazarus.³⁴ According to him, oxygen atoms may occupy either vacancy site

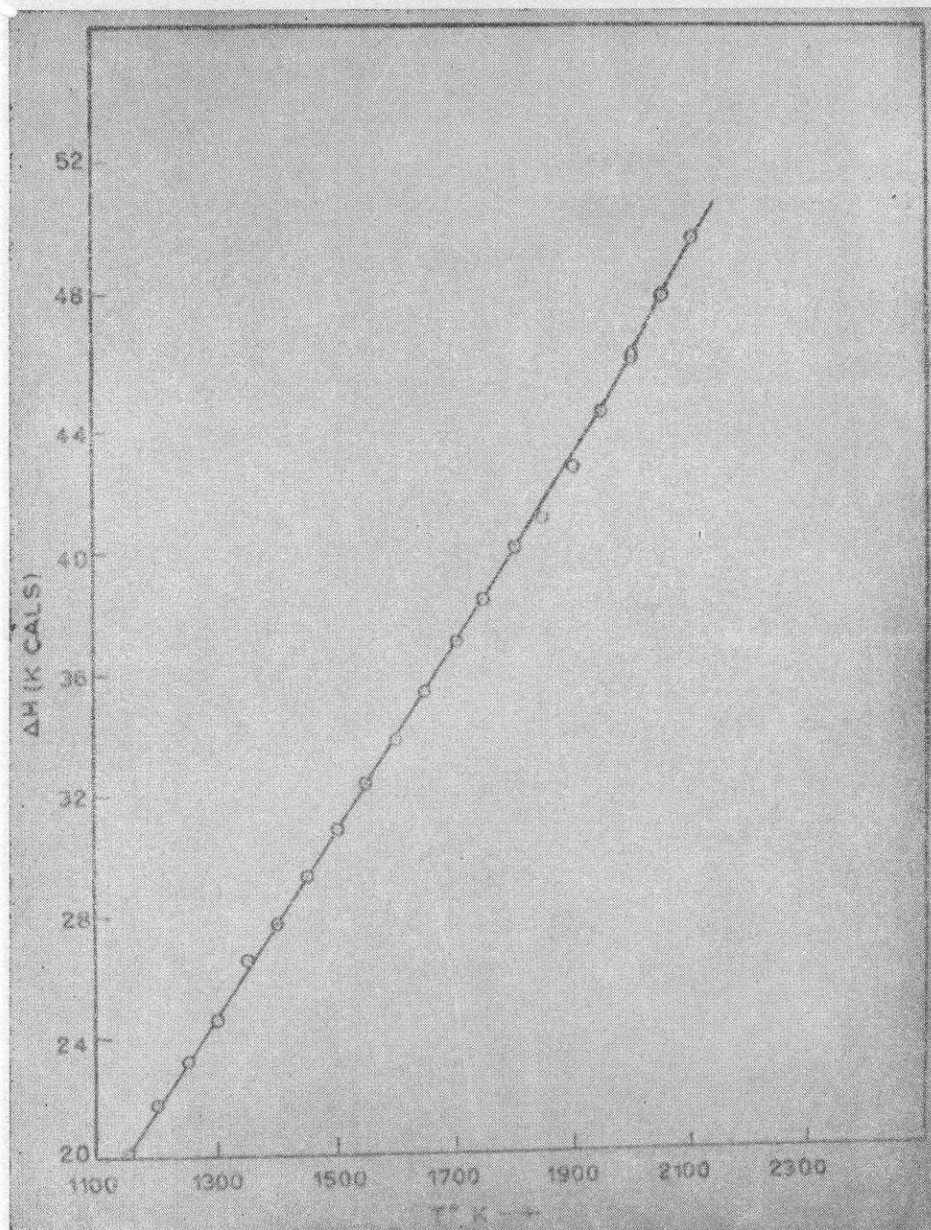


6 Assumed bimodal analysis for diffusivity in β -Zr

itself or form oxygen-vacancy complex whose mobility would be limited with the interstitial diffusion of oxygen. Direct evidence for the role of oxygen in diffusion in β -Zr and β -Ti is contradictory. Whereas oxygen enhances the marker movement in Mo-Ti binary diffusion³⁵, sponge and iodide zirconium containing varying oxygen content exhibit identical diffusion co-efficients. A serious objection to Kidson's hypothesis lies in the large oxygen-vacancy binding energy necessary for the required extrinsic vacancy concentration. The known values of interstitial-vacancy binding energy values are given in Table III.

TABLE III Interstitial vacancy binding energy in some systems

Type	Binding energy (exptd.) cal/gm ml	Ref.
C-Vacancy in Fe	9200	36
C-Vacancy in Ag	8000	37
C-di-interstitial in Fe	2000	36
C-Fe interstitial in Fe	12000	36
O-vacancy in Zr	30000	Kidson's model



7 Activation energy (ΔH) vs absolute temperature T graph for self-diffusion in β -Zr

Such a high value of oxygen-vacancy binding energy in Zr has been justified by Kidson on the basis of covalent bonding between Zr and oxygen atoms which gives rise to strong directional bonds.

