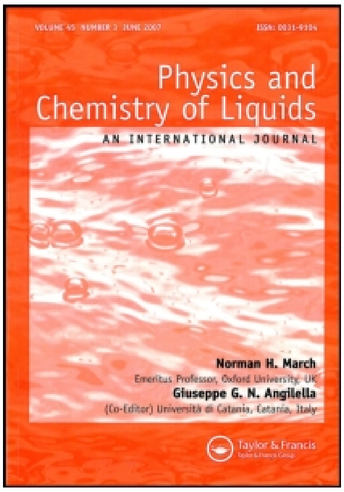

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Predictions of the "Relaxation Mechanism" for Self Diffusion as a Function of d-Bandfilling in Solid and Liquid Transition Metals

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In this note we show that the relaxation mechanism for self diffusion in solid transition metals leads quite naturally to a minimum in self diffusion coefficient at the half filled 3d, 4d and 5d-bands. We also loosely apply this concept to liquid transition metals where the relaxation is modelled as a local region of vaporization in the liquid (i.e. S(q) for large q is locally fluctuating wildly) and show that, if one can assume an Arrhenius $D = D_0e^{-\phi/kT}$ to a liquid metal, then the relaxation mechanism also predicts a minimum in self diffusion coefficient at the half filled 3d, 4d and 5d-bands for liquid transition metals. This prediction is shown to agree with the limited, scattered data for self diffusion in liquid transition metals.

The relaxation mechanism for self diffusion coefficient, D, in solid metals was first proposed by Nachtrieb and Handler.[1,2] It envisions a self diffusion event in a solid to consist of a vacancy surrounded by a relaxed cluster of nearest neighbors which approximates a 12 to 14 atom liquid drop. This mechanism leads to a relation between the activation energy for self diffusion in a solid, Q, and the latent heat of melting, L_m, of the form $Q = 16.5\ L_m$. Out of this proportionality 12 to 14 L_m was assigned to the relaxation formation energy, H_f, leaving 2.5 to 4.5 L_m for the motional energy, H_m, so that $(H_m/H_f)_{FCC} = 0.375$. Rothman and Mundy[3] have recently challenged the mechanism and its resultant correlations on the basis that the Nachtrieb-Handler assumption that log D versus T^{-1} is a straight line is not true for many solids, such as $\beta - \mathrm{Ti}$, $\beta - \mathrm{Zr}$, V, Na and K. Also, they quote recent measurements leading to a value of $(H_m/H_f)_{FCC} = 0.75$ and point out the "vague" details about the relaxation structure, likening the liquid drop region to melting and freezing one or two atoms at a time with an activation energy of order L_m (equivalent to the activation energy for self diffusion in monatonic liquids) causes great suspicion about its validity. They further conclude that the correlation between self diffusion coefficient and melting applies only to a limited class of diffusion phenomena in solids.

Even in the light of this reasoning Rothman and Mundy cannot dismiss the correlation of Q with L_m, of form $Q = 16.5\ L_m$ of Nachtrieb and Handler, nor the slightly poorer $Q = 18\ RT_m$ of Sherby *et al.*[2] Even if $Q^S = 16.5\ L_m$ or $Q^S = 18\ RT_m$ is not as experimentally accurate as one would like, it still approximately holds for many solid transition and non-transition metals.

