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Universal Binding Energy Relations in Metallic Adhesion

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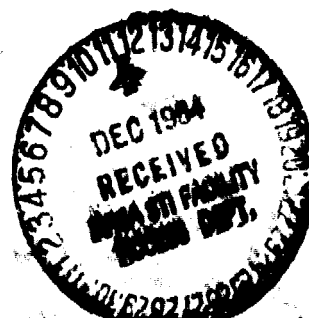

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UNIVERSAL BINDING ENERGY RELATIONS IN METALLIC ADHESION

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ABSTRACT

Rose, Smith, and Ferrante have discovered scaling relations which map
the adhesive binding energy calculated by Ferrante and Smith onto a single
universal binding energy curve. These binding energies are calculated for
all combinations of Al(111), Zn(0001), Mg(0001), and Na(110) in contact.
The scaling involves normalizing the energy by the maximum binding energy
and normalizing distances by a suitable combination of Thomas-Fermi screen-
ing lengths. Rose et al. have also found that the calculated cohesive
energies of K, Ba, Cu, Mo, and Sm scale by similar simple relations, sug-
gesting the universal relation may be more general than for the simple
free-electron metals for which it was derived. In addition, the scaling
length was defined more generally in order to relate it to measurable phys-
ical properties. Further this universality can be extended to chemisorp-
tion and molecular binding. The implications of this scaling have been
explored and have produced some interesting results and verifications. A
simple and yet quite accurate prediction of a zero temperature equation of
state (volume as a function of pressure for metals and alloys) is presented.
Thermal expansion coefficients and melting temperatures are predicted by
simple, analytic expressions, and results compare favorably with experiment
for a broad range of metals. All of these predictions are made possible by
the discovery of universality in binding energy relations for metals.
Finally some results of other researchers concerning universality in Van
der Waals forces are referred to.

DISCUSSION

The adhesive forces between metals in contact play an important role
in, for example, friction and wear and bonding of metal films and in inter-
face properties such as grain boundary energies or fracture strengths [1,2].
Metals in intimate contact interact strongly, leading to significant
changes in interfacial electronic structure. In many situations such as in
friction and wear, grain boundary energetics, and fracture, binding energy
as a function of separation between surfaces is of interest. However this
information is generally inaccessible experimentally. The ranges of the
strong forces are quite small [3], and mechanical deformations of the
solids add complexity to the interpretation of experiments. Consequently
it would be useful if theory could accurately give information concerning
the shape of such binding energy curves, which would complement the infor-
mation obtained from mechanical deformations.

Ferrante and Smith [3-5] have calculated the adhesive binding energy
versus separation for a number of simple metals in contact, Al(111),
Zn(0001), Mg(0001), Na(110), using the jellium model. Figure 1 shows an

example of Al and Mg "jellia" in contact. Crystallinity is introduced into the jellium model through first order perturbation theory and lattice sums. These calculations have used the Hohenburg-Kohn-Sham theory. Details can be found in Refs. 3, 4, and 6 to 8.

The adhesive energy is defined as

$$E_{ad} = \frac{E(a) - E(\infty)}{2A} \qquad (1)$$

where E is the total energy, a is the separation, and A is the interfacial cross-sectional area. The results of these calculations are shown in Fig. 2. E_{AD} at the energy minimum for the same metal with perfect matching at the interface is the surface energy. The values for the binding energies at the minimums are given in Table I. From the binding energies we can see that the strength of the bond for dissimilar contacts is comparable to that for "perfect registry" same-metal contacts. Perfect registry refers to cleaving an ideal single crystal. Nonregistry refers to separating two pieces of metal in contact with arbitrary relative orientation. These curves represent brittle fracture at absolute zero and do not include effects such as ductile extension, which occurs in real contacts. We further note that the derivative of these curves gives the tensile force versus separation.

These calculations are limited, however; the results apply only to simple metals and not to transition metals, which may include directional effects. In addition, because they are only quasi-three-dimensional, only the densest-packed planes for which variations in the plane are a minimum are considered. Consequently it would be of interest to see if these results have more generality than the materials considered.

There is a wide variety of shapes and well depths in the plots of total energy versus separation for the 6 bimetallic contacts shown in Fig. 2. We have found that all of these curves could be scaled into the single universal curve shown in Fig. 3. The scaled separation is given by

$$a^* = \frac{(a - a_0)}{\ell} \qquad (2)$$

where a is the equilibrium separation and ℓ is the scaling length. The scaled binding energy is given by

$$E_{ad}^* = \frac{F_{ad}(a^*)}{\Delta E} \qquad (3)$$

where ΔE is the well depth.