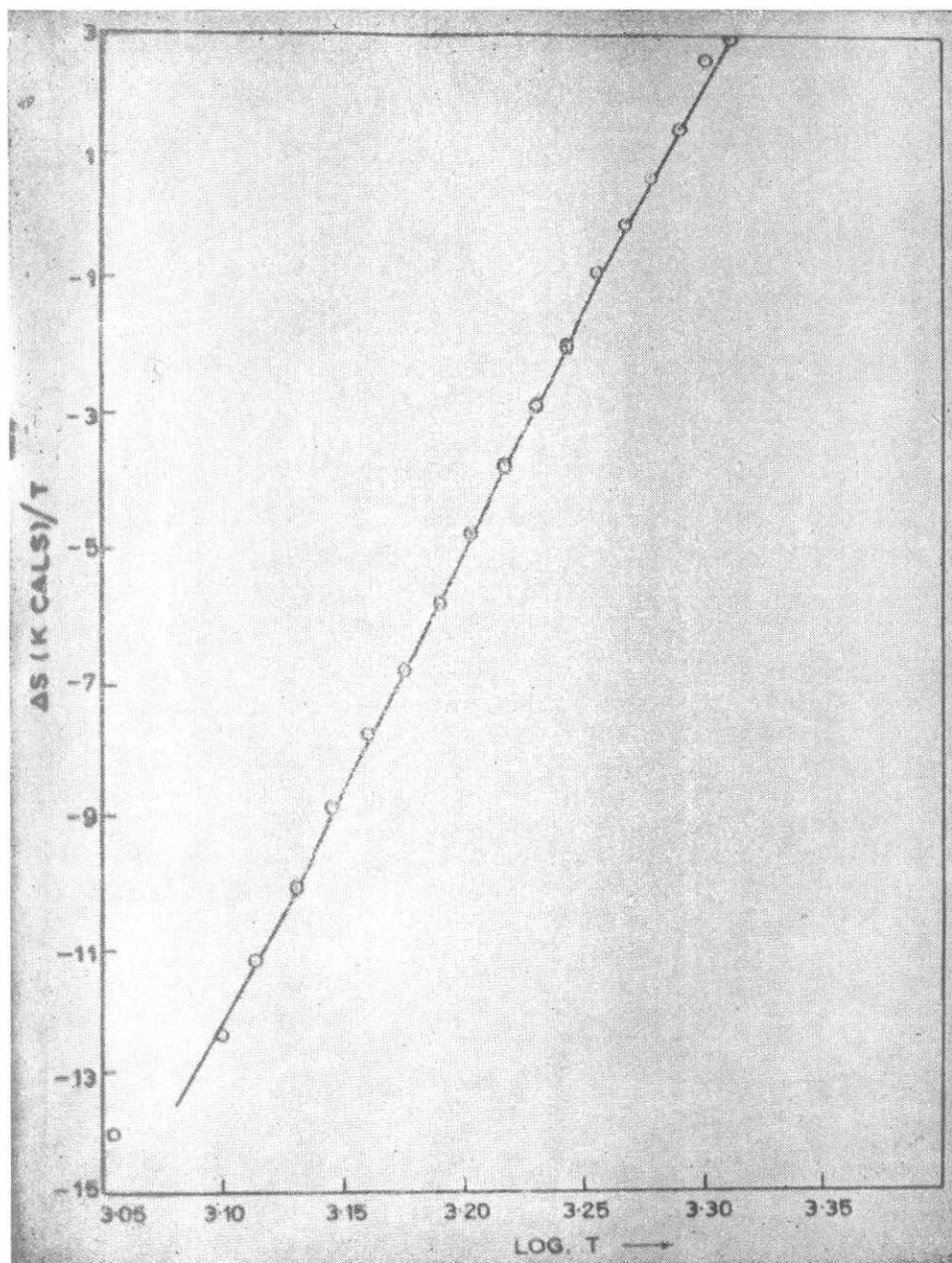
(ii) Dislocation-enhanced diffusion

The dislocation controlled enhancement of volume diffusivity has been suggested as an alternative to extrinsic vacancy model and has received fairly wide support.¹⁵ According to Hart the enhancement arises due to difference in the jump frequencies of the atoms along the dislocations and in the lattice. During its random walk the diffusing atom encounters disloca-

tions, and the total distance travelled is a function of time spent in lattice and in dislocation sites. If the diffusing atom spends an average time \bar{t} in making $n = n_1 + n_d$ jumps, then the diffusion co-efficient D can be written as

$$D = D_d \left(\frac{t_d}{\bar{t}} \right) + D_1 \frac{(1-t_d)}{\bar{t}} \approx g^d d + (1-g) D_1 \quad \dots \text{(ix)}$$

where t_d is time spent in dislocations, D_d and D_1 are diffusivity values along dislocations and through the lattice. Diffusion through dislocations is more likely for diffusion because of stronger solute-dislocation interac-



8 ΔS vs log T graph for self-diffusion in β-Zr

tion. In the temperature range where diffusion through dislocation is predominant

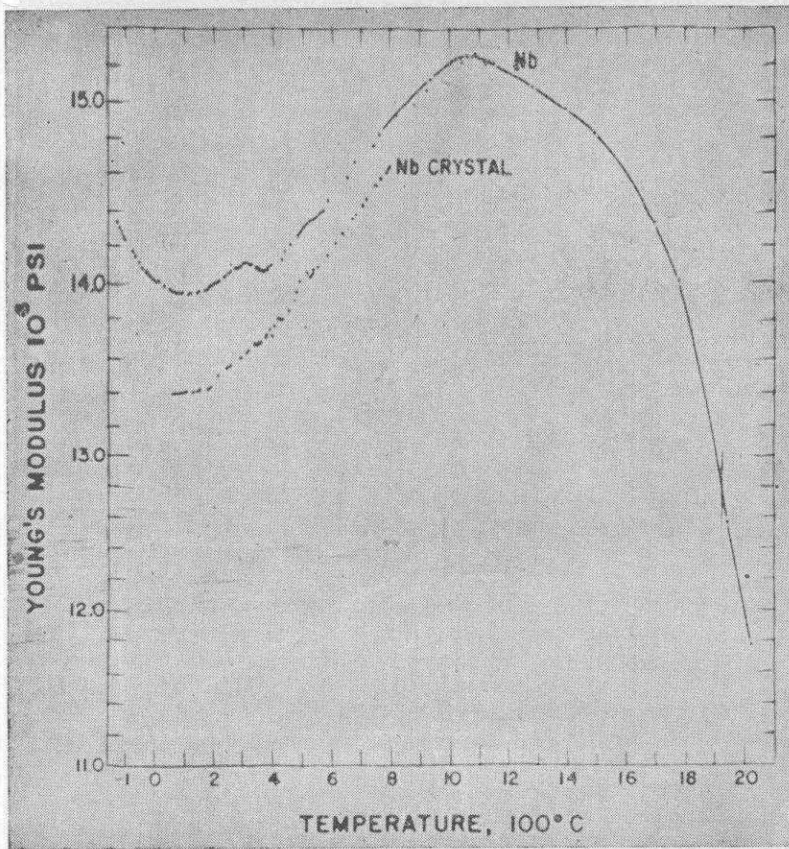
$$D_i \ll g^{\alpha} d \quad \text{and} \quad \bar{D} = g^{\alpha} d$$

