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Universal model for the surface energy of solids

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The surface energy σ is considered as the work done in reversibly cleaving a bulk solid. Let $F(z)$ be the force per unit area required to increase the spacing between the end planes from a to $a+z$. For small z, $F(z)=Az$, where we show how A can be determined from the bulk phonon spectrum, and for large z, $F(z)=C/z^3$, where C can be determined from the bulk frequency-dependent dielectric constant. We assume that, apart from scale, the function $F(z)$ has a universal shape $f^*(z)$. It then follows that $\sigma=\alpha^*(AC)^{1/2}$ where α^* is a universal constant. Preliminary comparison with experiment gives good results with $\alpha^*=0.476$.

I. INTRODUCTION

This paper represents a contribution to the theory of surface energy. Our point of view is to regard the surface energy as the work done in reversibly cleaving a bulk solid along some crystallographic plane. This general approach is quite natural and estimates along this line can be found in earlier works.[1]

Thus, one can write, very roughly, that the cleavage force per unit area is

$$F=\begin{cases} E(z/a)\,, & \text{for } z\leqslant a \\ O\,, & \text{for } z>a \end{cases} \tag{1.1}$$

where E is an appropriate elastic modulus, a is the lattice interplanar spacing, and z is the separation of the two half crystals during the cleavage. This gives for the surface energy per unit area

$$\sigma\equiv\tfrac{1}{2}\int_0^\infty F(z)dz=\tfrac{1}{4}Ea\,, \tag{1.2}$$

which does provide a rough correlation with experiment. (The factor of $\frac{1}{2}$ in the above expression is due to the fact that two surfaces are created during this cleavage process.) The estimate (1.2) focuses on the *short-range* behavior of the cleavage force.

Another approach emphasizes the *long-range* behavior of the cleavage force. Lifshitz has shown[2] that when the two halves of the crystal are far apart, there exists an attractive polarization force per unit area of the form

$$F=C/z^3\,. \tag{1.3}$$

Here the constant C is related to the frequency-dependent dielectric function $\epsilon(\omega)$ by

$$C=\frac{\hbar}{64\pi^2}\int_0^\infty du\int_0^\infty ds\, s^2\left[\left(\frac{\epsilon(iu)+1}{\epsilon(iu)-1}\right)^2 e^s-1\right]^{-1}. \tag{1.4}$$

(For a jellium-type metal with plasma frequency ω_p, $C=1.79\times10^{-3}\hbar\omega_p$). A simple approximation, analogous in spirit to Eq. (1.1), is

$$F(z)=\begin{cases} C/z^3, & \text{for } z\geqslant z_0 \\ O, & \text{for } z<z_0 \end{cases} \tag{1.5}$$

giving

$$\sigma=C/4z_0{}^2\,. \tag{1.6}$$

In this form the theory can be related to some recent ideas of Schmidt and Lucas,[3] and of Craig.[4] These authors gave arguments (whose validity has been questioned) for effectively setting $z_0=0.33v_F/\omega_p$ for the case of metals, where v_F is the effective Fermi velocity of the metal electrons. With this choice they obtain semiquantitative agreement with experiment.

A simple functional form for the force F, which has the correct small z behavior ($F=Az$) and large z behavior ($F=C/z^3$), is

$$F=dU/dz\,, \tag{1.7}$$

where

$$U=-\frac{1}{2}\left(\frac{C}{d^2+z^2}\right) \tag{1.8}$$

and

$$d^2=(C/A)^{1/2}\,. \tag{1.9}$$

By Eq. (1.2), this form gives

$$\sigma=\tfrac{1}{2}\int_0^\infty F(z)dz=-\tfrac{1}{2}U(0)=\tfrac{1}{4}(AC)^{1/2}\,. \tag{1.10}$$

The constant A was computed by Zaremba[5] in terms of the lattice-phonon spectrum, by modeling the cleavage process as a rigid displacement of one-half of the crystal with respect to the other half. Again, qualitative agreement with experiment is obtained for metals, although the theoretical values are substantially (~40%) too low.