The scaling length ℓ was initially defined in terms of the Thomas-Fermi screening length [9]. However, in extending these results we found that universality applied not only to adhesion, but also to chemisorption, cohesion, and chemical bonding [5]. In these cases the Thomas-Fermi screening length is no longer a simply defined quantity. Therefore a different definition of scaling length was selected, given by

$$\ell = \left\{ \Delta E \left[\frac{d^2 E(a)}{d^2 a^2} \right]^{-1} \right\}^{1/2} \qquad (4)$$

This particular selection for scaling length was chosen since it can be related to experimentally measurable properties such as the bulk modulus for bulk solids or the vibration frequency for molecules. In Fig. 4 we show the scaled binding energy for adhesion, chemisorption, cohesion, and molecular bonding plotted on a single curve. We can see that for these four diverse types of bonding the shape of the binding energy curve is the same (i.e., there is a universal shape). These results indicate that there is an underlying simplicity in nature that had not been realized previously.

At this point it is worth backtracking and reiterating what has been demonstrated. These results are correlations between theoretical calculations of each property. These binding energy curves are not accessible experimentally. As partial evidence that these results are not some artifact of the theoretical techniques used, we point out that the calculation of the binding energy for H_2^+ is exact. There is another avenue of verification, however. The fact that the shapes of the binding energy curves are the same permits interrelationships to be obtained between different physical properties. A notable success is the correct prediction of the vibration frequency for a chemisorbed atom on a given symmetry lattice site in terms of a known vibration frequency as determined by experimental techniques such as high-resolution energy loss spectroscopy [5]. Another is the derivation of the empirically determined relationship between surface and cohesive energy [5].

$$\frac{4\pi r_{ws}^2 \sigma}{E_{coh}} = \frac{\ell_s}{\ell_b} \frac{2C_{11}'}{2d} \frac{r_{ws}}{3B}$$ (5)

where r_{ws} is the Wigner-Seitz radius, σ is the surface energy, E_{coh} is the cohesive energy, the ℓ's are the appropriate scaling lengths for the surface and bulk, C_{11}' is the elastic constant appropriate to strain normal to the surface, d is the interplanar spacing, and B is the bulk modulus. In Fig. 5 we show a plot of the theoretical relationship along with experimental data. More such plots are given in Ref. 5.

These relationships test the proposed concepts at the minimums of the binding energy curves. If an analytical expression for the universal shape were known, further experimental implications of universality could be derived. We have found that the gross features of the curves could be fit reasonably well by Morse or Rydberg functions [10]. To fully examine the experimental properties, a more detailed analytic form is needed. In the spirit of the Rydberg function we propose a polynomial times an exponential. In Ref. 13 we examine the further experimental implications in terms of the equation of state of metals and alloys at zero temperature (the compressive region of the binding energy curve), the melting temperature in terms of the cohesive energy (the inflection point), and the coefficient of thermal expansion (the anharmonic near-minimum region). In Fig. 6 we show the equation of state, in Fig. 7 the melting temperature as a function of cohesive energy, and in table II the coefficient of thermal expansion. As can be seen the theoretical results and experimental predictions agree quite well.

At this point no complete theoretical justification for universality is available. In addition, it would be useful to obtain some semiempirical predictions of well depth by merging these results with those of Miedema [14]. Such a merger would enable a complete specification of the binding energy curve and give more complete prediction of the physical properties of materials. Similar observations have been made by Cole, Vidali, and

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Klein for physical as opposed to strong bonding forces [15]. Smith, Gay, Arlinghouse, and Richter are currently calculating surface energies and adhesive energies by using fully three-dimensional models [16]. We hope to have a sufficient understanding of universality to provide experimentalists with simple theoretical relationships for predicting material properties.

REFERENCES

1. D.H. Buckley, J. Colloid and Interface Sci., 58, 36 (1977).

2. D. Tabor in "Surface Physics of Materials." Vol. 2, ed. by J.M. Blakely, Academic Press, New York, (1975) chap. 10.

3. J. Ferrante and J.R. Smith, Surf. Sci., 38, 77 (1973).

4. (a) J. Ferrante and J.R. Smith, Phys. Rev. B 19, 3911 (1979).
    (b) J. Ferrante, J.R. Smith, and J.H. Rose in "Microscopic Aspects of Adhesion and Lubrication," ed. by J.M. Georges, Elsevier Scientific, Amsterdam (1982).

5. J.H. Rose, J.R. Smith, and J. Ferrante, Phys. Rev. B 28, 1835 (1983).

6. N.D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970).

7. W. Kohn and L.J. Sham, Phys. Rev. A 140, 1133 (1965).

8. A.J. Bennett and C.B. Duke, Phys. Rev. 162, 578 (1967).

9. J.M. Ziman, Principles of the Theory of Solids. Cambridge University Press, New York (1964).

10. J.C. Slater, Quantum Theory of Molecules and Solids. Vol. 1. McGraw-Hill, New York (1963).

11. J.K. Norskov and N.D. Lang, Phys. Rev. B 21, 2131 (1980).

12. A.E. Carlsson, C.D. Gellatt, Jr., and H. Ehrenreich, Phil. Mag. A. 41, 241 (1980).

13. F. Guinea, J.H. Rose, J.R. Smith, and J. Ferrante, Appl. Phys. Lett. 44, 53 (1984).

14. (a) A.R. Miedema, R. Boom, and F.R. DeBoer, J. Less. Comm. Met. 41, 283, (1975).
    (b) A.R. Miedema, Phillips Tech. Rev., 36, 217 (1976).