for self-diffusion, g is written as $(\rho\alpha/d)$ where ρ is density of dislocations, α is number of sites along the impurity dislocations cross-section and 'd' is total exchange site density. Putting second term of eqn. (vi) equal of gD_d , one can write

$$\left(\frac{\rho\alpha}{d}\right) D_d = 8.5 \times 10^{-5} \quad \text{and} \quad Q_d = 27\,7000 \text{ cal/gm. mol}$$

Further for $d=10^{15}$, $D^{\circ}d \approx 1.0$, and $\alpha=10$, dislocation density would be of the order of 10^{10} dislocations/cm².

Zirconium and titanium both undergo phase transformation which is known to be martensitic type. Using thin film microscopy Howe³⁸ has shown that it introduces copious dislocations tangles in Zr. According to Kidson, solute diffusion in β-Ti supports dislocation diffusion concept. It is found that $D_{Ni} > D_{Co} > D_{Fe} > D_{Mn} > D_{Cr} > D_{Nb} > D_{Mo}$ for diffusion in β-Ti. The solubility of these are, in decreasing order, i. e. the solute showing maximum diffusivity is least soluble. The main objection to this model lies in high dislocation density required to explain the observed enhancement. A dislocation density of $10^{10}/\text{cm}^2$ seems improbable in



9 Showing temperature dependence of elastic constants of niobium

β -Zr and β -Ti at such high temperatures. To explain the enhanced diffusivity in γ -U, still higher dislocation densities of the order of $10^{12}/\text{cm}^2$ would be needed.

(iii) *Monovacancy-divacancy concept for enhanced diffusion*

Bimodal diffusion, on the assumption that monovacancies and divacancies make predominant contribution to atom movement in low and high temperature ranges respectively of β -Zr and β -Ti have been suggested by Newmann³⁹, Askill and Gibbs¹⁷ and Peart and Askill⁴⁰. It was pointed out by Gibbs⁴⁶ that 'anomalous' metals have weak elastic bond strength and as such $Q=34 T_m$ rule may not be applicable for vacancy diffusion. Further, the negative entropy of diffusion at low temperatures may arise in these cases but to the suppression of certain modes of vibrations at the saddle point. The contribution of divacancies to self-diffusion in nickel has been estimated by Seeger⁴¹ and has been found to be negligible. However, it has been argued that whereas the diffusion in fcc metals has been measured over a small temperature range ($0.7-1.0 T_m$), in bcc metals the range is quite large ($0.5-1.0 T_m$) and with favourable energy parameters, the contribution of divacancies at high temperature can be substantial. Configurationally, a correlated diffusion of divacancy in fcc lattice is possible involving nearest neighbours. In a bcc lattice for divacancy diffusion to occur, the next nearest

neighbours have to be involved. It is, therefore, suggested that probability of next near neighbour jumps in bcc lattice are also quite high.

Peart and Askill⁴⁶ have shown that corresponding to Arrhenius diffusion equation for monovacancies

$$D_s = \gamma_a f_a^2 v \exp\left(\frac{\Delta S^s}{R}\right) \exp\left(-Q_s/RT\right)$$

