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A New Approach for the Relative Surface Free Energy of Cubic Material with Terrace, Step, and Kink Structures

J. C. Canullo,[†] H. L. Tignanelli,[‡] A. Plastino,[§] and A. J. Arvia[*]

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Casilla de Correo 16, Sucursal 4, 1900 La Plata, Argentina

A new relationship between the relative surface free energy and the surface structure of a cubic material with terrace, step, and kink structures based upon the application of the information theory is presented. Any surface of a face centered cubic crystal exists as combinations of (111), (100), and (110) microfacets with a certain concentration of kinks, corners, and border of terraces. By use of the most dense atomic array, the entire crystallographic surface can be described, including the corresponding relative surface free energy of each kind of site. The results can be correlated with existing experimental data.

Introduction

The question of chemical activity and atomic surface structure of metals is of great importance in heterogeneous catalysis and, in general, in the formation of surface chemical bonds. The chemical activity is directly related to the surface energy distribution which in turn depends on the distribution of the various pieces of surface, that is, on the terrace–step–kink structure. These structures are characterized via the Miller indices. The description and notation of the crystal surfaces have been the matter of a series of publications,[1-3] the most recent one referring to high-Miller index surfaces of cubic materials.[3] On the other hand, a considerable number of publications have dealt with the evaluation of the surface free energy of metals, either theoretically[4-6] or experimentally.[7]

The present paper brings forth a new relationship between the relative surface free energy and the surface structure of a cubic metal with terrace, step, and kink structures by recourse to the information theory formalism.[8] For this purpose the notation recently proposed by Van Hove and Somorjai[3] for the surface structures of cubic materials has been considered. The results are in a good agreement with those reported in earlier theoretical and experimental works[7-9] and become useful to extend previous conclusions derived on the matter.[4,5]

As the subject of this paper covers two very specific aspects, namely, the crystallography of metal surfaces and the information theory (statistical inference), it is convenient to present a concise introductory survey of those aspects independently, to make the specific question described in the paper more easily understandable for the nonspecialist.

Crystallography and Crystal Surface Area

When a hanging liquid metal bead produced by melting one extreme of a metal wire is cooled down, it tends to produce a spherical single crystal with flat surfaces and, from a macroscopic point of view, to attain the minimum surface energy condition.[9] The surface of an ideal spherical single crystal offers all possible crystalline orientations which are characterized in each direction (pole) by definite Miller indices (*hkl*). In the absence of contaminants the minimum surface free energy condition extends flatness to the true atomic level[10] where, on account of the material discretness (atoms) and emergent crystalline (*hkl*) plane, the surface breaks into microfacets, that is, terraces, steps, and kinks, following on the long range the surface curvature (parts b and c of Figure 1). Each microfacet is made up of only one of the fundamental atomic arrangements, namely the (111), the (100), an probably the (110). Due to the microfaceted breakage, the real surface area may differ from the calculated geometric area for a unit cell of the emergent (*hkl*) plane, and this difference depends on the distance between the fundamental crystallographic poles. In this way, one denotes plane, surface, or pole (*hkl*) to an ideal geometric plane tangent to the spherical surface in the intersection of the [*hkl*] pole direction with a spherical single crystal surface. The (*hkl*) plane emerging from the bulk crystalline structure, will be called the

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[†] Member of CICBA–INIFTA, UNLP.

[‡] Permanent address: Observatorio Astronómico, Universidad Nacional de La Plata, Paseo del Bosque S/N, 1900 La Plata, Argentina. Member of CICBA.

[§] Permanent address: Physics Departament, Universidad Nacional de La Plata, C.C. 67, 1900 La Plata, Argentina. Member of the Researcher Career (CONICET).

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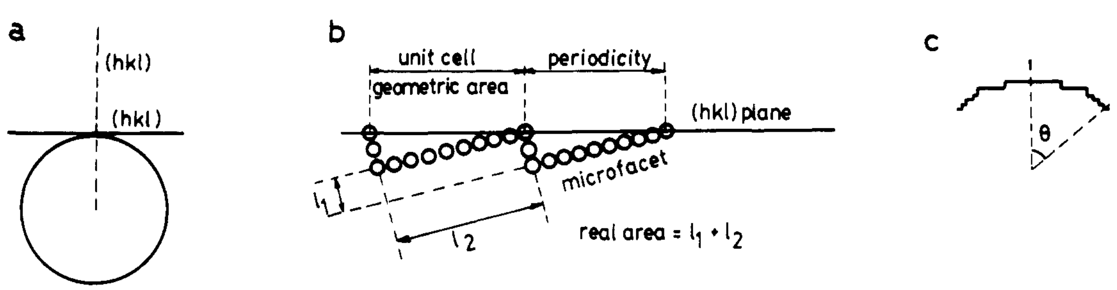

