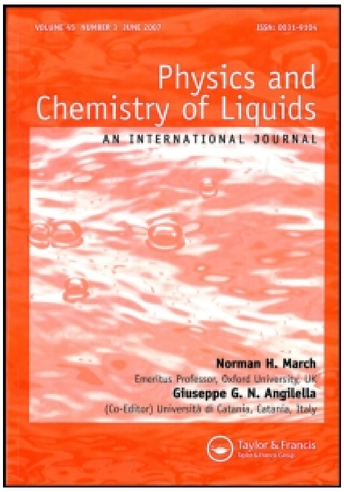

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Edward Siegel

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Liquid Transition Metal Surface Tension and Viscosity Maxima at the Half Filled d-Band; a Manifestation of Solid Transition Metal Cohesive Energy and Melting Temperature Maxima

EDWARD SIEGEL
24 Fifth Avenue, N.Y., N.Y. 10011

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In this note we point out that the maxima in surface tension and viscosity that liquid transition metals exhibit versus d-electron to atom ratio (d-bandfilling) via a sharp peak at the half filled 3d, 4d or 5d-band is related to the peak in cohesive energy and melting temperature at the half filled d-band exhibited for solid transition metals of all three transition series. We argue that this provides evidence for the concept that d-electron bonding carries over from the solid to the liquid state as the transition metal melts.

Allen[1] has recently shown that the surface tension γ of liquid transition metals has pronounced maxima at between 1500 and 2700 dynes/cm near the half filled d-band. In the 3d transition series Mn has an anomalous dip in γ and in the 4d transition series Tc has a smaller anomalous dip in γ. However, with these two exceptions, the 3d, 4d and 5d liquid transition metal series show similar trends, with the 5d $\gamma_{\max}$ at Re (2700 dyne/cm) being larger than the 4d $\gamma_{\max}$ at Mo (or Ru) (2250 dyne/cm), which in turn is larger than the 3d $\gamma_{\max}$ at V (1900 dyne/cm). In Figure 1 we illustrate Allen's correlation. Allen has also plotted γ versus $T_M/V^{2/3}$, where T_M is the melting temperature and V is the molar volume. A nearly straight line relation, of form

$$\gamma = 3.6T_M/V^{2/3}$$

is obtained, as illustrated in Figure 2.

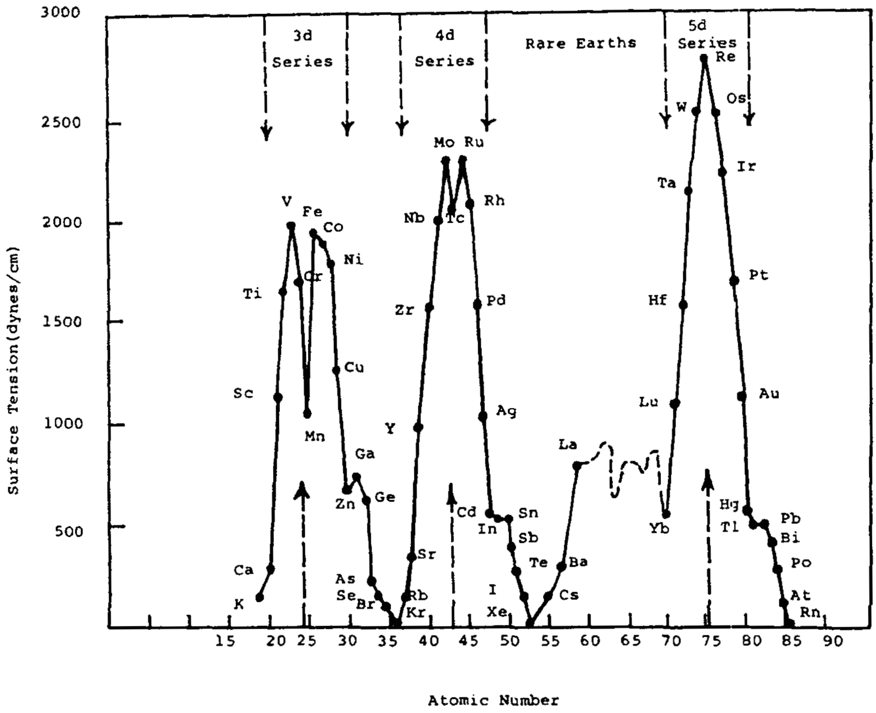

FIGURE 1 Surface Tension as a Function of Atomic Number for Liquid Elements. The 3d, 4d and 5d Transition Metal Series (indicated on top of Figure) exhibit maxima in surface tension at the half filled d-bands (indicated on bottom of Figure).