15. G. Vidall, M.W. Cole, and J.R. Klein, Phys. Rev. B 28, 3064 (1983).

16. (a) J. Gay, J.R. Smith, R. Richter, F.J. Arlinghaus, and R.H. Wagoner, J. Vac. Sci. Tech. A 2, 931 (1984).
    (b) R. Richter, J.R. Smith, and J. Gay, Proc. First Int. Conf. on the Structure of Solid Surfaces, U. of California, Berkeley, 1985.

TABLE I. - BINDING ENERGY COMPARISON

[All energy values taken from the
minimums in the adhesive energy
plots (Figs. 3 and 4).]

Metal combination	Nonregistry	Perfect registry
	Binding energy, $ergs/cm^2$	
Al(111)-Al(111)	490	715
Zn(0001)-Zn(0001)	505	545
Mg(001)-Mg(0001)	460	550
Na(110)-Na(110)	195	230
Al(111)-Zn(0001)	520	
Al(111)-Mg(0001)	505	
Al(111)-Na(110)	345	
Zn(0001)-Mg(0001)	490	
Zn(0001)-Na(110)	325	
Mg(0001)-Na(110)	310	

TABLE II. - COMPARISON OF THERMAL
EXPANSION COEFFICIENTS PRE-
DICTED WITH EXPERIMENTAL
VALUES AT 293 K

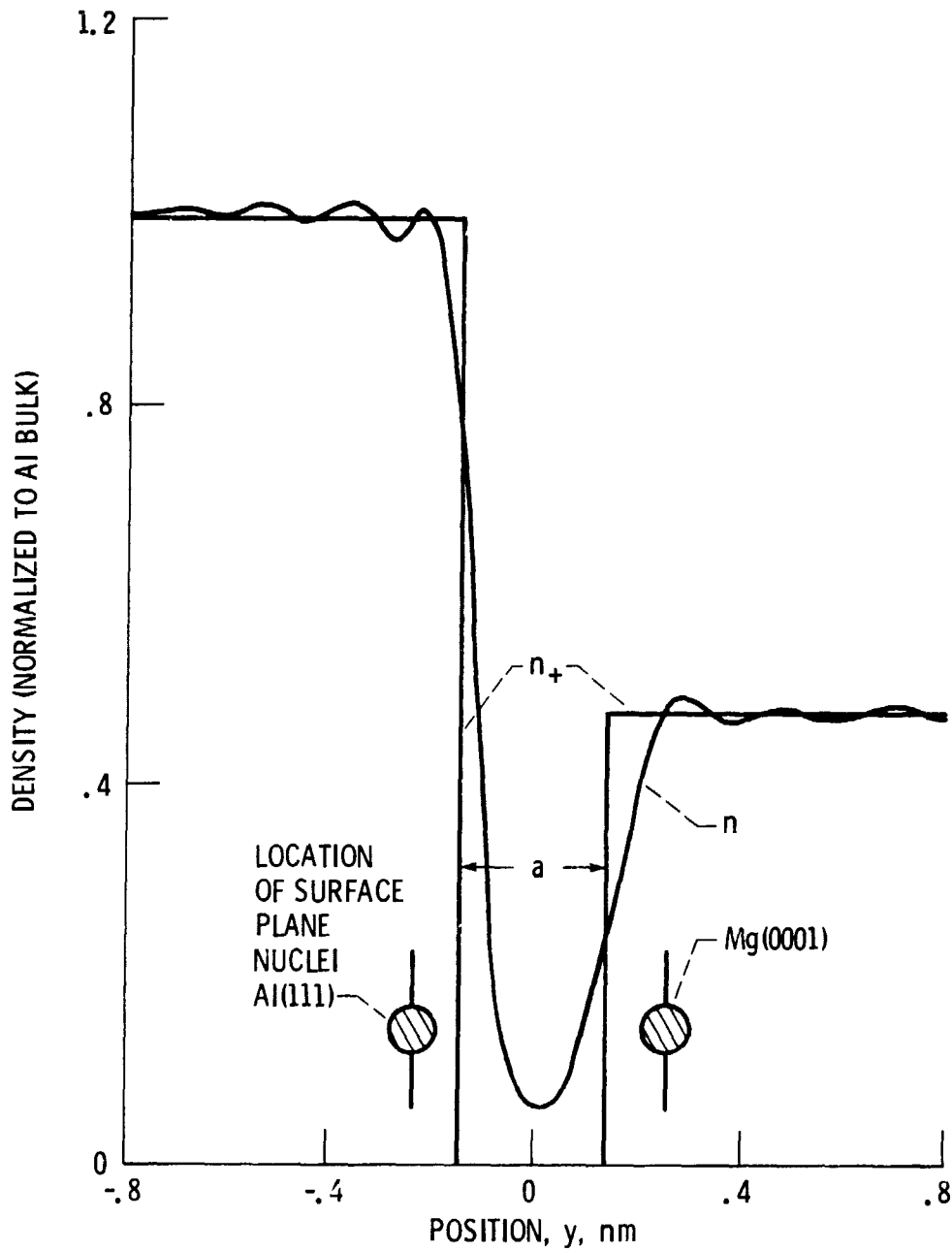| Metal	$\alpha(10^{-6} K^{-1})$	
	Theory	Experiment
W	6.0	4.5
Ir	6.7	6.5
Mo	7.7	5.0
Ta	8.0	7.3
Nb	8.4	7.1
V	11.8	7.8
Pd	12.1	11.6
Fe	12.1	11.8
Au	12.2	14.2
Ni	13.3	12.8
Cu	16.7	16.7
Ag	17.5	19.0
Al	19.6	23.0
$Cu_{0.7}Zn_{0.3}$	20.2	19.9
Pb	23.6	28.7
U	60.9	46.6
Na	75.5	69.0
K	86.0	82.0
Cs	89.9	100.0