Figure 1. (a) Bidimensional scheme of an ideal crystalline plane (*hkl*) emerging from the bulk and tangent to the spherical surface in the intersection with the [*hkl*] direction. (b) Geometric unit cell and its corresponding microfacets. (c) Microfaceted curvature.

geometric area of the crystallographic surface area unit cell defined by Nicholas[1] and calculated by Somorjai's[3] formulas (Figure 1).

The geometric surface area of the unit cell of a simple cubic crystal, $A^{uc}{}_{sc}$, of a (*hkl*) pole is given by the equation

$$A^{uc}{}_{sc} = [h^2 + k^2 + l^2]^{1/2} \tag{1}$$

and for the face centered cubic (fcc) crystalline structure

$$A^{uc}{}_{fcc} = (1/2)[h^2 + k^2 + l^2]^{1/2} \tag{2a}$$

for *h*, *k*, and *l* not all odd numbers, and

$$A^{uc}{}_{fcc} = (1/4)[h^2 + k^2 + l^2]^{1/2} \tag{2b}$$

for *h*, *k*, and *l* all odd numbers. Equations 1, 2a, and 2b are expressed according to Somorjai's notation.[3]

Let us denote by $A_g(hkl)$ the geometric area of the (*hkl*) pole. Then

$$A_g(hkl) = A^{uc}{}_{sc} = [h^2 + k^2 + l^2]^{1/2} \tag{3}$$

and let us further consider that $A_r(hkl)$, i.e. the real area of the (*hkl*) pole is the sum of the real areas of the fundamental atomic arrangements (111), (100), and (110) from which the real area is constructed. Under these conditions, ExcA(*hkl*), the excess of geometric area at the (*hkl*), pole can be expressed by the ratio

$$\mathrm{ExcA}(hkl) = A_r(hkl)/A_g(hkl) \tag{4}$$

In order to make the problem easier to solve, a simple cubic crystallographic structure will be considered. Notwithstanding, eq 4 remains the same for the fcc system provided that the fundamental poles are properly corrected.

The definition of Ar for each fundamental pole is based upon the fact that for fcc crystals the most compact atomic arrangement, that is, (111), corresponds to that of the lowest surface free energy. Correspondingly, one should expect, that in the absence of constrains, any fcc surface should tend to approach the (111) arrangement. This means that in this case, one can write

$$A_r(111) = A_g(111) \tag{5}$$

Let us consider now the unreconstructed (110) fcc surface. The latter can be expressed as the following combination of (111) surfaces

$$(110) = (1/2)(111) + (1/2)(11\bar{1}) \tag{6}$$

then, $A_r(110)$ is given by

$$A_r(110) = (1/2)A_r(111) + (1/2)A_r(11\bar{1}) = A_r(111) \tag{7}$$

On the other hand, for the unreconstructed (100) fcc surface, as it also involves a compact arrangement, Ar(100) can be expressed in terms of Ar(111) times the geometric factor $\delta = (2/3)(3)^{1/2} = 1.1547$. The value of δ is the ratio between $A_g{}^{uc}{}_{fcc}(100)$, the geometric area of the fcc (100) unit cell, and $A_g{}^{uc}{}_{fcc}(111)$, the geometric area of the fcc (111) unit cell. Thus

$$\delta = \frac{A_g{}^{uc}{}_{fcc}(100)}{A_g{}^{uc}{}_{fcc}(111)} = \frac{0.5a^2}{0.433a^2} = 1.1547 \tag{8}$$

where *a* is the constant translation distance of the unit cell. The correction factor δ plays a significant role in the definition of ExcA

$$\mathrm{ExcA}(100) = \frac{A_r(100)}{A_g(100)} = \delta \tag{9}$$

because it is directly related to the relative surface free energy value, which is considered further on. It should be noted that several noble metals (100) surfaces exhibit the trend to reconstruct,[11] yielding a superlattice that corresponds to the following combination

$$[5{*}20](100) = (111) \tag{10}$$

that is, the reconstructed surface tends to reach the minimum surface free energy of the (111) arrangement.