Wilson[2] has shown that, as a function of d-bandfilling, viscosity also exhibits a peak at the half filled d-band for 3d, 4d and 5d liquid transition metals. He also showed that the molar volume V has a minimum in the same spot for all three transition metal series. Thus Allen's correspondence in γ versus d-bandfilling to $T_M/V^{2/3}$ versus d-bandfilling is partially a consequence of the $V^{2/3}$ denominator exhibiting its minimum near the half filled d-band. However T_M still has a maximum near the half filled d-band for the 3d, 4d and 5d transition metal series, so that $T_M/V^{2/3}$ maximum there is more pronounced than that of T_M alone. Wilson also showed that another measure of the cohesive energy, the enthalpy of sublimation, has peaks at the half filled d-band for the 3d series (with an anomalous dip at Mn), 4d series and 5d series also.

Presumably these maxima in surface tension, viscosity, melting temperature and enthalpy of sublimation in liquid transition metals at the half filled d-band are attributable to the same cause, a maximum in the cohesive energy at the half filled d-band in each of the 3d, 4d and 5d liquid transition metal

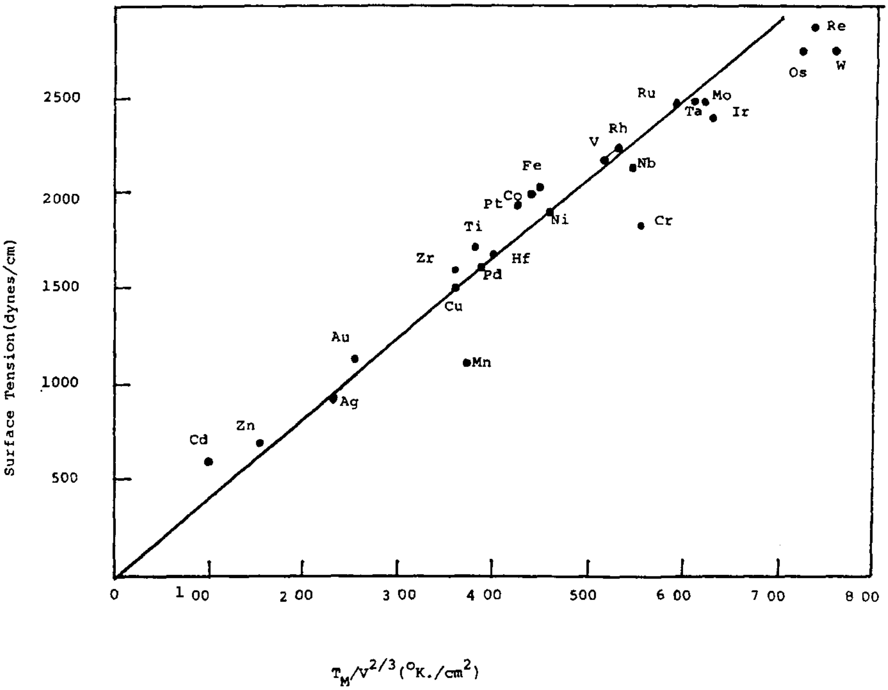

FIGURE 2 Proportionality of Liquid Transition Metal Surface Tension to $T_M/V^{2/3}$ for 3d, 4d and 5d Transition Metals.

series. Siegel[3] has recently explained the solubility maxima at the half filled d-band for all three series in this way. In this note we attempt to link up these trends with a recent theory of cohesive energy of solid transition metals, in which d-bandfilling and other more basic considerations clearly come into play in producing the cohesive energy maximum at the half filled 3d, 4d or 5d band.

