could lead to a Jahn-Teller–like electronic instability which lifts the degeneracy and thereby lowers the total energy. In view of the bonding character of this band one expects that the Mo_6 octahedron undergoes a triclinic distortion, such that the shortening of the Mo-Mo *intracluster* bonds corresponds to a localization of the conduction electrons in one of the split subbands. Such a mechanism is consistent with the observed semiconducting behavior of $EuMo_6S_8$ at ambient pressure,[4] and could explain the absence of superconductivity in triclinic $BaMo_6S_8$. It could perhaps also explain the onset of superconductivity in $EuMo_6S_8$ at high pressure,[3,4] because the rhombohedral to triclinic lattice transformation could be suppressed by the application of hydrostatic pressure. If this is true one expects that $BaMo_6S_8$ also becomes superconducting under pressure. Its critical temperature could be even higher than that of $EuMo_6S_8$ because its Mo_6 clusters are further apart from each other [$d_{\text{Mo-Mo}}{}^{\text{inter}} = 3.27$ Å, $d_{\text{Mo-S}}{}^{\text{inter}} = 2.58$ Å (HT $EuMo_6S_8$); $d_{\text{Mo-Mo}}{}^{\text{inter}} = 3.41$ Å, $d_{\text{Mo-S}}{}^{\text{inter}} = 2.62$ Å (HT $BaMo_6S_8$)][7] and thus its conduction bands are narrower.[11]

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Universal Binding Energy Curves for Metals and Bimetallic Interfaces

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We provide evidence for a universal relationship between metallic binding energies and lattice parameters. By a simple scaling of a universal relationship, one can obtain binding energies as a function of atomic separation for bimetallic interfaces and bulk metals.

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Solid-state energetics are fundamentally described by the relation between the total energy and an appropriate atomic separation. Equations of state, reaction kinetics, and relative atomic configurations are examples of quantities which depend sensitively on the energy as a function of separation. Such energy-distance relations cannot be obtained for solids with use of modern experimental techniques. They can, however, be determined by *ab initio* calculations. However, such calculations are difficult and quite rare.[1-4]

In this Letter we suggest that there is a simple universal form for the relation between binding energy and atomic separation.[5] This universal form permits the simple analytic prediction of the binding-energy–distance relationship relative to equilibrium. The only necessary inputs are the equilibrium binding energy and the equilibrium interstitial electron density.

Two of us[2] have recently computed the electronic structure and adhesive energetics for contacts between all combinations of Al(111), Zn(0001), Mg(0001), and Na(110). The Kohn-Sham equations were solved self-consistently with use of methods similar to those discussed in Ref. 1. Computed binding energies agreed well with experimental surface energies and very good agreement was obtained between computed elastic constants and experiment. In Fig. 1 are plotted the adhesive binding energies as a function of separation in bimetallic contacts made between all combinations of the four metals. The adhesive energy is defined as

$$E_{\rm ad}(a) = [E(a) - E(\infty)]/2A, \tag{1}$$

where E is the total energy, A is the cross-sectional area, and a is the distance between the surfaces of the metals ($a = 0$ when surface atoms of the two half-spaces are separated by the average of the two bulk lattice spacings).

It is clear that there is considerable variation in shape and depth of these curves. It will now be shown that these curves, as well as those of the identical metal contacts[1] [Al(111)-Al(111), etc.], can be simply scaled into a universal curve. This scaling is motivated by the expectation that metals having shorter screening lengths would have adhesive energy curves which rise faster with separation. That is, the metals would screen the disturbances caused by creating the surface over a shorter distance. This suggests that for identical metal contacts the separation is scaled by the Thomas-Fermi screening length $\lambda = (9\pi/4)^{1/3} r_s^{1/2}/3$ a.u., where the bulk electron density is $n_+ = 3/4\pi r_s^3$. When we encounter bimetallic contacts as represented in Fig. 1, a length scaling appropriate to both metals must be considered. In that case, we chose to scale by an arithmetic average, $(\lambda_1 + \lambda_2)/2$. The energy amplitude was scaled by its equilibrium value, $\Delta E \equiv E_{\rm ad}(a_m)$ where a_m is the equilibrium separation. Explicitly we have

$$E_{\rm ad}(a) = \Delta E\, E_{\rm ad}^*(a^*). \tag{2}$$

Here $E_{\rm ad}^*(a^*)$ is the universal adhesive energy function and $a^* = 2(a - a_m)/(\lambda_1 + \lambda_2)$.