The foregoing analysis of (111), (100), and (110) fcc surfaces can be presented in terms of a generalized equation for the real area of the pole (*hkl*) as follows

$$\begin{aligned} A_r(hkl) &= n_1A_r(111) + n_2A_r(110) + n_3A_r(100) \\ &= n_1A_r(111) + n_2A_r(111) + (2/3)n_3A_r(111) \\ &= (n_1 + n_2 + (2/3)n_3)A_r(111) \end{aligned} \tag{11}$$

where $n_1 = l$, $n_2 = k - l$, and $n_3 = h - k$ denote the number of microfacets of poles (111), (110), and (100), respectively, and $h \geq k \geq l$. Hence, one can write[3]

$$(hkl) = l(111) + (k - l)(110) + (h - k)(100) \tag{12}$$

and

$$f(N) = n_1 + n_2 + (2/3)n_3 \tag{13}$$

so that

$$\mathrm{ExcA}(hkl) = \frac{f(N)A_r{}^{sc}(111)}{A_g{}^{sc}(hkl)} \geq 1 \tag{14}$$

for any set of (*hkl*) values. Obviously, ExcA = 1 for (*hkl*) = (111).

An Outline of Information Theory

The term information implies a quantitative as well as a qualitative concept which reflects the quantity of information carried by a message and its quality. Then,

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both concepts are to some extent interrelated. The information contained in the message constitutes the basis for developing a model that allows description of the phenomenology of the message's origin. Therefore, the model becomes an intellectual invention interposed between the message and that phenomenon which has produced it.

The information theory attempts to analyze the information contained in a message independent of any conceptual framework. This theory has been formally described by Shannon in 1948.[8c] According to this author, the symbols used in the message must obey certain laws in order to be able to transmit a given quantity of specific information.

The information generator can be mathematically described as a source S emitting a sequence of symbols related to a certain fixed alphabet or code, s_i, obeying a fixed probabilistic law

$$S = \{s_1, s_2, ..., s_q, ...\} \tag{15}$$

where q can be finite or infinite. In the simplest case the symbols of the message become statistically independent. Such an information source is denoted as a *null memory source*, and it can be described by using the alphabet of the source S, and $P(s_1)$, $P(s_2)$, ..., $P(s_q)$, ..., where $P(s_i)$ denotes the appearance probability of each symbol.

The quantity of information $I(s_i)$, associated with the symbol s_i, is defined as

$$I(s_i) = \log\,[P(s_i)]^{-1} \tag{16}$$

and by a judicious choice of the logarithm base, different units for the quantity of information can be established. Thus, for a logarithm of base 2, for $P(s_i) = {}^1/_2$, $I(s_i) = 1$ bit. One bit is the quantity of information resulting from two possible alternatives which are equally probable. Otherwise, for $P(s_i) = e^{-1}$, $I(s_i) = 1$ nat, and for $P(s_i) = 0.1$, $I(s_i) = 1$ hartley, using natural or decimal logarithm, respectively. The latter is used in the following section.

The information theory, which has been traditionally applied to communication networks, electronics, and structural aspects of computational languages, has also been found to constitute an important tool to deal with problems of astronomy, taxonomy, X-ray diffraction, statistical mechanics, and physical chemistry, including crystallography.[12,13]

The information theory provides a definite criterion for building up a unique solution for a probabilistic problem by recourse to the maximum entropy principle which asserts that out of the all available solutions there is only one which maximizes the function S, denoted as the "entropy", which is the sum over all distinguishable emsembles of the integral involving the corresponding distribution functions.[14]

Results and Interpretation

Let us consider a null memory information source situated in the fundamental crystallographic triangle comprised between the [111], [110], and [100] direction poles (Figure 2). The fundamental crystallographic triangle contains all the information about the surface structure and associate properties. It should be noted that the 48 fundamental crystallographic triangles are required to cover completely the surface of a fcc single crystal sphere. In this case the symbols of the message emitted from the source are the (hkl) Miller indices. Then, for this system, according to the precedent definitions, one can write

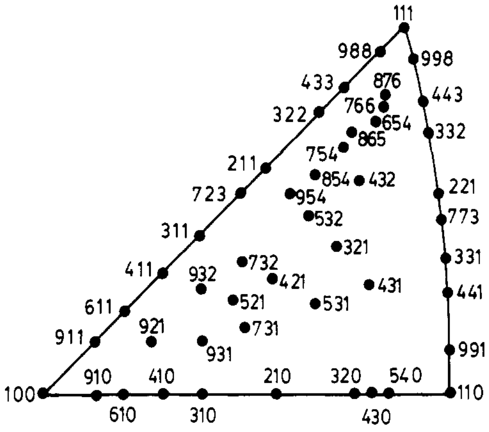

Figure 2. Fundamental fcc crystallographic triangle. The locations of representative poles are included. Adopted from ref 16.