Figure 1. - Electron number density n and jellium ion charge density n_+ for an Al-Mg contact. When $a = 0.0$, the distance between Mg and Al atomic planes is $(d_{Al} + d_{Mg})/2$, where d_{Al} and d_{Mg} are the respective bulk interplanar spacings.
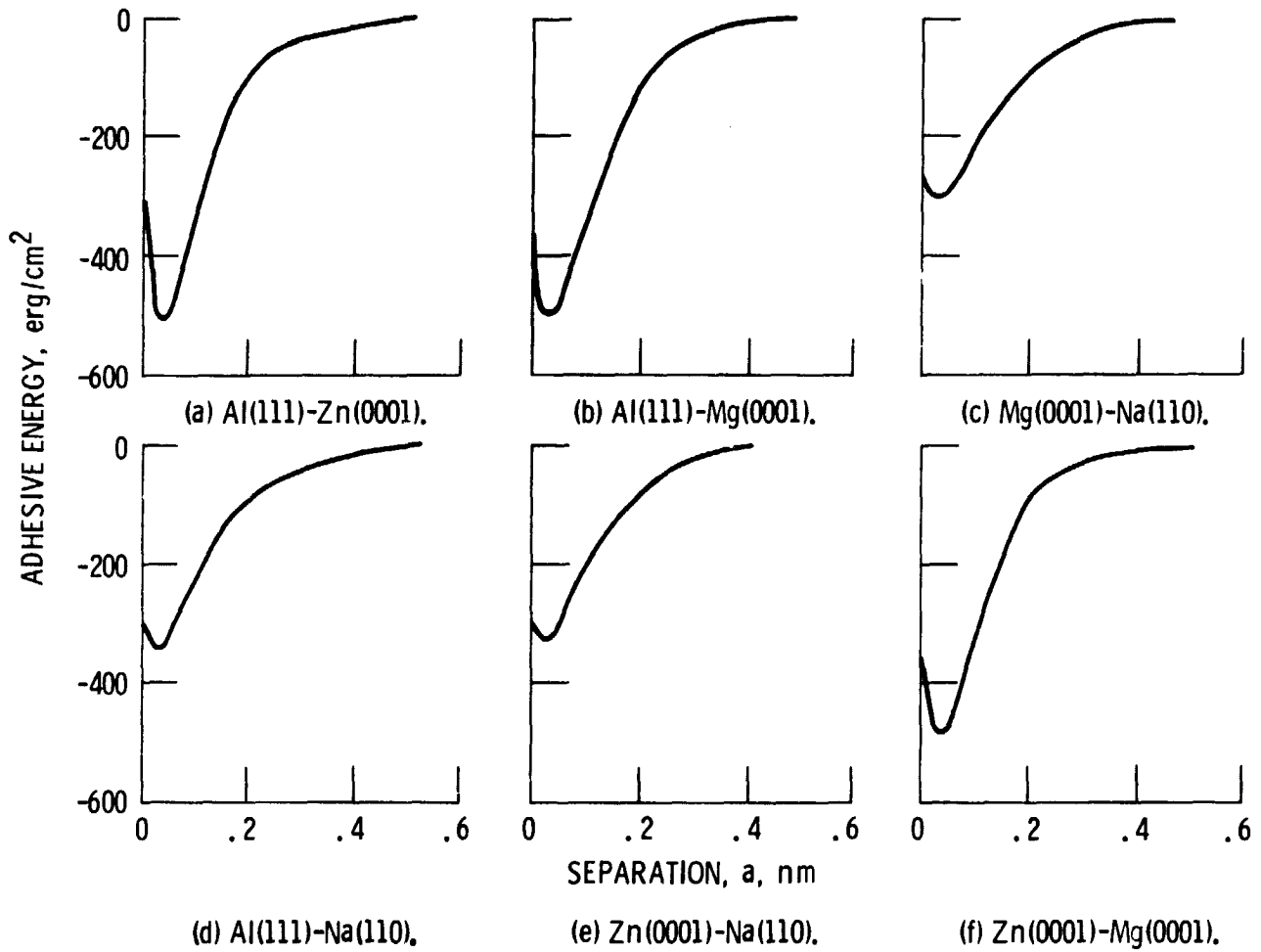
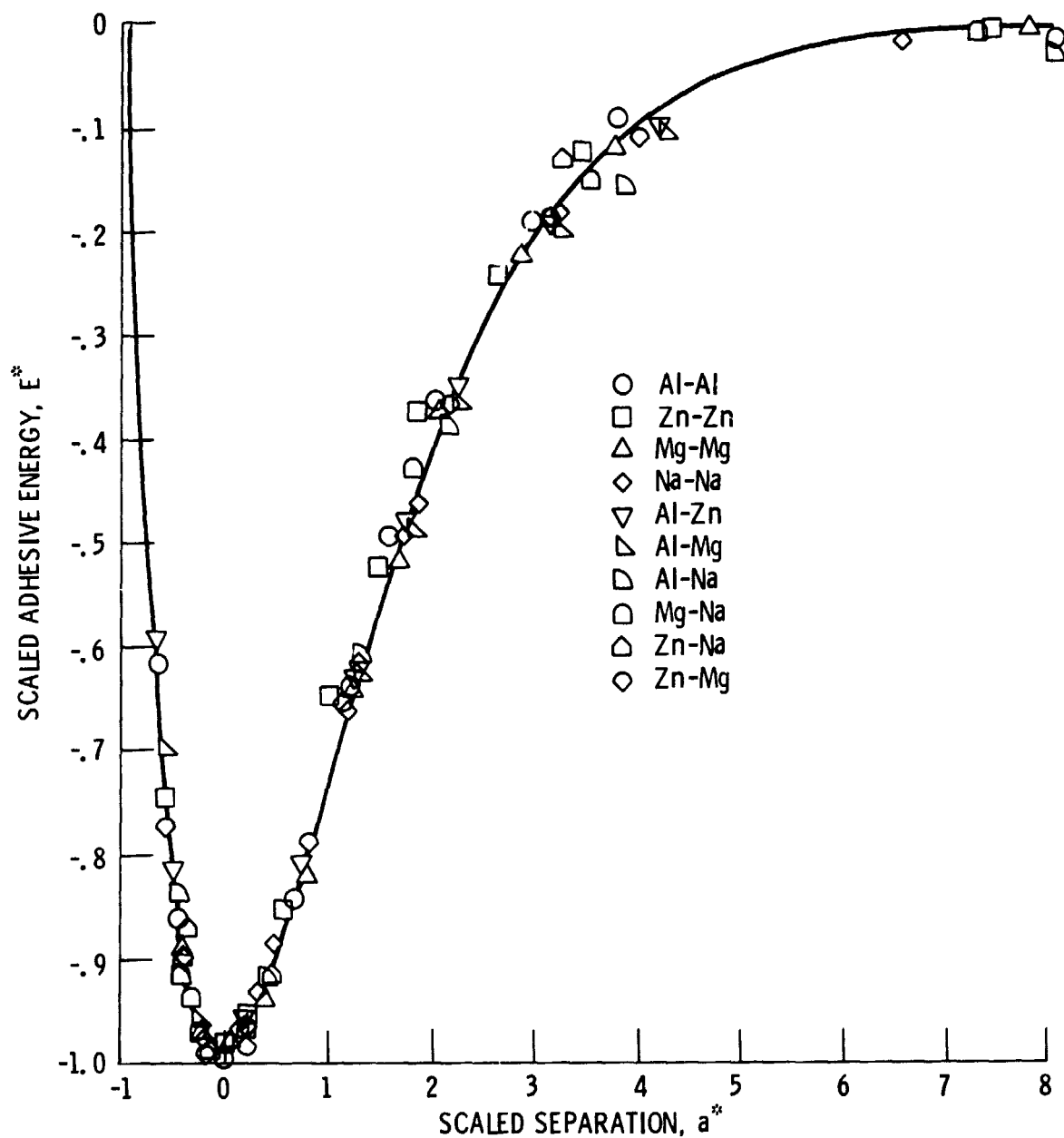Figure 2. - Adhesive binding energy versus the separation between the surfaces indicated.