Figure 2 shows the results of scaling the calculated adhesive energies. An analytic fit is given by $E_{\rm ad}^* = -(1 + \beta a^*)\exp(-\beta a^*)$ with $\beta = 0.90$. The universality of the scaled adhesive energy curve is truly remarkable. One can see that the results for all ten bimetallic contacts lie very close to the universal curve. This is true even though the bulk metallic densities in the various metals vary

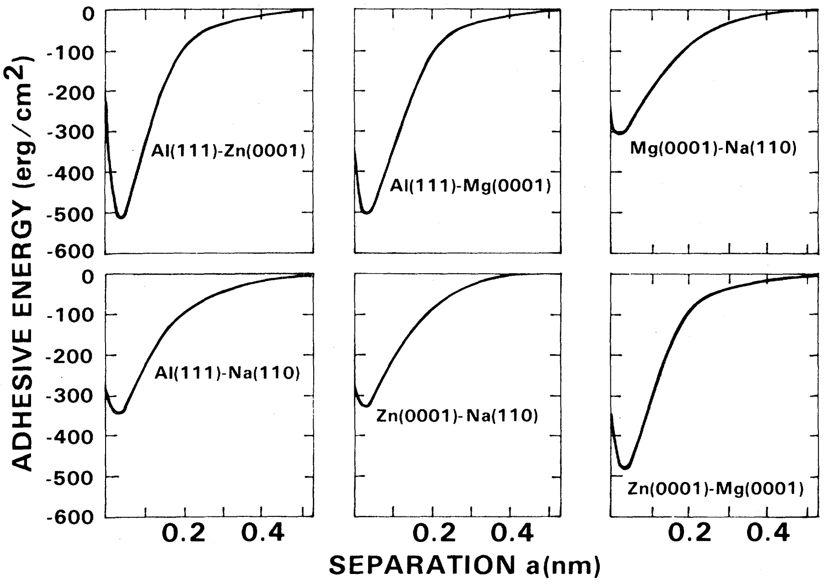

FIG. 1. Adhesive binding energy vs the separation a between the surfaces indicated.

by a factor of 8.

It is important to understand how the fortunate result of a universal energy curve comes about. In the following, we attempt to provide a plausibility argument within the jellium model. First, we have found that solid-vacuum density distributions, $n(x)$, scale rather accurately with λ. That is, there is, to a good approximation, a universal number density distribution $n^*(x-a/2)$ where

$$n(x-a/2)=n_+n^*[\lambda^{-1}(x-a/2)]. \tag{3}$$

Here $a/2$ is the coordinate of the jellium surface. There is a similar scaling for the Kohn-Sham effective one-electron potential:

$$V_{\rm eff}(x-a/2)=v_B v_{\rm eff}^*[\lambda^{-1}(x-a/2)]. \tag{4}$$

We were motivated to look for this scaling by the fact that the Thomas-Fermi equation scales[6,7] exactly with x in units of λ. Secondly, we have found[2] that the total number density in the bimetallic interface is given to a fair accuracy by a simple overlap of the corresponding solid-vacuum distributions. This, and the stationary property of $E[n]$, indicate that it would be a good approximation to use overlapping solid-vacuum number density and potential distributions.

Thus, in a first-order perturbation approximation, we have for identical metal contacts,

$$E_{\rm ad}(a)\cong(1/A)\int_{-\infty}^{\infty}n(x-a/2)v_{\rm eff}(x+a/2)\,dx. \tag{5}$$

Combining Eqs. (3)–(5), we have

$$E_{\rm ad}(a)\cong(1/A)(n_+v_B)\int_{-\infty}^{\infty}n^*(x-a^*/2)v_{\rm eff}^*(x+a^*/2)\,dx. \tag{6}$$

The integrand in Eq. (6) is independent of r_s. The constants in front of the integral are independent of a, and thus Eq. (6) scales exactly as we scaled the adhesive energy curve to give Fig. 2. Although our plausibility argument is restricted to jellium interfaces, we note that the calculated adhesive energies include the ion-ion term exactly for a rigid-lattice model and the electron-ion term in first-order perturbation theory.

It seems that the universal nature of the binding-energy–distance relation is not limited to metal interfaces or to simple metals.[8] Recently, theoretical binding energy curves have become available for several bulk metals [Carlsson, Gelatt, and Ehrenreich[3] (Mo, K, and Cu) and Herbst[4] (Sm^{+2}, Sm^{+3}, and Ba)]. These total cohesive energy curves were calculated as a function of the separation between atoms for a uniformly dilated lattice. We characterize the density of the lattice in terms of the Wigner-Seitz radius, $r_{\rm WS}=(3/4\pi n_A)^{1/3}$, where n_A is the atom

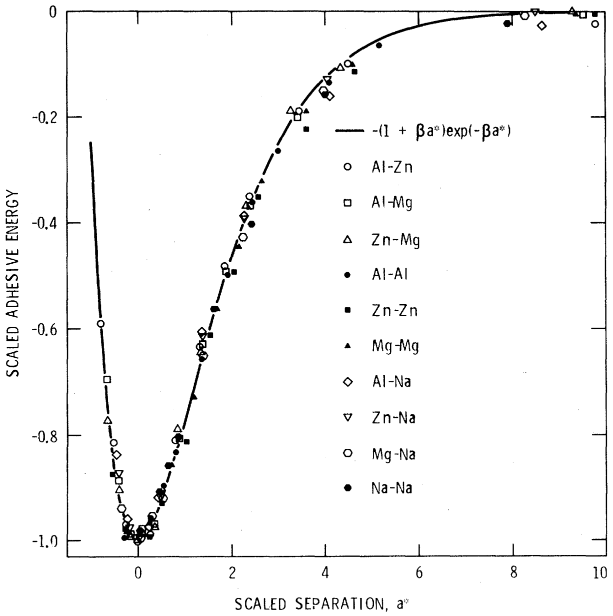

FIG. 2. Adhesive energy results from Fig. 1 (above) and Fig. 4 of Ref. 1 scaled as described in the text: $a^*=2(a-a_m)/(\lambda_1+\lambda_2)$.