$$S(hkl) = \{(hkl)_1, (hkl)_2, ...\} \tag{17}$$

In the case, one can define $I(hkl)$, the quantity of information, as the excess of area with respect to the geometric area. This definition is justified from the fact that LEED surface crystallography data have shown that under vacuum virtually all clean metal surfaces relax inward. The more open or rough the structure of the surface is, the larger the inward relaxation. The latter is a function of the surface roughness, which is the inverse of the packing density.[15] Therefore, from eq 4 for any (hkl) pole, the result is

$$I(hkl) = \log \mathrm{ExcA}(hkl) = \log \frac{A_r(hkl)}{A_g(hkl)} \tag{18}$$

where $I(hkl)$ is given in Hartley units. According to eq 18, ExcA (hkl) appears as the unnormalized reciprocal probability of the (hkl) pole. The values of ExcA for the microfacets related to the different (hkl) poles of the fcc system are assembled in Table I.

Following the same procedure, energetic information from the fundamental crystallographic triangle can also be derived. Thus, let $\gamma(hkl)$ denote the surface free energy of the (hkl) pole, and let us also define $E_{\mathrm{rel}}(hkl)$, the relative surface energy of the (hkl) pole with respect to the (111) pole, as follows

$$E_{\mathrm{rel}}(hkl) = \gamma(hkl)/\gamma(111) \tag{19}$$

where $E_{\mathrm{rel}}(hkl) \geq 1$ for any (hkl) pole and $E_{\mathrm{rel}}(hkl) = 1$ for $(hkl) = (111)$. Hence, $I'(hkl)$, the quantity of information related to the relative surface free energy of the (hkl) pole, is given by

$$I'(hkl) = \log \frac{\gamma(hkl)}{\gamma(111)} \tag{20}$$

Let us now consider the ExcA values given in Table I, and the relative surface free energy of the different poles

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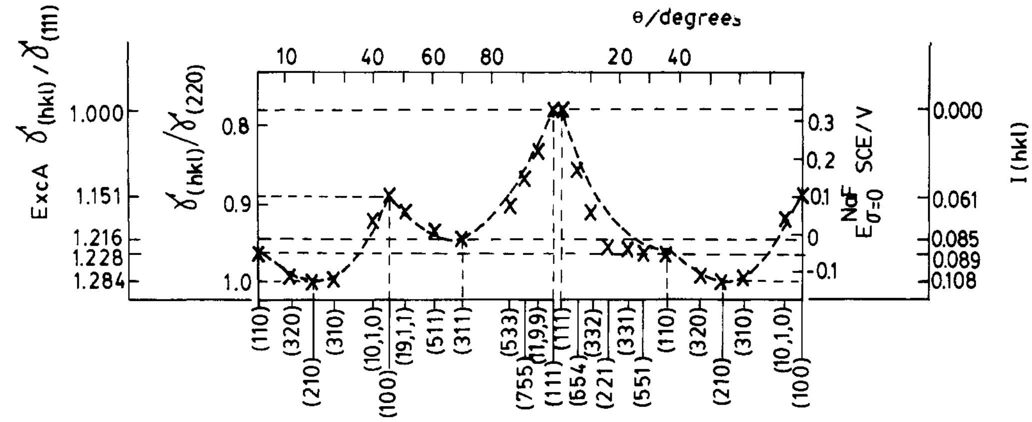

Figure 3. Relative surface free energy of gold and its dependence on crystallographic orientation, according to Hamelin et al.[9b] The y axis displays the $\gamma(hkl)/\gamma(111)$, ExcA(hkl), and $I(hkl)$ scales. $E^{NaF}_{\sigma=0}$ denotes the potential of zero charge in 0.1 M NaF at 298 K.