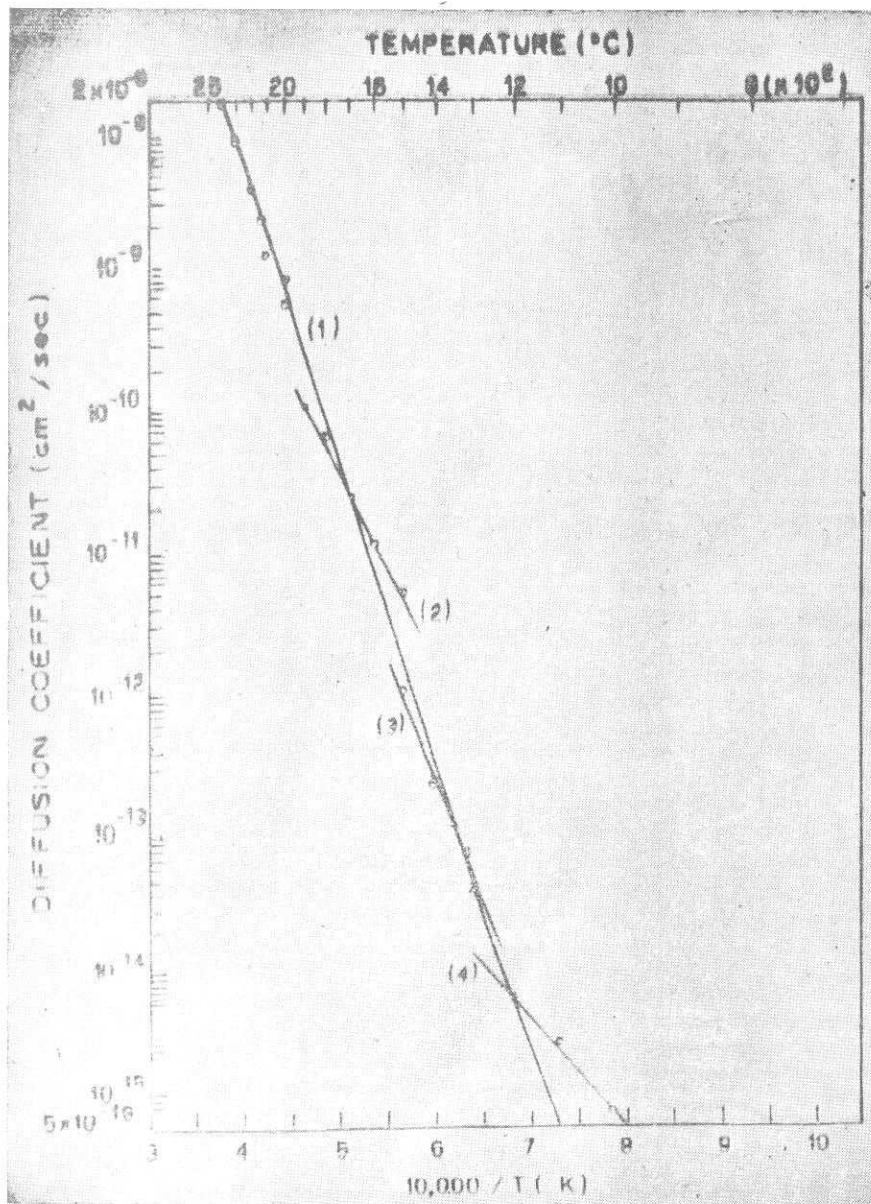
an identical equation for divacancy diffusion is written as

$$D_d = \gamma_d f_d a^2 v_d \exp\left(\frac{\Delta S^d}{R}\right) \exp\left(-Q^d/RT\right) \quad (x)$$

where terms with subscript 'd' and 's' are divacancies and monovacancies respectively. The activation energy Q^d is related to that for monovacancies by eqn.

$$Q^d = 2Q^s - E_B + Q_m^d \approx 1.54Q^s \quad (xi)$$

E_B and Q_m^d are divacancy binding energy and its migration energy respectively. Similar relationships for frequency factor terms have also been derived. Table IV gives the activation energy and frequency factors for monovacancies and divacancies for different bcc metals.



10 Temperature dependence of diffusion of niobium —95 in niobium

TABLE IV Activation energy and frequency factor values for mono- and divacancies in bcc transition metals (after Peart and Askill)

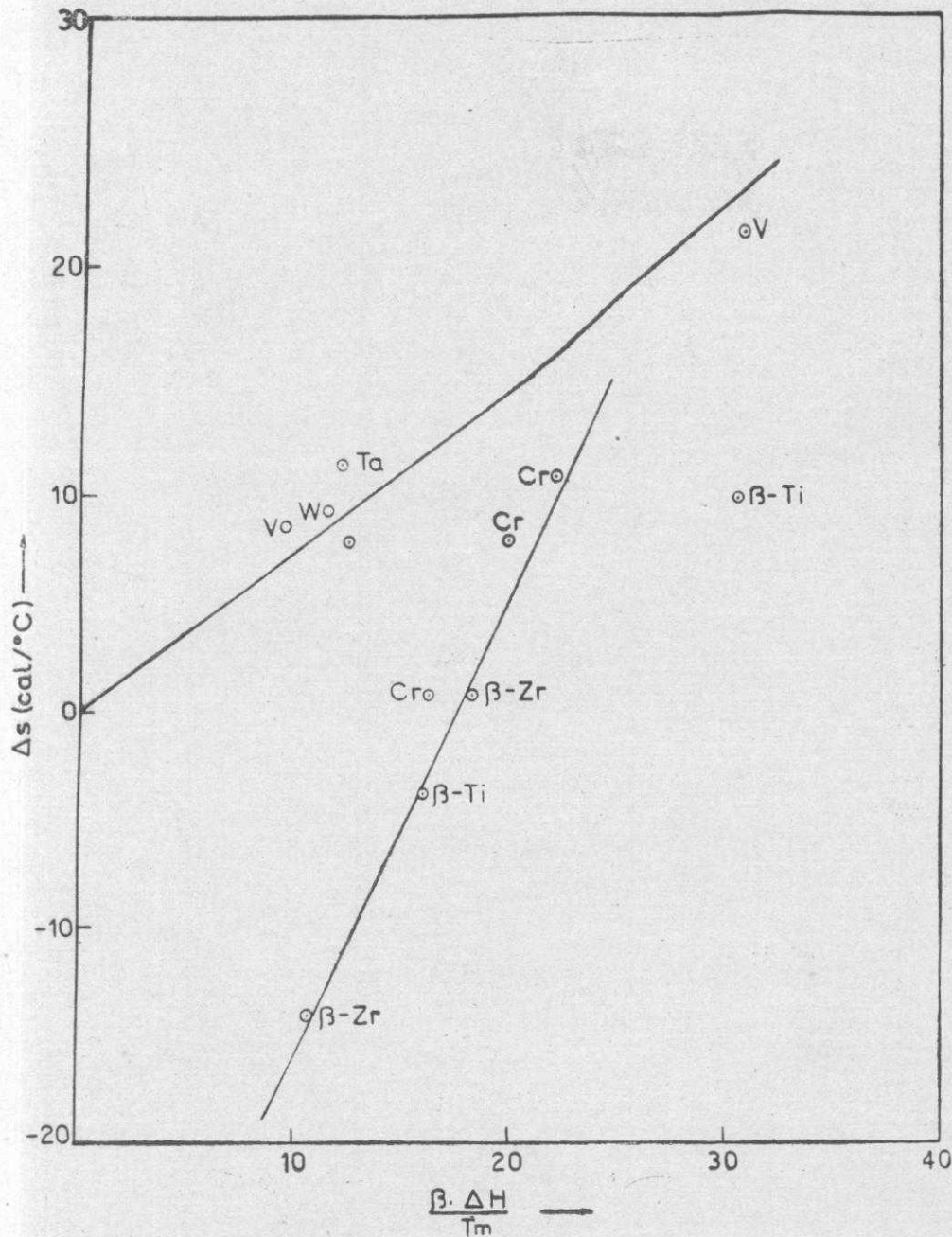
Metal	Monovacancy		Divacancy		Transition temp. (T_c) corresponding to 10% divacancy contribution
	D_0	Q	D_0	Q	
β -Zr	1.4×10^{-3}	35	0.35	60	1450
β -Ti	1.7×10^{-3}	35	0.20	55	1350
V	0.36	73.6	2.5×10^3	109	1400
Ta	1.24	98.7	—	—	2200
Cr	1.3	81.0	10^4	138	1700
γ -U	2.3×10^3	28.5	0.2	43	1050