Kollar and Solt[4] have recently proposed a theory of solid transition metal bonding trends which predicts a maximum in the cohesive energy, as measured by the melting temperature or sublimation energy, and its derivative, the bulk modulus, as measured by the hardness. Their theory is outlined as follows. They assume a separate s-band and d-band, with s–d hybridization and d–d direct Coulomb or exchange interaction not allowed. The cohesive energy is expressed as

$$-E_c = E^d + E^s \tag{2}$$

where the d-electron contribution is

$$E^d = E^d_{om} - E^d_a + E^d_{bs} + E^d_c$$

and the s-electron contribution is

$$E^S = E^s_0 + E_{es} + E_k + E_{ex} + E_{corr} - E^s_a \tag{3}$$

Here E^d_{om} is the d-band center in the metallic state, E^d_a is the atomic d-level, E^d_{bs} is the sum of the one electron energies of the d-band, E^s_0 is the bottom of the s-band, E_{es} is the electrostatic self energy of the s-electrons, E_k, E_{ex} and E_{corr} are the kinetic, exchange and correlation energies of the s-electrons, E^s_a is the atomic s-level, and E^d_c is the difference between the correction terms arising when summing up one-electron energies to obtain the total energy in the metallic and atomic cases; E^d_c contains the d–d and s–d Coulomb and exchange energies. All terms except E^d_a and E^s_a depend upon the atomic radium proportionately $R_a = V^{1/3}$ and the d-bandfilling ζ. The tight binding d-band is chosen to be

$$E(k) = E^d_{om} + 4\,I\left[\prod_{\substack{i=x,y,z\\ j=y,z,x}} \cos k_i a/2 \cos k_j a/2\right] \tag{4}$$

where a is the lattice constant and I is the overlap integral

$$I(R_0, \zeta) = \lambda \int \phi_\zeta(r - R_l)\, V_\zeta(r)\, \phi_\zeta(r)\, dr = \lambda\, I_0 \tag{5}$$

with λ being constant over each transition series, R_l being the position vector of the l^{th} nearest neighbor, $V_\zeta(r)$ being the lattice potential of form

$$V_\zeta(r) = \left|\begin{array}{ll} -Z^*_d(\zeta)\left[r^{-1} - (R_0/2)^{-1}\right], & r < R_0/2 \\ 0 & , r > R_0/2 \end{array}\right| \tag{6}$$

and R_0 is the nearest neighbor distance. The Slater effective charge is expressed in terms of the d-bandfilling by

$$Z^*_d = 0.65\,\zeta + 0.35 \tag{7}$$

and the d-electron Slater wave function

$$\phi_\zeta(r) \cong r^2 \exp[-(0.65\,\zeta + 0.35\,r)/3] \tag{8}$$

The d-bandstructure is expressed as

$$E^d_{bs} = \int (E - E^d_{om})\, N(E)\, dE = 120\, A(\zeta)\, I_\zeta(R_0) \tag{9}$$

where N(E) is the d-electron density of states and

$$A(\zeta) = (V/3N(2\pi)^3) \int_\zeta dk \left[\prod_{\substack{i=x,y,z\\ j=y,z,x}} \cos k_i a/3 \cos k_j a/3\right] \tag{10}$$

The density of states is defined as

$$N(E_F) = (dE_F/d\zeta)^{-1}_{\zeta=\zeta(E_F)} = (120\, I\, d^2A/d\zeta^2)_{\zeta=\zeta(E_F)} \tag{11}$$

which peaks parabolically near the half filled d-band. The s-band energy is

$$E^s = E_0^s + 2.21/R_a^2 + 1.2/R_a - 0.916/R_a - (0.115 - 0.031 \ln R_a) - E_a^s \quad (12)$$

and

$$R_a = (3/2^{5/2}\pi)^{1/3} R_0 \quad (13)$$

The calculated cohesive energy was found to peak parabolically near the half filled d-band ($\xi \approx 5{,}5$) for the 3d, 4d and 5d transition metal series. It was shown to agree with empirical trends in the 3d, 4d and 5d series. The shrinking atomic volume was caused by d-band cohesion contributions and was strongest near the half filled d-band, where s–d interactions play only a small part.