Table I. Values of ExcA(*hkl*) and *I*(*hkl*) for Different fcc (*hkl*) Surfaces

poles	microfacets			distance from poles, deg			ExcA-	
(hkl)	100	110	111	100	110	111	(hkl)	$I(hkl)$
(111)	0	0	1	54.7	35.2	0	1	0
(988)	1	0	8	51.4	33.7	3.23	1.03833	1.63395E–02
(988)	0	1	8	51.4	33.7	3.23	1.07827	3.27297E–02
(988)	0	0	9	51.4	33.7	3.23	1.07827	3.27298E–02
(433)	1	0	3	46.6	31.9	8.04	1.08916	3.70924E–02
(322)	1	0	2	43.3	30.9	11.4	1.12022	4.93049E–02
(211)	1	0	1	35.2	30	19.4	1.17851	7.13335E–02
(733)	4	0	3	31.2	30.2	23.5	1.19908	7.88507E–02
(311)	2	0	1	25.2	31.4	29.4	1.21854	8.58408E–02
(411)	3	0	1	19.4	33.5	35.2	1.22474	8.80454E–02
(611)	5	0	1	13.2	36.5	41.4	1.21756	8.54906E–02
(911)	8	0	1	8.93	39.0	45.8	1.20407	8.06536E–02
(100)	1	0	0	0	45	54.7	1.15469	6.24691E–02
(910)	8	1	0	6.34	38.6	50.3	1.21139	8.32854E–02
(610)	5	1	0	9.46	35.5	48.3	1.2339	9.12812E–02
(410)	3	1	0	14.0	30.9	45.5	1.26025	0.100457
(310)	2	1	0	18.4	26.5	43.0	1.27801	0.106536
(210)	1	1	0	26.5	18.4	39.2	1.29099	0.110923
(320)	1	2	0	33.6	11.3	36.8	1.28102	0.107556
(430)	1	3	0	36.8	8.13	36.0	1.27016	0.10386
(540)	1	4	0	38.6	6.34	35.7	1.26233	0.101173
(110)	0	1	0	45	0	35.2	1.22474	8.80438E–02
(991)	0	8	1	45.1	4.49	30.7	1.22097	8.67077E–02
(441)	0	3	1	45.8	10.0	25.2	1.20604	8.13623E–02
(331)	0	2	1	46.5	13.2	22.0	1.19207	7.63038E–02
(773)	0	4	3	47.4	16.8	18.4	1.1721	6.89658E–02
(221)	0	1	1	48.1	19.4	15.7	1.15469	6.24685E–02
(332)	0	1	2	50.2	25.2	10.0	1.10782	4.44698E–02
(443)	0	1	3	51.3	27.9	7.32	1.082	3.42282E–02
(998)	0	1	8	53.2	32.1	3.11	1.03692	1.57486E–02
(111)	0	0	1	54.7	35.2	0	1	0
(321)	1	1	1	36.6	19.1	22.2	1.23442	9.14645E–02
(432)	1	1	2	42.0	23.1	15.2	1.17932	7.16324E–02
(532)	2	1	2	35.7	23.4	20.5	1.21756	8.54903E–02
(421)	2	1	1	29.2	22.2	28.1	1.25987	0.100329
(531)	2	2	1	32.3	17.0	28.5	1.26866	0.103347
(431)	1	2	1	38.3	13.8	25.0	1.2455	9.53443E–02

of a fcc metal such as gold.[9] The comparison of these data (see Figures 3 and 4) show that $E_{rel}(hkl)$ and ExcA(hkl) exhibit the same dependence with respect to the pole's indices. Therefore, for any (hkl) pole

$$I(hkl) - I'(hkl) = \Delta I(hkl) = 0 \qquad (21)$$

This means that the difference in terms of information between the relative surface free energy and the geometrical structure of the surface is zero for any crystalline pole.

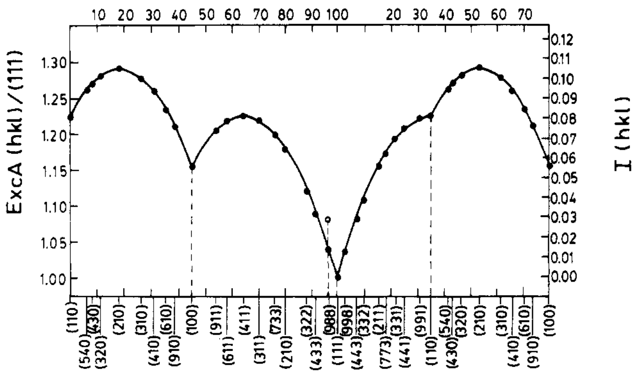

Figure 4. Dependences of ExcA(hkl) and $I(hkl)$ on crystallographic orientation. Data corresponds to zones between [110]–[100], [100]–[111], and [111]–[110] directions. The (988) = 8*(111) + 1*(111) face (open circle, O) displays an excess of geometric area and relative surface free energy larger than the (988) = 8*(111) + 1*(100) microfacets configuration.