Siegel[4] has recently correlated D with d-bandfilling in liquids, showing

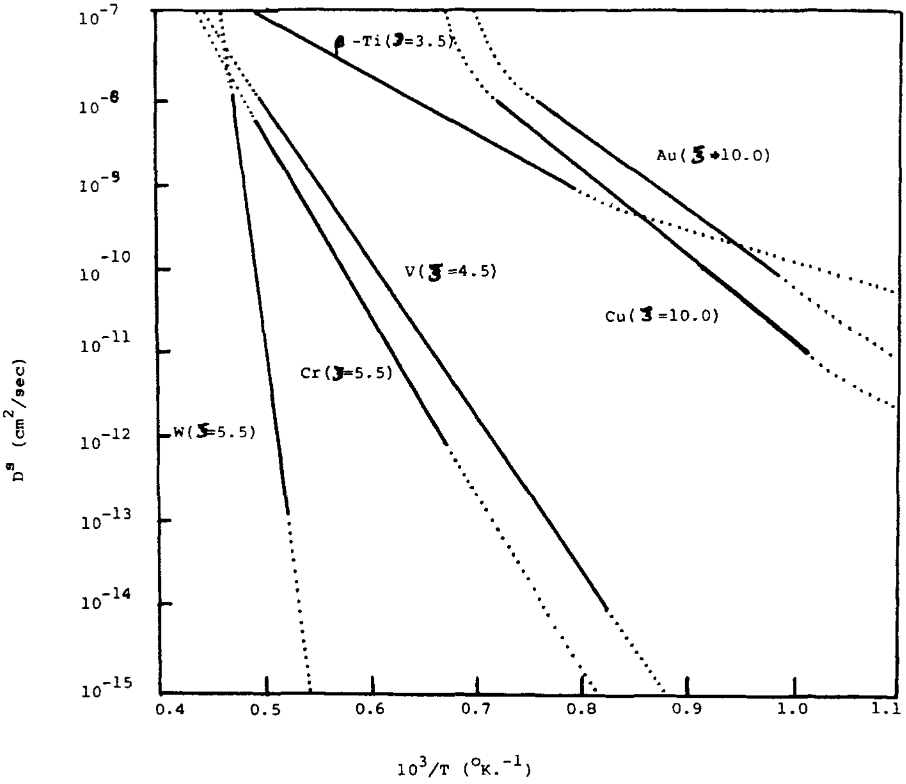

FIGURE 1 Some representative self diffusion coefficients of solid transition metals illustrating a maximum in activation energy near the half-filled d-band. (Cr, W).

evidence for a pronounced minimum near the half filled d-band. He did this by using Swalin's[6] and Egelstaff's[7] separate relation of D to inverse heat of vaporization, ΔH_v^{-1} and to inverse viscosity η^{-1}, which Wilson[5] has shown have pronounced maxima at the half filled 3d, 4d and 5d-bands for liquid transition metals.

We here wish to point out that, since L_m and T_m exhibit maxima at the half filled 3d, 4d and 5d-bands, as Wilson emphasized, Q^S, in either the Nachtrieb-Handler relation to L_m, or the Sherby *et al.* relation to T_m, must also have a pronounced maximum. Arrhenius behavior, $D = D_0 e^{-Q/RT}$ would then imply that $D(\xi) = D_0 e^{-Q(\xi)/RT}$ (in terms of the d-bandfilling ξ) would have a pronounced minimum near the half filled 3d, 4d or 5d-bands. Thus, a series of plots of log D versus T^{-1} should have a maximum slope for Cr, Mo and W and a minimum slope for Sc, Y, and La (or V, Zr and Hf) and Cu, Ag and Au (or Ni, Pd and Pt). In Figure 1 we plot some available log D^S versus T^{-1} slopes[8] for some 3d, 4d and 5d solid transition metals and note an increase in slope. In Figure 2 we plot self diffusion Q^S values versus d-band-filling for 3d, 4d and 5d transition metals and see that a pronounced peak does exist near the half filled d-band, comparing well with Siegel's correla-