It is further suggested that wherever Q^d for diffusion is high, the diffusion would be primarily monovacancy controlled. Hence a curvature in the Arrhenius plot may not be seen. It is also suggested that in β -Zr and β -Ti which exhibit negative entropy, dislocation controlled diffusion occurs near $\alpha \rightarrow \beta$ transformation temperature.

'Anomalous' diffusion as a consequence of intrinsic property of the material

Explanations, attributing anomalous diffusion characteristics to the intrinsic properties of the metals, are based on either the thermodynamical properties or 'anomalous' temperature dependence of elastic constants observed in bcc transition metals.

Thermodynamics does not impose any restrictions on the variations of enthalpy and entropy with tem-



11 Plot of Zener's relationship for self-diffusion in bcc metals

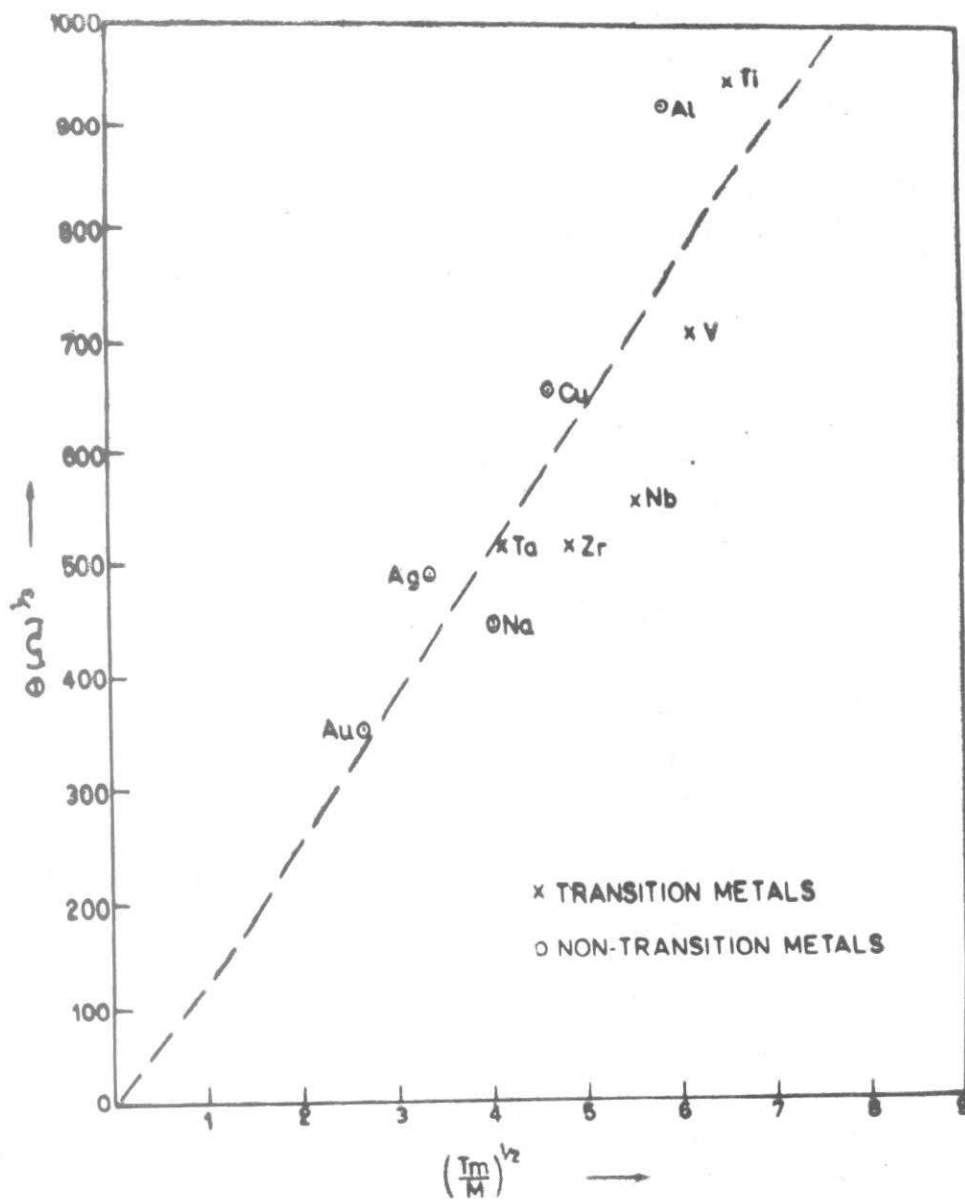
perature. Federer and Lundy⁸ have applied this concept to their study of self-diffusion in β -Zr, and have shown that the effective activation energy varies linearly with temperature as shown in Fig. 7. Tiwari and Sharma¹⁸ have further pointed out that if the diffusion were to occur by a unique process, the temperature dependence of entropy and enthalpy should be related according to