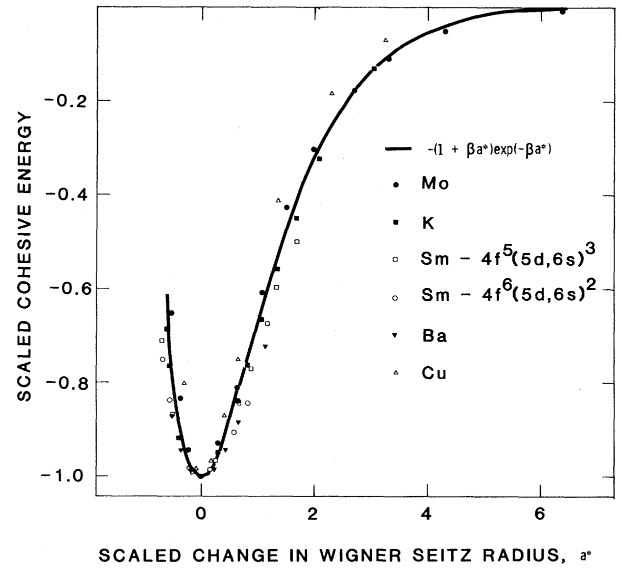

FIG. 3. Bulk energy of various metals scaled and described in the text: $a^*=(r_{\rm WS}-r_{{\rm WS}m})/\lambda$. A value of $\beta=1.16$ was obtained by a least-squares fit to the data.

density. As shown in Fig. 3, these quite disparate cohesive energy curves can be approximately scaled into a universal function, $E_c{}^*$, which is also defined in Eq. (2) if we replace $E_{\rm ad}$ by E_c everywhere. ΔE is the cohesive energy at the equilibrium spacing $r_{{\rm WS}\,m}$ and $a^* = (r_{\rm WS} - r_{{\rm WS}\,m})/\lambda$, where λ is again the Thomas-Fermi screening length. The value of r_s used to determine λ was determined by the equilibrium interstitial electron density.[4,9] The binding energies of Mo, K, Ba, $\mathrm{Sm}^{+2}[4f^2(5d,6s)^2]$, and $\mathrm{Sm}^{+3}[4f^2(5d,6s)^3]$ fall closely on a single curve with $\beta = 1.16$ where we have used the same analytic form as for the adhesive energies. The value of β differs from that appropriate for adhesive energies, presumably in part because all atoms change their positions in the bulk cohesive energy calculations while the adhesive energy curves assume that atomic planes are moved rigidly. The result for Cu has the same shape, but a somewhat different β than the other metals. We do not understand this variation.

The cohesive energy calculations of Carlsson, Gelatt, and Ehrenreich[3] (augmented–spherical-wave functional theory) and Herbst[4] (relativistic Hartree-Fock) are quite different from each other and from the perturbative density-functional results of Refs. 1 and 2 for $E_{\rm ad}$. The nature of cohesive bonding in these metals is quite varied. Ba is a divalent band-overlap metal; Sm is an f-electron metal; Mo and Cu have important d-band interactions; while K is a simple metal. That results for such different metals calculated in quite different ways fall on a single curve indicates the generality of the scaling relations. We note that the "tail" region of the screening charge distribution around metal ion cores can be represented by electron gas parameters. It is known that the screening charge density and potential in this region scale as $r_s{}^{1/2}$ to a fair approximation.[10] Then the argument of Eqs. (3)–(5) applies to the long-range interaction of screened bulk ions with $\pm a/2$ referring to the relative lattice positions and x replaced by $\vec{r}$.

The use of the electron density at $r_{\rm WS}$ is reminiscent of the approach of Miedema and Boom,[11] whose work complements our own. They calculate equilibrium energies (e.g., heats of formation). We, on the other hand, use similar equilibrium quantities to determine the form of the binding-energy–distance relation.

The plotted energies of Fig. 3 were computed for the same electronic configuration at all atomic separations as were the interface calculations. The adhesive energy scaling was illustrated for simple metals. However, the appearance of an analogous scaling relation for the bulk energy of transition metals indicates that the adhesive energy scaling may well extend beyond simple metals. As more accurate adhesive and bulk binding energy results become available, we expect to find systematic deviations from the proposed universal curves for different crystal directions and for different classes of metals. Figure 3 suggests that these deviations might be included by establishing different values of β.

Many analytic physical relationships are implied by the form of the scaling. In a forthcoming publication we will discuss a universal, volume-dependent pair potential for metals and show how cohesive energies, surface energies, and brittle fracture parameters can be written simply in terms of known quantities for metallic elements and alloys.

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