Their prediction agrees perfectly with the plot of V versus ξ in Figure 3, since $V = R_0^3 = 2^{5/2}\pi R_a^3/3$, and empirically V shrinks most near the half filled d-band. The excess d-electron cohesion which predominates near the half filled d-band derived from quite basic principles in the Kollar–Solt theory and agrees empirically with the maximum in surface tension and viscosity of liquid transition metals near the half filled d-bands in the 3d, 4d and 5d series. However, a word of caution must be given, since the Kollar–Solt theory is strictly true for solid transition metals, that while such a theory possibly could be applied to liquid metals as is, with suitable redefinition of all terms, this has not been done yet. Since the agreement is so striking we are tempted to tentatively conclude that liquid transition metals must have a fairly narrow, semi-tight binding d-band structure so that the Kollar–Solt theory can apply, or else that the cohesive properties of a liquid transition metal are directly attributable to filling of the atomic d-level in the transition metal atoms, be they in the liquid or solid states. Figure 4 shows the melting temperature, another measure of E_c, versus d-bandfilling and again peaks are seen at the centers of the 3d, 4d and 5d bands.

In another, unrelated, field (that of transition metal superconductivity) Gambino and Seiden[6] have convincingly argued that atomic properties determine the superconducting transition temperature, T_c, completely, but whether such a correlation holds for surface tension and viscosity of a liquid transition metal is an unanswered question at present. We tend to favor the former version, since it allows us to use the Kollar–Solt theory which predicts the expected E_c maximum and $V(R_0)$ minimum near the half filled band directly,

Altmann, Coulson and Hume-Rothery[5] evolved a more empirical theory to support the predominance of d-bonding near the half filled d-band in terms of hybrids of gerade and ungerade orbitals (eg. sd^3), the latter having