$$1/T \times dQ/dT = d \Delta S/dT \quad (\text{xii})$$

Putting $dQ/dT = \text{constant } (K_1)$, and integrating eqn. (xii), one gets

$$\Delta S = K_1 \log T + K_2 \quad (\text{xii a})$$

Eqn. (xii a) predicts a linear relationship for ΔS and $\log T$. Fig. 8 shows that eqn. (xii a) holds good for β -zirconium. Gibbs has, however, argued that this approach cannot be conclusive as equation (xii) is valid even for those cases where two or more mechanisms are operating simultaneously. Eqn. (xii) is significant if from other considerations it is known that ΔS and Q values correspond to a single mechanism. There are 'extrinsic' factors to support Tiwari and Sharma's¹⁸ assumption of the same. For example, recent impurity diffusion data in β -Zr (Table V) exhibit normal diffu-



12 Lindmanns relationship for Debye temperature and melting point

TABLE V Characteristic parameters for diffusion of Cr, Sn, Ag and U in β -Zr in 900-1200°C temperature range

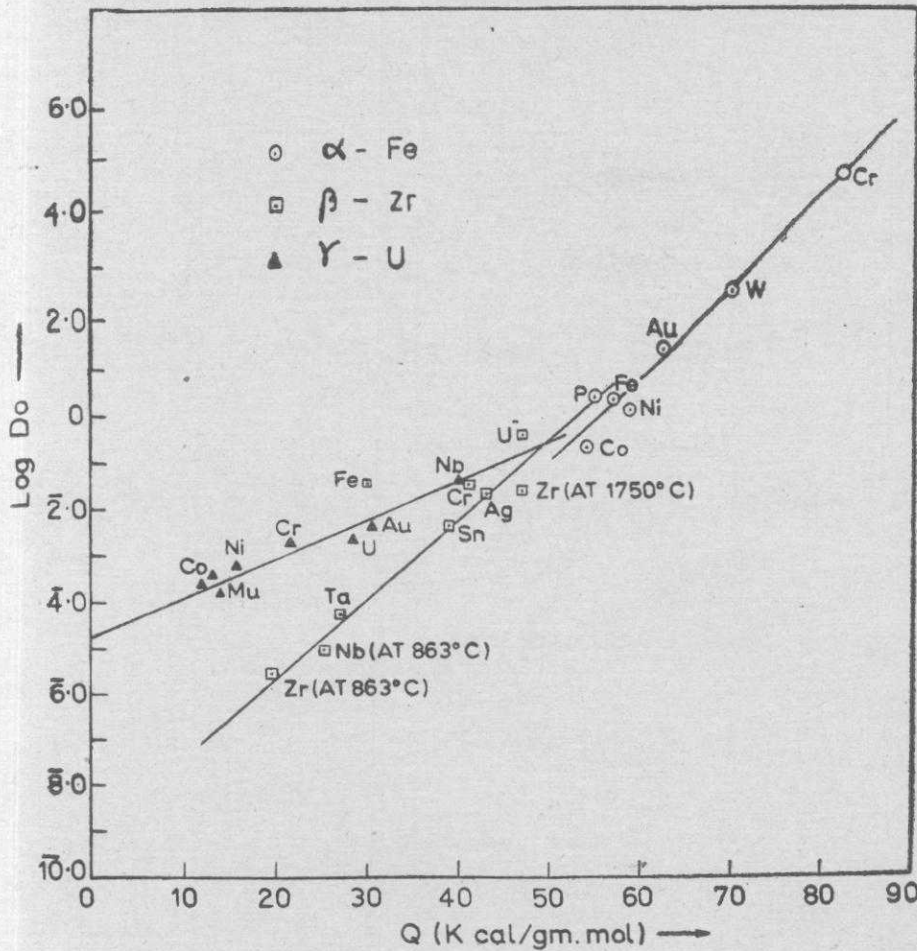
Diffusing atom	D_0	Q	Ref.
Sn	0.005	39 000	49
Sr	0.038	41 000	50
Ag	0.002	43 000	51
U	0.46	47 000	52

sion parameters and no enhancement. If the 'extrinsic' vacancy or dislocation induced enhancements were true for 'anomalous' self-diffusion in β -Zr, these factors should have influenced impurity diffusion as well,

specially when it is known that solute-dislocation interaction is usually quite strong.