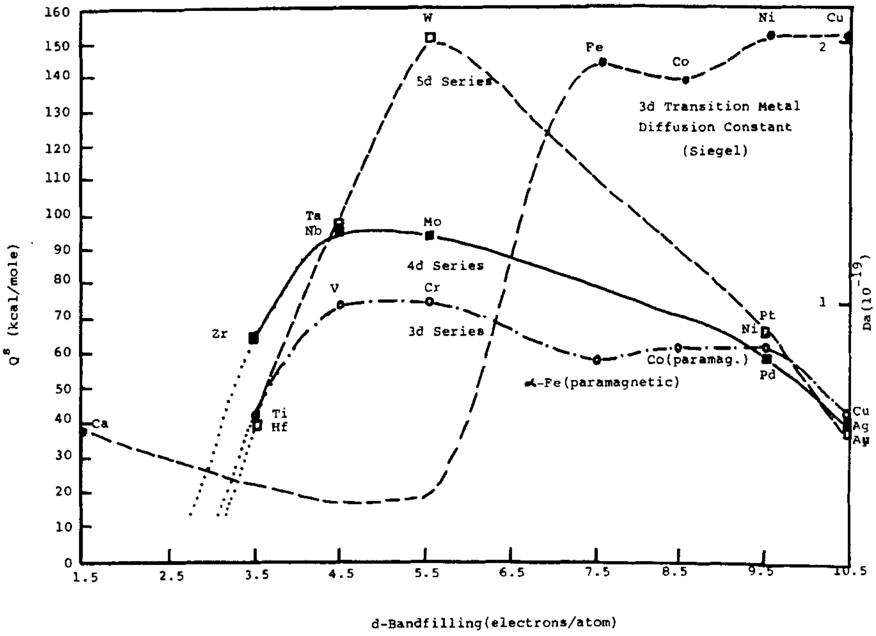

FIGURE 2 Activation energies for self diffusion in 3d (·-·-·-), 4d (——) and 5d (---) solid transition metals illustrating maxima near the half-filled d-band. Da[4] (——) of 3d transition metals shows a minimum at the half-filled 3d-Band.

tion in terms of η^{-1} and ΔH_v^{-1} of D versus d-bandfilling which had a minimum near the half filled d-band.

In liquid transition metals the theories of diffusion are considerably more open to question, as are the experimental data. We can, however, explain the minimum in D^L for liquid transition metals at the half filled 3d, 4d and 5d-bands, previously predicted because of maxima in η and $\Delta H_v(\approx D^{-1})$ there, by loosely applying the relaxation concept, where here a local fluctuation in the short range (high q) liquid structure factor S(q) results in a local "gaseous region". With purposely vague definition of this liquid relaxation we see that we should, in analogy to the Nachtrieb-Handler relation in solid diffusion, predict $Q^L \cong 16.5\ L_v$, where L_v is the latent heat of vaporization. An alternative would be in analogy with the Sherby et al. relation in solids, $Q^L \cong 18\ RT_B \cong 36\ RT_m$, where T_B is the boiling temperature ($\approx 2T_m$) in many solids. Since L_v and T_m have maxima at the half filled d-band, Q^L should. Thus an Arrhenius $D^L = D_0e^{-Q^L/RT_m}$ predicts D^L as having a