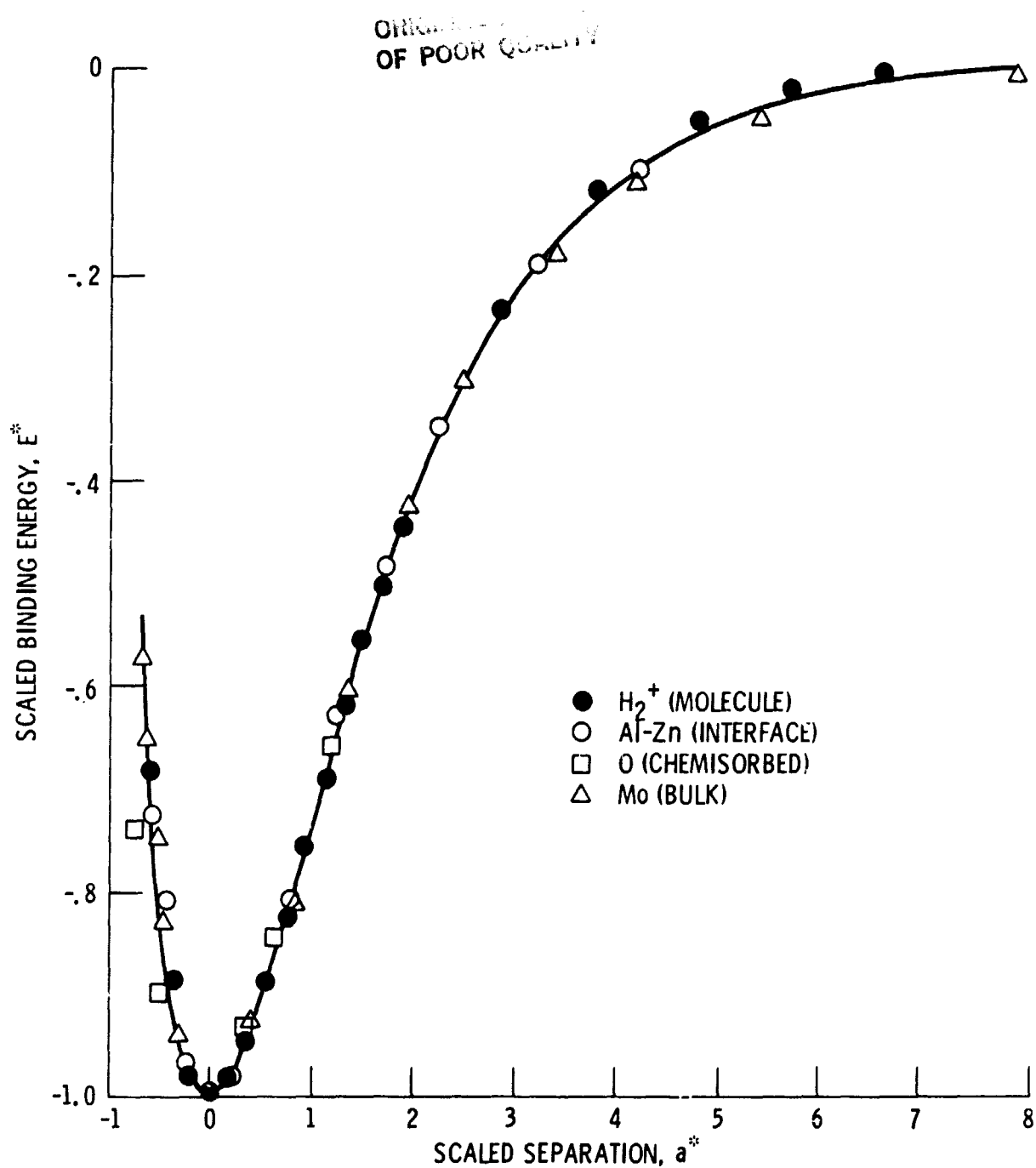Figure 3. - Adhesive energy results scaled as described in the text (see Eqs. (2) to (5)).