The present paper differs from the work of Zaremba in two respects: (1) In computing the force constant A for small cleavage separation, we do not make the rigid lattice assumption but allow for relaxation of the interplanar spacings near the cleavage plane; (2) instead of the particular form (1.7)–(1.9) for $F(z)$ we postulate that $F(z)$ can, to a good approximation, be expressed in terms of an as yet unknown universal function $f^*(z)$. These two points are discussed in the following two sections. The result is a universal approximate theory of the surface energy of all simple solids with nonreconstructing surfaces, involving a single dimensionless parameter α^*, one-half of the integral of the universal function $f^*(z)$. Section IV makes a very preliminary comparison of this theory with experimental data on cubic metals, which gives agreement to within about 16%. This is of the same order as the error in the experimental surface energies. Section V discusses the significance of the results and suggests future directions of research.

II. INITIAL CLEAVAGE FORCE

For simplicity we consider here only crystals with one atom per unit cell. We imagine that equal and opposite forces are applied to all atoms on two adjacent planes.[6] As the forces are slowly increased, the crystal is cleaved. We denote by $F(z)$ the force per unit area being exerted on the right portion when the distance between the two outermost planes has increased from a to $a+z$ (see Fig. 1). For finite z, the spacing between other lattice planes near the cleavage plane will differ somewhat from their equilibrium spacing in the bulk to minimize the total energy.[7] Including these relaxation effects, the surface energy per unit surface area equals one-half the total cleavage work per unit cross-sectional area, and is thus given by

$$\sigma = \tfrac{1}{2} \int_0^\infty F(z)dz \,. \tag{2.1}$$

For small z, F has the form

$$F(z) = Az \,. \tag{2.2}$$

As shown in the Appendix, A is given by

$$A = \tfrac{1}{4}\rho a \omega_0^2 \,, \tag{2.3}$$

where ρ is the density, a is the equilibrium interplanar spacing parallel to the cleavage plane, and ω_0^2 is given in terms of the frequencies $\omega(q)$ of the longitudinal phonons perpendicular to the cleavage plane by the expression

$$\frac{1}{\omega_0^2} \equiv \frac{a}{\pi} \int_0^{\pi/a} \frac{\sin^2(qa/2)}{\omega^2(q)}\, dq \,. \tag{2.4}$$

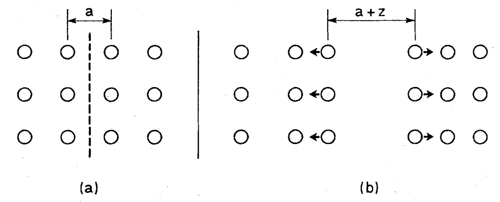

FIG. 1. Reversible cleavage of the crystal. (a) Shows the uncleaved crystal, with all interplanar spacings parallel to the cleavage plane (shown dashed) equal to a. (b) Shows the crystal during cleavage, with a spacing of $a+z$ between the two outermost planes, and naturally relaxed spacings between the other planes.

Equations (2.3) and (2.4) are general and exact.

Note that if only nearest-neighbor interplanar forces are significant, then

$$\omega(q) = \bar{\omega} \sin(qa/2) \,, \tag{2.5}$$

where $\bar{\omega}$ is the maximum frequency. In this case, $\omega_0 = \bar{\omega}$.

We also compare our result with that of Zaremba,[5] who modeled the cleavage process by a *rigid* shift of one portion of the crystal relative to the other. His result for the coefficient A can also be written in the form (2.3), but with ω_0 given by

$$(\omega_0^2)_r = \frac{a}{\pi} \int_0^{\pi/a} \frac{\omega^2(q)}{\sin^2(qa/2)}\, dq \,, \tag{2.6}$$

where the index r refers to the rigid cleavage. Clearly, for the nearest-neighbor spectrum (2.5), $(\omega_0)_r = \bar{\omega}$; i.e., in this case (understandably) there is no difference between the two values of A. However, whenever there are interactions between planes beyond nearest neighbors it is obvious that

$$\omega_0^2 < (\omega_0^2)_r \text{ and } A < A_r \,. \tag{2.7}$$

In typical cases A is about 20 to 40% smaller than A_r.