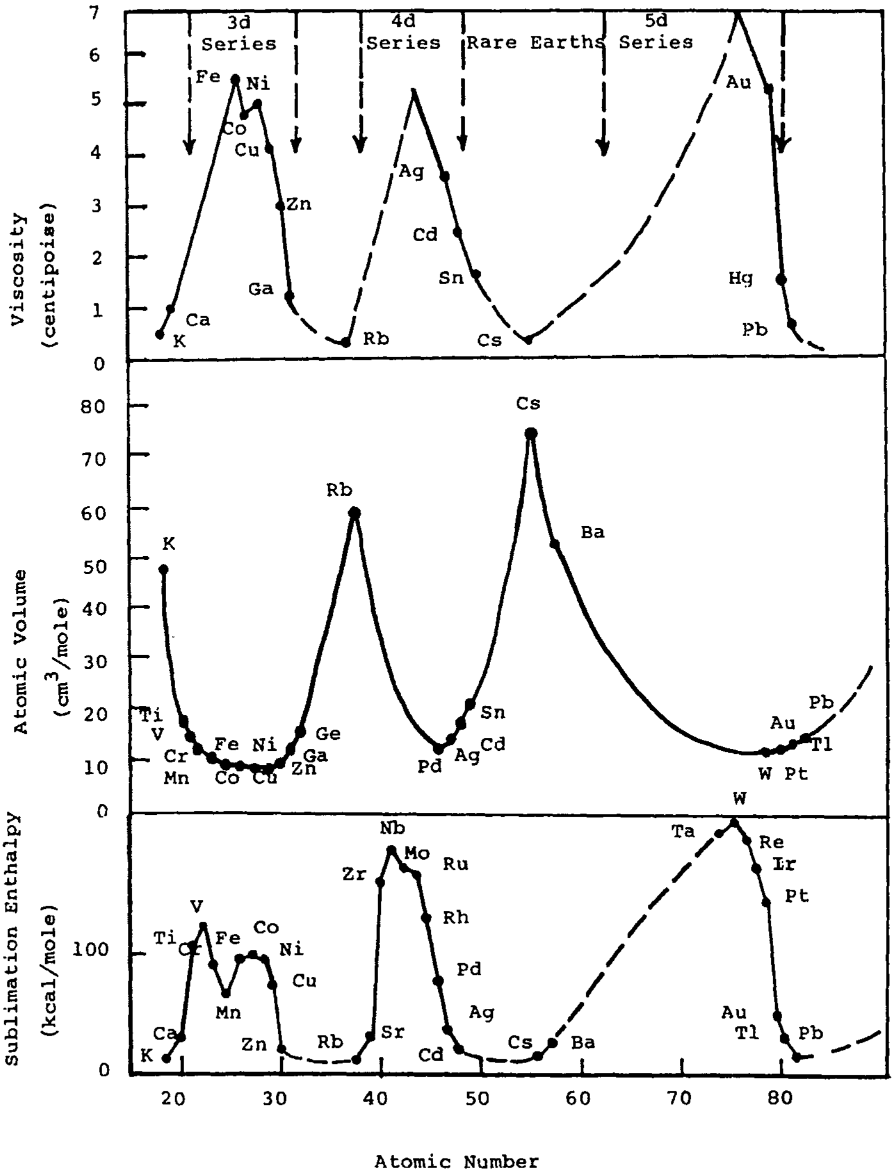

FIGURE 3 Trends in Viscosity, Atomic Volume and Sublimation Enthalpy as a Function of Atomic Number for 3d, 4d and 5d Liquid Transition Metals.

strong directional properties. The sd^3 ungerade hybrid has four tetrahedral directions, yielding directed bonds to eight neighbors (b.c.c. structure) near the half filled d-band.

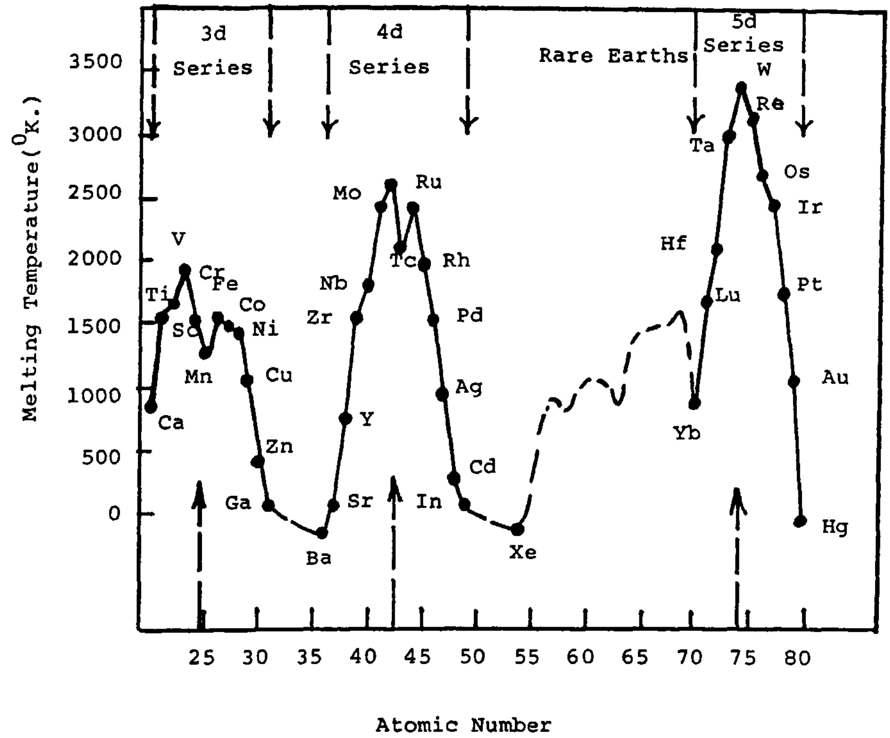

FIGURE 4 Melting Temperature versus Atomic Number for Liquid Elements. Pronounced peaks are exhibited at the half filled d-bands (indicated on bottom of Figure) in the 3d, 4d and 5d Transition Metal Series (indicated on bottom of Figure).

Skapski[7] defined the molar surface energy as

$$E_M^E = (Z-Z_s)/Z\Delta H_V \qquad (14)$$

where ΔH_V is the molar heat of vaporization, Z is the atomic coordination number in the liquid metal and Z_s is the surface coordination number. Thus $(Z-Z_s)$ represents the number of atomic bonds broken in bringing an atom from the bulk liquid to the liquid surface. For an f,c.c. liquid transition metal $(Z-Z_s)/Z = 0.25$, for a h.c.p. liquid transition metal $(Z-Z_s)/Z = 0.33$ and for a b.c.c. liquid transition metal $(Z-Z_s)/Z = 0.36$. (14) shows that $(Z-Z_s)/Z$ is a maximum when E_M^E and ΔH_v are, i.e. when the cohesive energy is a maximum. This is of course at the half filled d-band in 3d, 4d and 5d transition metals since Allen showed that E_M^E and ΔH_V are linearly related. Thus, *if* the Kollar–Solt theory can loosely be applied to liquid transition metals, it predicts a maximum in $(Z-Z_s)/Z$, the number of bonds broken in bringing a liquid metal atom from the bulk to the surface, and thus in the number of directional bonds broken (and thus in γ) at the half filled d-band from first principles.