Figure 4. - Binding energy as a function of interatomic separation for four systems as noted, scaled as described in the text. The H_2^+ results were taken from Ref. 10, the Ai-Zn interface energies from Ref. 4, the oxygen chemisorption binding energy from Ref. 11, and the Mo binding energy from Ref. 12
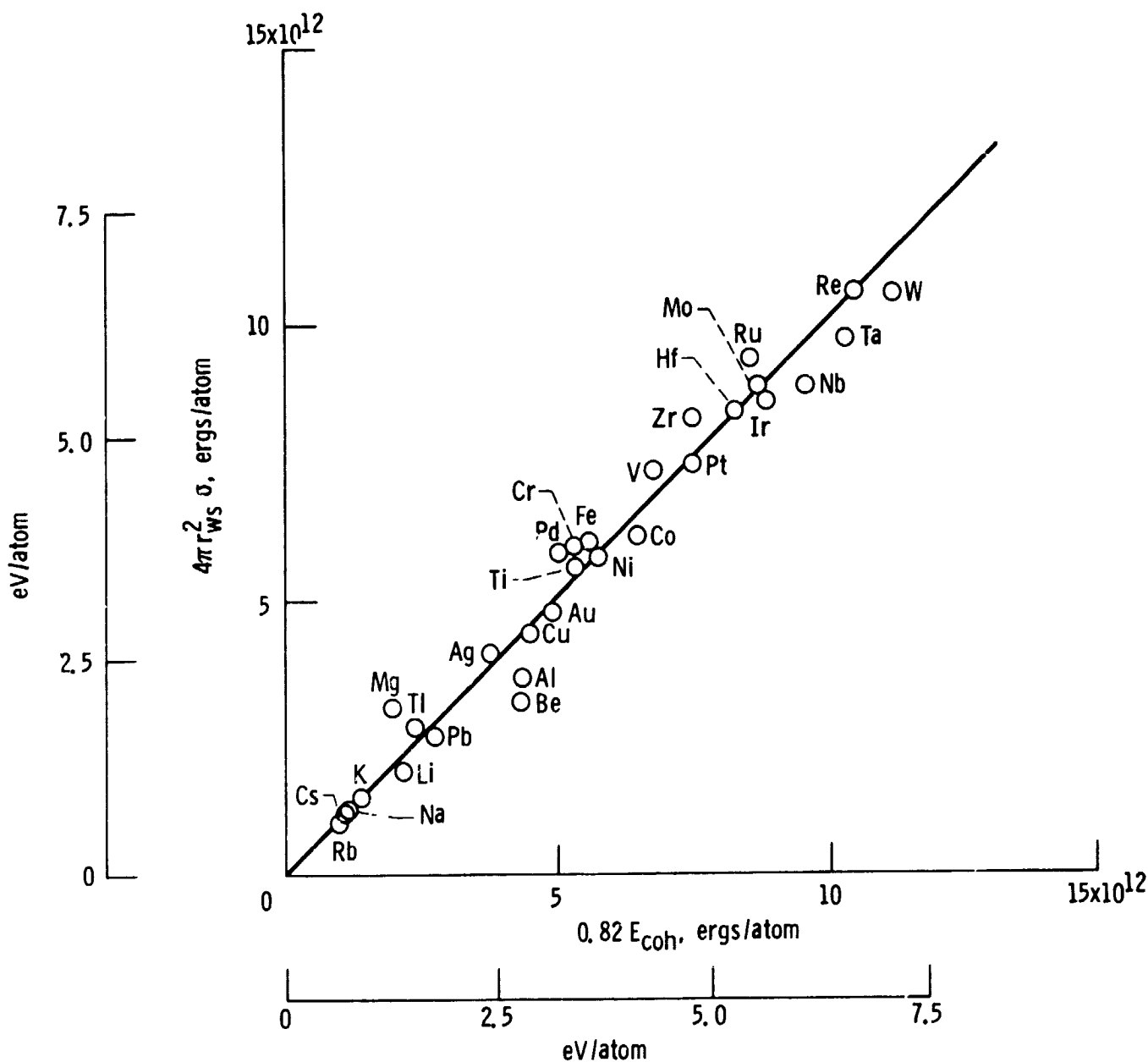
Figure 5. – A plot of equation (5) along with experimental results relating surface and cohesive energies.