III. UNIVERSAL MODEL FOR THE CLEAVAGE FORCE

We have seen that, for small and large z, the cleavage force behaves, respectively, as

$$F(z) = \begin{cases} Az & (z \ll a) \\ C/z^3 & (z \gg a) \,, \end{cases} \tag{3.1}$$

where the coefficients A and C differ from material to material. Let us now scale the force F in units of $(A^3C)^{1/4}$ and the distance z in units of $(C/A)^{1/4}$,

$$F = (A^3C)^{1/4} f[z/(C/A)^{1/4}], \tag{3.2}$$

so that

$$f(z)=\begin{cases} z & \text{for } z\ll 1 \\ 1/z^3 & \text{for } z\gg 1\,. \end{cases} \tag{3.3}$$

It can be directly verified that (3.2) and (3.3) lead to (3.1). The curve $f(z)$ is plotted schematically in Fig. 2.

The surface energy of any solid is then given exactly by

$$\sigma=\alpha(AC)^{1/2}\,, \tag{3.4}$$

where A is given by Eqs. (2.3) and (2.4), C is the Lifshitz constant [Eq. (1.4)], and

$$\alpha\equiv\tfrac{1}{2}\int_0^\infty f(z)dz\,, \tag{3.5}$$

which will be characteristic of each material and each crystal face.

The function $f(z)$ has, by construction, the same behavior for both small and large z for all materials. In the absence of additional information it is reasonable to try the simple hypothesis that, to a good approximation, $f(z)$ equals a *universal function*, $f^*(z)$, for all materials. Then α, Eq. (3.5), becomes a universal constant, α^*, and

$$\sigma\approx\alpha^*(AC)^{1/2} \tag{3.6}$$

for all materials.

If Eq. (3.6) is indeed an accurate representation of surface energies, a plot of σ vs $(AC)^{1/2}$ for different materials should fall on a single straight line, passing through the origin, whose slope determines α^*. The functional form

$$f(z)=\frac{z}{(1+z^2)^2} \tag{3.7}$$

corresponding to the simple form (1.6)–(1.8) for $F(z)$ gives $\alpha^*=\frac{1}{4}$, and one would expect the best universal α^* to be not too different from this value.

IV. COMPARISON WITH EXPERIMENT

A test of our hypothesis (3.6) requires a reliable knowledge of σ from surface-energy measurements, of A from measured phonon spectra, and of C from the measured bulk optical constant $\epsilon(\omega)$. The overall experimental situation is not too good. In this preliminary comparison with experiment, we choose the (110) faces of 10 cubic metals for which reasonably reliable data exist. We find that the plot of σ vs $(AC)^{1/2}$ does indeed fall reasonably well on a straight line passing through the origin (see Fig. 3). A least-squares fit gives the value

$$\alpha^*=0.476\,, \tag{4.1}$$

which, surprisingly, is almost twice as large as that obtained with the simple form (3.7).

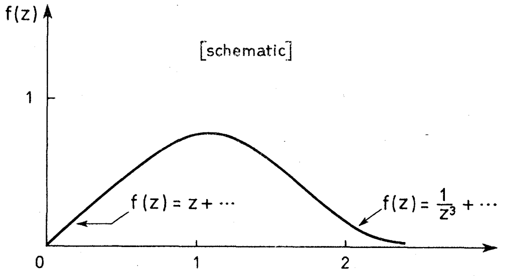

FIG. 2. The scaled force function $f(z)$. Note the behavior for small and large values of z.