Lastly, a plot of surface tension versus melting temperature directly is shown in Figure 5. There a near linearity is exhibited. It can be seen, by connecting the transition metals of the 3d, 4d and 5d series respectively, that T_M and γ both peak at the half-filled d-band (Cr–Fe in the 3d series, Mo–Ru in the 4d series and W–Re in the 5d series). In all three series γ peaks at the group VIIB or VIII elements (Fe, Ru, Re) while T_M peaks at the group VIB elements (V–Cr, Mo, W) and in increasing order of γ and T_M the series are 3d, 4d and 5d, as they are for cohesive energy.

In conclusion, the Kollar–Solt prediction of maxima in E_c at the half filled 3d, 4d and 5d bands from "first principles," which thus predicts the similar maxima in empirically measured T_M or ΔH_V or enthalpy of sublimation, also can be used to imply the half filled d-band maxima observed in the surface tension and viscosity of liquid transition metals for the 3d, 4d and 5d series if we assume that these Kollar–Solt bonding theory assumptions are valid for the liquid transition metal phase. The major unanswered question is whether this result holds for the cohesive properties (viscosity,

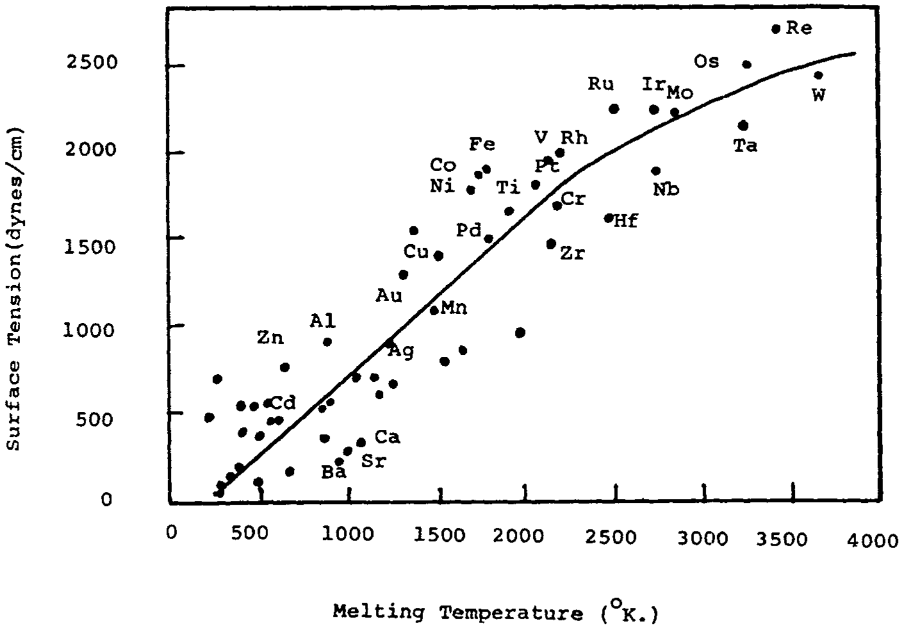

FIGURE 5 Proportionality of Liquid Transition Metal Surface Tension to Melting Temperature, T_M, in the 3d and 4d Transition Metal Series. This proportionality *fails* for the 5d Transition Metal Series.

surface tension) of liquid transition metals because these cohesive properties are purely functions of the trends in atomic properties of the transition metal ions in the liquid or because the liquid transition metal still retains the necessary details of the electronic band structure (narrow d-bands etc.) so that the Kollar–Solt theory of cohesion trends in solid transition metals is readily extended to liquid transition metals with only minor quantitative changes in parameters. This will be attempted from first principles in a later paper.

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