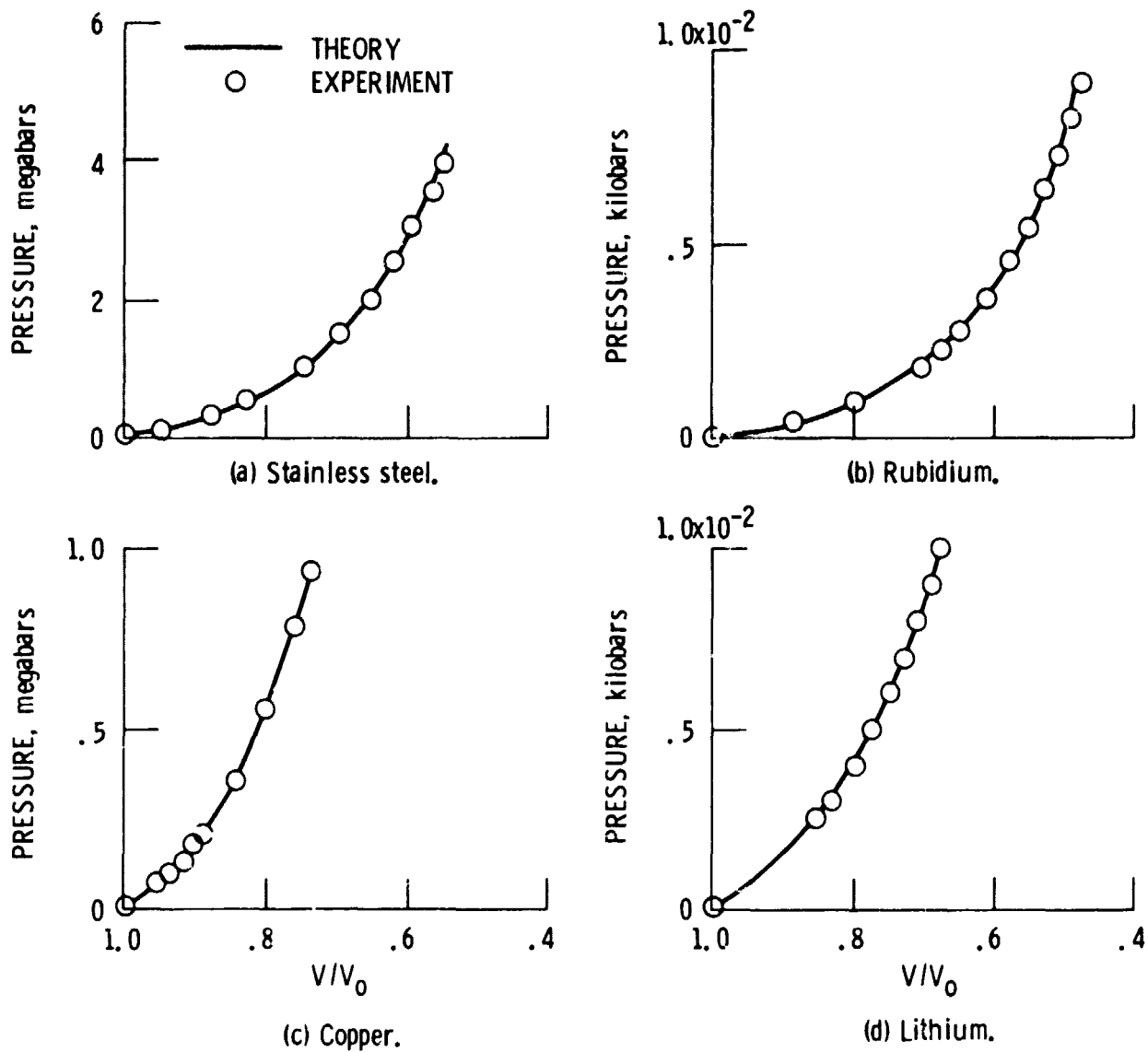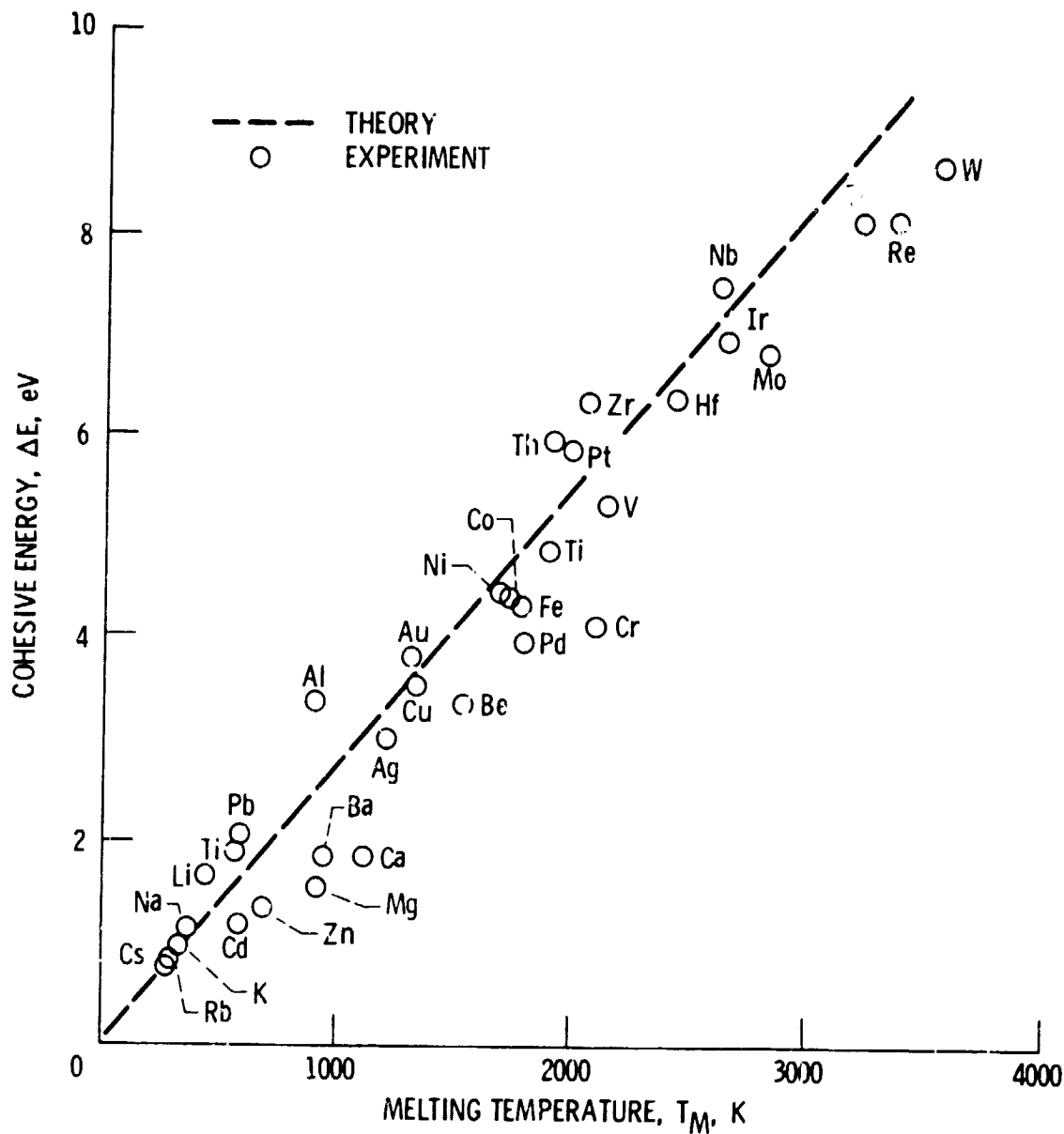Figure 6. – Predicted equation of state and experimental values shown for four metals.

Figure 7. - Predicted and experimental melting temperatures as a function of cohesive energy.