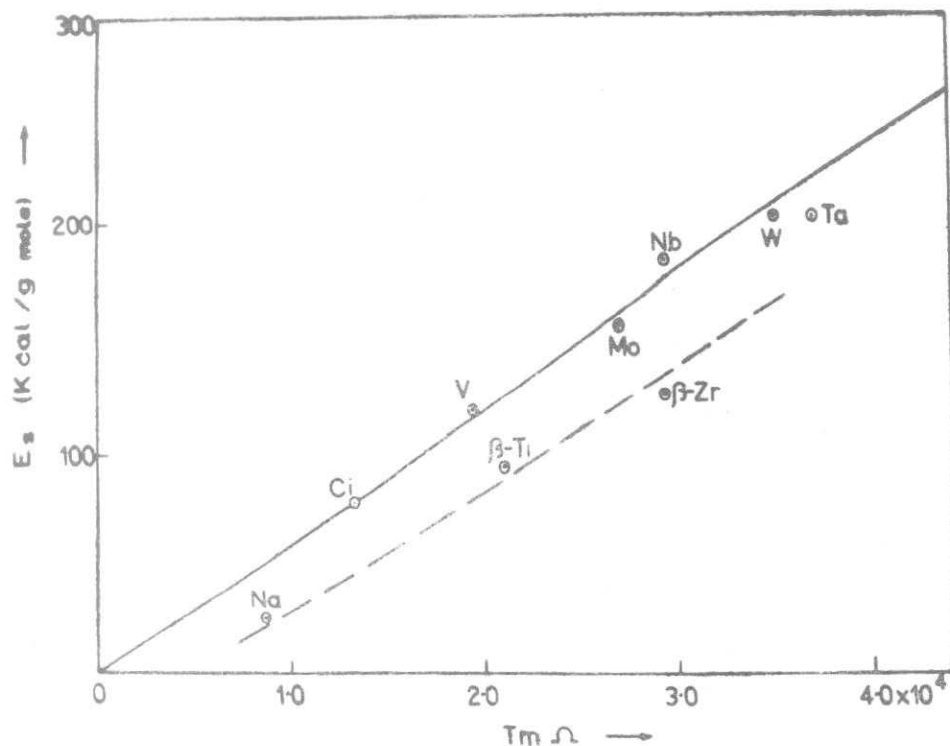
Fig. 2 shows that the estimated value of activation energy $Q=53$ Kcal/gm mol for β -Zr at m. p. fits very well in the Q vs (E_s/Ω) relationship for other bcc metals where monovacancy diffusion is known to be the controlling factor. In view of this mono- and divacancy model also appears to be speculative. ΔS and Q values corresponding to different temperatures could well be the true entropy and enthalpy values of an unique process for β -Zr.

Bcc transition metals exhibit 'anomalous' temperature dependence of elastic constants. Fig. 9 shows the variation of Young's modulus of niobium with temperature as reported by Armstrong and Brown.⁴² It shows the unusual positive value of dE/dT in 600-1000°C range. Even in higher temperature range dE/dT shows large variations. Other transition metals such as V and Ta also exhibit some 'anomalous' features in


 13 Log D_0 vs diffusion activation energy for α -Fe, β -Zr and γ -U

elastic constant data.⁴³ There is some evidence that vanadium exhibits a tendency for 3d \rightarrow 4s electron transition at elevated temperatures. This could cause changes in elastic constant behaviour. Tiwari and Sharma²¹ have considered the effect of nonlinear temperature dependence of elastic constants on entropy and enthalpy of diffusion. Using Zener's relation (eqn. iv) and dE/dT values from Armstrong and Browns' data for vanadium, they found that $(\Delta_s)_{1500}/(\Delta_s)_{800} = 4.9$. This ratio from experimental diffusion data is found to be 6.3 which is in fairly good agreement with same obtained from elastic constant data. Similarly, although diffusion data in niobium (Fig. 10) can be represented by an average straight line, it is in fact anomalous, as the changes in slopes of diffusivity correlate well with temperature variation of elastic constants. These are shown in Fig. 10. Further, since dE/dT is positive in 600–1000°C range for Nb, the entropy of diffusion according to equation (iv) should be negative. Lundy et al.'s low temperature data (segment 4) can be fitted to an equation $D = 6.7 \times 10^{-4} \exp(-77000/RT)$ which gives a negative entropy of -3.61 cal/°C for diffusion. Using Armstrong and Browns' data for dE/dT , the entropy of diffusion is estimated to be -2.53 cal/°C.

Both these values are in good agreement. Thus the anomaly in the diffusion behaviour of vanadium niobium and tantalum could be a manifestation of their unusual elastic constant data. However, such an argument does not hold good for β -Zr and β -Ti, both of which exhibit negative entropy at low temperatures. dE/dT for β -Zr is found to be -0.55 psi/°C, and application of Zener's equation (iv) yields a positive entropy of diffusion. Fisher and Renken⁴⁴ have shown that the elastic constant parameters $C' = (C_{11} - C_{12})/2 \rightarrow 0$ as $\alpha \rightarrow \beta$ transformation temperature is approached from α -side. ΔH_m is closely related to the shear parameter C' , and if $C' \rightarrow 0$ as one approaches transformation temperature from high β -side, $\Delta H_m \rightarrow 0$. Arrowson and Shewmon²⁰ have suggested that this change in the value of shear elastic parameter could explain the small activation energy for diffusion at low temperatures in β -Zr and β -Ti. In a recent study Mundy et al.⁴⁵ have shown that self-diffusion in sodium occurs by relaxed vacancy, in which case though the total entropy is positive, the entropy for migration is negative. The relative activation volume for diffusion in this case is found to be 0.52. Using $Q = K(E_s/\Omega)$ relationship (Fig. 2), Ray et al. have shown that the


 14 Cohesive energy vs $T_m \Omega$ plot for bcc metals

relative activation volume for self-diffusion in β -Zr at m.p. is 0.43 as compared to 0.39 estimated for Na; the same for other bcc transition metals being higher in the range of 0.6 to 0.8. This led Tiwari and Sharma²¹ to suggest that diffusion mechanism in β -Zr, β -Ti and γ -U could be identical to that of Na.

The preceding discussion has shown that the problem of diffusion in β -Zr, β -Ti and γ -U is difficult to explain in a self-consistent manner. Is diffusion in these cases controlled by thermally induced point defects or by short-circuiting paths like dislocations? The question cannot be answered categorically yet as the evidence in support of each model is not conclusive. Very recently Campbell and Huntington⁴⁰ have studied the thermo-migration and electro-migration in β -Zr. These workers report large thermo-migration effects with mass flow towards the central hot region with an activation energy of 26 to 29 Kcal/gm. mol. The activation energy for electro-migration was 30 Kcal/gm. mol. This forced motion of atoms did not exhibit any evidence of high temperature mechanism. It led Campbell and Huntington⁴⁰ to conclude that diffusion occurs through dislocations under these conditions. These workers have, however, not discarded the possibility of a bimodal defect mechanism based on monovacancy and divacancy.