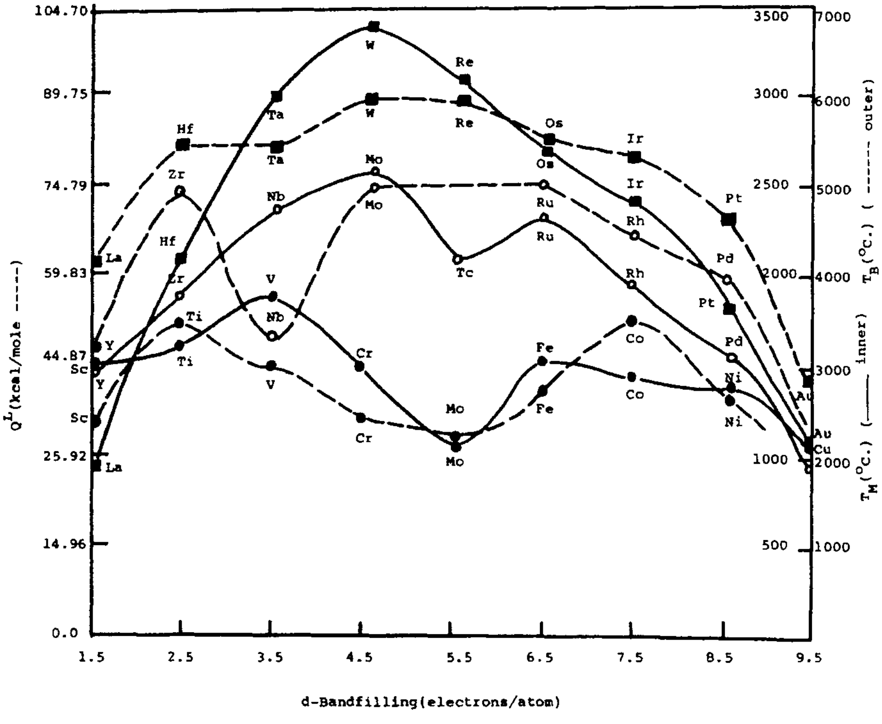

FIGURE 3 T_M (——), T_B (---) and Q^L_{self} (· · · · · ·) (= 18 RT_B) for 3d (●), 4d (○) and 5d (■) transition metals illustrating common maxima near the half filled d-bands with the exception of T_B of the 3d and 4d transition metals.

deep minimum at the half filled d-band. Unfortunately a complicated spectrum of activation energies is usually prevalent in a liquid rather than one specific Q^L, so

$$D^L = \sum_i D_{0i} e^{-Q_i^L/RT_m} \tag{1}$$

is the correct form, but each Q_i^L should peak at the half filled d-band.

In Figure 3 we plot Q^L as estimated by $18\ RT_B = 36\ T_mR$ and $16.5\ L_v$ versus ζ. We notice a pronounced maximum at the half filled d-band since T_m and L_v each have such a maximum. In Figure 4 we plot transition metal impurity (solute) diffusion activation energies in β – Ti and observe some peaking near $\zeta = 4.5$ to 5.5 in the 3d and 4d solute series. In addition to Q^s_{self} peaks (and therefore D^s_{self} dips) at $\zeta = 5.0$ it appears that Q^s_{solute} also

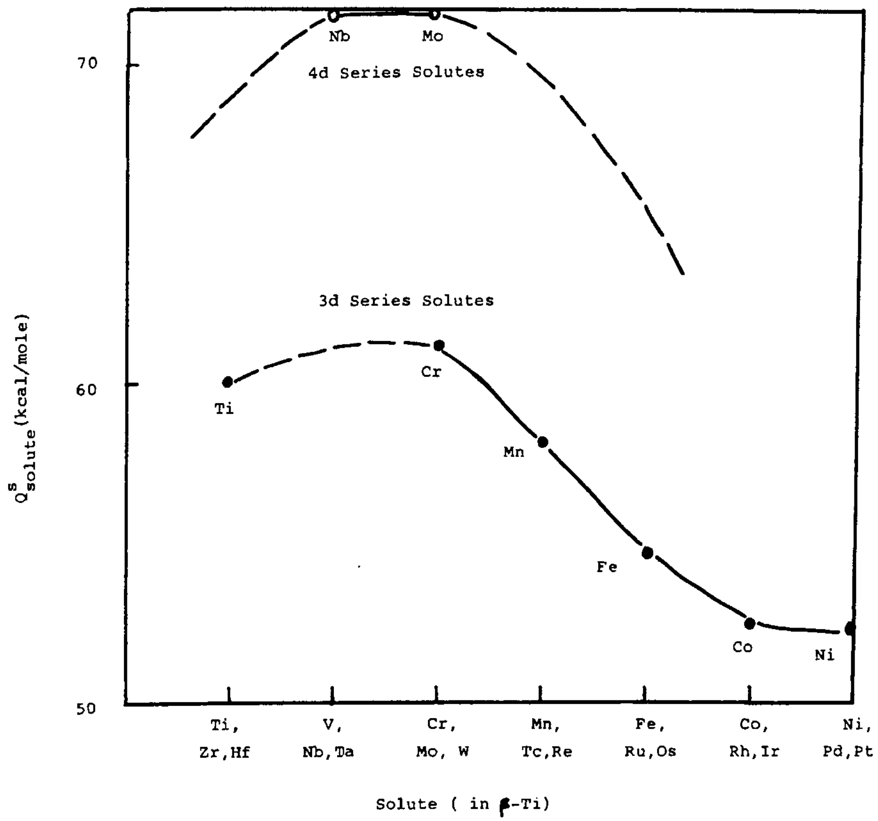

FIGURE 4 Q^S_{solute} versus solute type in solid β – Ti^8(---) illustrating maximum near the half filled d-band.