Table II. Values of *I*(988) for Different Microfacet Composition

pole		microfacets	$I(988)$
(988)	=	8*(111) + 1*(100)	0.0163395
(988)	=	8*(111) + 1*(110)	0.0327297
(988)	=	8*(111) + 1*(111)	0.0327298

It should be noted that for the (hkl) pole, according to eq 16 and the maximum entropy principle,[13,14] $I(hkl)$ provides information about the most probable relative geometric composition of fundamental microfacets, i.e. that involving the smallest excess in geometry. This fact is illustrated for the (988) pole in Table II and in Figure 4. In this case, the first geometric composition corresponds to the minimum of either ExcA(988) or E_{rel}(988) value.

On the other hand, from eq 18 we obtain

$$I(hkl) = \log A_r(hkl) - \log A_g(hkl) = I_r(hkl) - I_g(hkl) \qquad (22)$$

where $I_r(hkl) = \log A_r(hkl)$, and $I_g(hkl) = \log A_g(hkl)$. Then from eq 21 one obtains

$$I_r(hkl) - I_g(hkl) - I'(hkl) = 0 \qquad (23)$$

Similarly, one can write

$$I'(hkl) = \log \gamma(hkl) - \log \gamma(111) = I''(hkl) - I''(111) \qquad (24)$$

where $I''(hkl) = \log \gamma(hkl)$, and $I''(111) = \log \gamma(111)$. Thus, from eqs 21, 22, and 24, one obtains

$$I_r(hkl) - I_g(hkl) - I''(hkl) + I''(111) = 0 \qquad (25)$$

Let us consider now that

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$$\log A_r(111) = K_1$$

$$\log \gamma(111) = I''(111) = K_2 \tag{26}$$

so that

$$\begin{aligned} I_r(hkl) &= \log f(N)\, A_r(111) \\ &= \log f(N) + \log A_r(111) = I_r(N) + K_1 \end{aligned} \tag{27}$$

where

$$I_r(N) = \log f(N) \tag{28}$$

Then, from eqs 25, 26, and 28, we obtain

$$I''(hkl) = I_r(N) - I_g(hkl) + K_1 + K_2 \tag{29}$$

where the terms $I_r(N)$, $I_g(hkl)$, and K_1 in eq 29 are all known. According to eq 29 the information associated with the surface free energy of the (*hkl*) pole is directly related to the geometry of the surface (the constant K_2 value poses no problem here). Then, the ratio between the geometric area of the (*hkl*) pole and Ar(111) furnishes the number of (111) unit cells involved in that surface. The term $f(N)$ corresponds to a correction factor indicating how far the surface structure of the (*hkl*) pole is from that of an ideal geometric surface with a (111) atomic arrangement. Therefore, from information theory it is possible to conclude that the relative surface free energy at each crystallographic pole is directly related to the real surface structure extracted from an ideal geometric area with (111) atomic array.

Finally, the present approach allows for the possibility of predicting the surface free energy of any (*hkl*) pole located in the fundamental crystallographic triangle if one knows just the value of a single pole. The corresponding equations are

$$\gamma(hkl)_1 \frac{A_g(hkl)_1}{f(N)_1} = \gamma(hkl)_2 \frac{A_g(hkl)_2}{f(N)_2} \tag{30}$$

and, by taking the (111) pole as reference, the result is

$$\gamma(hkl) = \frac{f(N)\, A_r(111)}{A_g(hkl)} \gamma(111) \tag{31}$$

Summing up one can assert that from the physical and chemical standpoints, any surface of a fcc crystal exists as a combination of only (111), (100), and (110) microfacets, and depending on the combinations of these microfacets, a certain concentration of kinks, corners, and border of terraces is accomplished. Then, by selection of the most dense atomic array the entire crystallographic surface can be described including the corresponding relative surface energy of each kind of surface site. The same approach is applicable for other crystalline structures such as simple cubic, bcc, and tetragonal structures.[17]

The present results can be satisfactorily compared to the scarce experimental data existing for metals such as gold, nickel, and lead[7b,7g,9b,9g,17] and are applicable at any temperature compatible with the corresponding crystalline state, provided that the thermal expansion of the lattice be considered.

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