Ray⁴⁷ has recently applied Zener's equation to self-diffusion in bcc metals as shown in Fig. 11. According to Zener's model, the constant for bcc and fcc metals is 1.0 and 0.55 respectively. Fig. 11 shows that whereas the diffusion data of V, W, Ta, and α -Fe can be represented by eqn. (IV) on the line with a slope of unity, β -Zr, β -Ti and even Cr exhibit considerable deviation from

this relationship even when enthalpy values for high temperature region are used. The diffusion entropy in these cases can be expressed as

$$\Delta S = -\lambda \frac{\Delta H}{T_m} + \frac{\delta(\mu/\mu_0)}{\delta(T/T_m)} - C \quad (\text{xiii})$$

The first term on R.H.S. of eqn. (xiii) is positive for β -Zr, and hence entropy would become negative only when ΔH becomes too small. Further, since ΔS_f for defect formation has to be positive, ΔS would be negative because of a negative ΔS_m value alone, which supports the arguments of Tiwari and Sharma.²¹ Recently Pellag⁴⁸ has compared the applicability of Zener's elastic model and Lazarus⁴⁹ screened vacancy concept for impurity diffusion in monovalent fcc metals. According to the screening theory, a vacancy in a metal is equivalent to a point charge $-Z$. In its interactions with other solutes it is screened in accordance with Hartree's theory. Pellag⁴⁸ finds that a plot of $\log D_0$ vs Q for solute diffusion in both monovalent and nickel is linear, and the slope can be used for calculating the screening constant. The main difficulty in the application of screening theory to transition metals lies in the value of Z which cannot be established with confidence due to unfilled d-shells. Recently Enderby and March⁵⁰ have shown that the screening theory can be applied for obtaining a correlation between the activation energy of vacancy formation in fcc metals and Debye temperature. It can also be used to establish Lindemann's relationship:

$$\theta = \left(\frac{h}{k} \right) \left(\frac{3}{4\pi\Omega} \right)^{1/3} \left(\frac{2KT_m}{3M\beta'} \right)^{1/2} \quad (\text{xiv})$$

between Debye temperature (θ) and melting point, h , and k are Planck's and Boltzmann's constants and β' is a constant factor. Fig. 12 shows that eqn. (xiv) is applicable to transition metals also. Thus even though the value of Z cannot be known for lattice diffusion in transition metals, $\log D_0$ vs Q plot should be identical to that in other fcc metals. Fig. 13 shows a plot of $\log D_0$ vs Q for solute diffusion in γ -U, β -Zr and α -Fe (after Ray⁴⁷). The data for β -Zr cover both low and high temperature regions. Diffusion in α -Fe is known to be monovacancy controlled. The $\frac{\delta(\log D_0)}{\delta Q}$

values for γ -U, β -Zr and α -Fe are 9.5×10^{-5} , 1.8×10^{-4} and 1.75×10^{-4} respectively and are quite comparable.

In the opinion of the present authors, the present situation with regard to diffusion in transition metals is due to the fact that till now no effort has been made to correlate it with the intrinsic nature of these metals. For example, the 'equation of state' for solids can be represented by Gruineison's equation

$$\gamma = (3\Omega/C_v) (\alpha/\beta) \quad (xv)$$

where α , β , C_v and Ω are thermal expansion co-efficient, compressibility, specific heat and atomic volume respectively. Hannemann and Gatos⁵¹ using eqn. (xv) have shown that α/β is a structure dependent ratio for metals. According to equation (v) this ratio is also important for diffusion process, being the ratio of diffusion entropy and activation volume. Table VI lists the thermal expansion and compressibility data for bcc metals. It shows that β -Zr, β -Ti and γ -U do not match up with other transition elements so far as 'equation of state' is concerned.

TABLE VI Thermal expansion and compressibility data for bcc metals (after Hannemann and Gatos)

Metal	$\alpha \times 10^6$ ($^{\circ}\text{K}^{-1}$)	$\beta \times 10^{13}$ cm ² /dyne	$\alpha/\beta \times 10^{-7}$
W	4.5	3.3	1.36
Mo	5.0	3.7	1.35
Ta	6.5	4.8	1.35
Nb	7.1	5.7	1.24
Cr	7.1	5.3	1.33
V	7.8	6.1	1.27
β -Zr*	64	10.5	6.09
β -Ti*	38 ?	11.1	3.42
γ -U	67.5	9.85	6.85

After Gibbs⁵²

The $Q = 34 T_m$ rule, and $Q = K (E_s/\Omega)$ relationship²⁶ can also be combined to give another empirical

relationship, $E_s = K_1 (T_m \Omega)$ where E_s is cohesive energy of metal. A plot of this correlation, as in Fig. 14 shows that β -Zr, β -Ti and Na align themselves together, away from other bcc transition metals.

In view of the above discussion an identical diffusion process vacancy type, in β -Zr, β -Ti, γ -U and Na cannot be ruled out. Rather it has a strong possibility. Thus it appears that the 'anomaly' in diffusion might not be caused by some extrinsic factors. Instead of asking why there appears a curvature in $\log D$ vs $1/T$ plot for β -Zr and β -Ti, one might ask why is it that despite strong closed shell repulsion (d-electron interaction) as reflected in high cohesive energy values, these metals also have comparatively large compressibility values? Why do these 'anomalous' metals behave intrinsically like sodium and unlike other bcc transition metals? Answer to these questions might be quite relevant to the diffusion behaviour of these metals.

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