The accuracy of the universality principle (3.6) can be judged by computing α for each of the 10 metals from Eq. (3.4) and then comparing this value with α^*. This results in the root-mean-square deviation

$$\Delta\alpha^*=\left(\frac{1}{10}\sum_{i=1}^{10}(\alpha_i-\alpha^*)^2\right)^{1/2}=0.16\alpha^*\,, \tag{4.2}$$

which is of the same order as the error in the experimental values for the surface energies.

We may ask how significant the inclusion of relaxation effects is in the use of the universality principle. If one attempts to fit the same 10 data

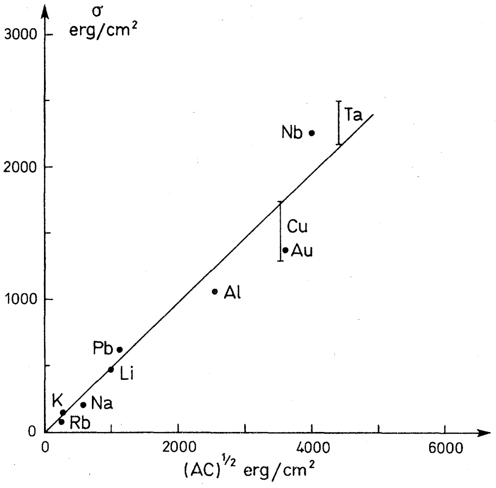

FIG. 3. Experimental surface energies vs $(AC)^{1/2}$. The straight line represents the best fit with $\alpha^*=0.476$. The sources of the experimental points were the following. Surface energies: Li (Ref. 8), Na, K, Rb (Ref. 9), Pb (Ref. 10), Al, Cu, Nb, Ta, Au (Ref. 11), Cu and Ta (Ref. 12). Dielectric constants: Li, Na, K. Rb, Al—free electron model with $\omega_p^2=(4\pi mn/e^2)$; Pb (Ref. 13); Cu, Au (Ref. 14); Ta (Ref. 15); Nb (Ref. 16). Phonon spectra: Li (Ref. 17), Na (Ref. 18), K (Ref. 19), Rb (Ref. 20), Pb (Ref. 21), Al (Ref. 22), Cu (Ref. 23), Nb (Ref. 24), Ta (Ref. 25), Au (Ref. 26).

by the formula

$$\sigma = \alpha_r^*(A_r C)^{1/2}\,, \tag{4.3}$$

where A_r is the *rigid*-lattice force constant (see Sec. III), one can partly compensate for the fact that $A_r > A$ by using a smaller value for α_r^*. However, the root-mean-square deviation of the data from (4.3) is about 50% larger than from (3.6).

V. DISCUSSION

A comparison with some limited data on metals indicates that the hypothesis of a universal value α^* in Eq. (3.6) for the surface energy may be of quantitative value for estimating the surface energy from independent experimental data about the elastic and the optical properties of the bulk material. Since direct measurements of surface energies are very difficult compared to those of the elastic and optical quantities A and C of the bulk materials, a sufficiently accurate, universal relationship of the form (3.6) could be of great value for surface physics. Evidently, more comprehensive tests of Eq. (3.6) would be of great interest.

Of course, the assumption of a universal α^*, derived from the postulated universal form of the normalized cleavage force $f^*(z)$, cannot be strictly exact. It would therefore be interesting to examine if there are systematic variations of the experimental quantity α, defined by Eq. (3.4), for different classes of surfaces, e.g., (001) and (111), or metals and insulators. At the present time such variations may be undiscernible because of uncertainties in experimental values of σ, A, and C. This reemphasizes the need for better data for these quantities. If, however, systematic variations of this sort were found, they would stimulate careful thinking about the nature of surface "bonds" for different classes of surfaces.

The large empirical value of α^* $(=0.476)$ is somewhat disturbing. If we use the schematic representation for $f(z)$,

$$f^{**}(z) = \begin{cases} z\,, & z < 1 \\ z^{-3}\,, & z > 1 \end{cases} \tag{5.1}$$

we obtain $\alpha^{**} = 0.500$. We conjecture that the near equality of the mean empirical α^* with α^{**} comes about by a near cancellation of two effects: a reduction of $f^{**}(z)$ for $z \lesssim 1$ by anharmonic (z^2) terms and an increase for $z \gtrsim 1$ by higher-order (z^{-4}) polarization terms.