peaks (and therefore D^S_{solute} also dips) at $\zeta = 5.0$, at least in this 3d β – Ti solvent. In Figure 5 we examine Q^L_{solute} for liquid transition metals. We plot Q^L_{solute} versus solute type (d-bandfilling) in liquid Fe, and some scattered points for the solvents Ag, Au and Cu. We note the reverse trends of maxima in Q^L_{solute} near $\zeta = 5.0$. This is constructed only from scattered data and is puzzeling.

In conclusion, while a simple Arrhenius activation energy for liquid self diffusion is probably not valid, we have described a way of predicting the Q^L versus d-bandfilling maxima near the half filled d-band that Siegel claimed exists. However there is no doubt that Q^S versus d-bandfilling does have a peak near the half filled d-band in solid transition metals in the solid relaxation mechanism model and therefore that D versus d-bandfilling has a pronounced minimum at the half filled 3d, 4d and 5d-band if a simple Arrhenius model for D is assumed to be valid. We have also shown that, in the isolated cases available, Q^S_{solute} exhibits similar half filled d-band

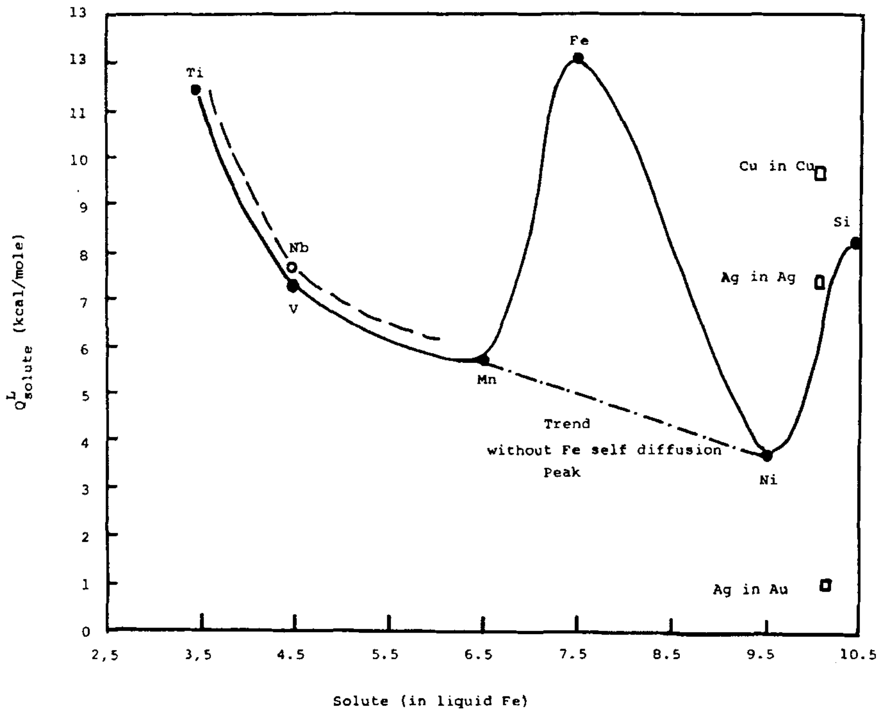

FIGURE 5 Q^L_{solute} versus 3d solute type in Fe[9,10](——) and 4d solute type in Fe[9,10](----). Also shown are assorted other activation energies (-·-·-) which are extrapolations of the 3d plot with the "spurious" Fe peak eliminated.

maximum trends for impurity diffusion in solid transition metals. The peak at Fe may be spurious since it is a Q^L_{self} point and Q^L_{self} (Ag in Ag) is greater than Q^L_{solute} (Ag in Au) so that the Fe peak may be at odds with the trend. However limited data on 3d solute diffusion in liquid Fe indicates that the *opposite* is true for Q^L_{solute} in liquid transition metals. So the Fe peak is an unsolved enigma, anomalous to transition metal trends presented here.

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