We turn next to the question of temperature dependence. If α is indeed a good universal constant α^* for different surfaces at zero temperature, because of the approximate universality of the function $f(z)$, it is natural to hypothesize that α is also approximately constant for a given material at different temperatures. Thus, if we denote by $\gamma(T)$ the surface Helmholtz free energy at temperature T, this suggests that

$$\gamma(T) = \sigma[A(T)C(T)/A(0)C(0)]^{1/2}\,,$$

so that the temperature dependence of $\gamma(T)$ would stem from the temperature dependence of A and C, Eqs. (2.3), (2.4), and (1.4).

A final remark about the constants A and C: When a phonon spectrum is not available, but the velocity of sound c perpendicular to the cleavage plane is known (e.g., from the elastic constants), a rough approximation to ω_0 can be obtained by postulating the nearest-neighbors type of dispersion spectrum, (2.5), which results in $\omega_0 = ca/2$. When the dielectric constant $\epsilon(\omega)$ is not available, one can attempt to represent the electrons by an effective plasma frequency, ω_p^{eff}, and then set $C = 1.79\times 10^{-3}\hbar\omega_p^{\text{eff}}$ [see Sec. I, Eq. (1.4) ff].

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APPENDIX: CALCULATION OF THE FORCE CONSTANT *A*

We wish to calculate the displacements u_1 and $u_0(=-u_1)$ when forces F (and $-F$) per unit area are applied to the lattice planes $m=1$ (and $m=0$). We therefore consider the equations of motion of the lattice planes under the action of a general force F_m:

$$M\ddot{u}_m = \sum_l A(l)u_{m+l} + F_m\,, \tag{A1}$$

where M is the mass per lattice plane per unit area,

$$M = \rho a \tag{A2}$$

($\rho =$ density, $a =$ interplanar spacing), and $A(l)$ are the interplanar force constants.

The normal modes of vibrations of the planes are given by

$$u_m = e^{i(kma-\omega t)}\,, \tag{A3}$$

where

$$\omega^2(k) = -\frac{1}{M}\sum_l A(l)e^{ikla}\,, \tag{A4}$$

Next we consider the static displacements u_m due to static forces F_m. We write

$$F_m=\sum_k F(k)e^{ikma}\,, \tag{A5}$$

$$u_m=\sum_k u(k)e^{ikma}\,. \tag{A6}$$

Substitution into (A1) gives

$$u_m=\sum_k \frac{F(k)}{M\omega^2(k)}e^{ikma}\,. \tag{A7}$$

For our case

$$F_m=F(\delta_{m,1}-\delta_{m,0})\,. \tag{A8}$$

If we impose periodic boundary conditions after N planes, we find

$$u_m=\frac{F}{NM}\sum_k \frac{1}{\omega^2(k)}\left[e^{ik(m-1)a}-e^{ikma}\right], \tag{A9}$$

and in particular

$$\begin{aligned} u_1&=\frac{Fa}{\pi M}\int_{-\pi/a}^{\pi/a}\frac{\sin^2(ka/2)}{\omega^2(k)}dk \\ &=F\frac{2}{\rho a}\frac{1}{\omega_0^2}\,, \end{aligned} \tag{A10}$$

where

$$\frac{1}{\omega_0^2}=\frac{a}{2\pi}\int_{-\pi/a}^{\pi/a}\frac{\sin^2(ka/2)}{\omega^2(k)}dk\,. \tag{A11}$$

Since $z=(u_1-u_0)=2u_1$, we have

$$F=\left(\frac{1}{4}\rho a\frac{1}{\omega_0^2}\right)z\,, \tag{A12}$$

which is used in Eqs. (2.2) and (2.3).

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