Broken-bond rule for the surface energies of noble metals

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Abstract. – Using two different full-potential *ab initio* techniques we introduce a simple rule based on the number of broken first-neighbour bonds to determine the surface energies of the three noble metals Cu, Ag and Au. When one bond is broken, the rearrangement of the electronic charge for these metals does not practically lead to a change of the remaining bonds. Thus the energy needed to break a bond is independent of the surface orientation, so that the surface energy is in good approximation proportional to the number of broken nearest-neighbour bonds.

The surface energy represents a fundamental material property. It is given by half the energy needed to cut a given crystal into two half crystals. As such the surface energy naturally depends on the strength of the bonding and on the orientation of the surface plane. A variety of experimental techniques have been developed to measure the surface energy [1], but all measurements are performed at high temperatures where surfaces are badly defined. The most comprehensive data stem from surface tension measurements in the liquid phase and by extrapolating the resulting orientation-averaged surface free energies to zero temperature [2,3]. The knowledge of the orientation-dependence of the surface energies is necessary to predict the equilibrium shape of a mesoscopic crystal and to study a series of important phenomena in materials science like crystal growth, creation of steps and kinks on surfaces, growth, stability and alloy formation of thin films or surface-melting faceting.

The lack of experimental data can be replaced by *ab initio* calculations. Due to the development of the density functional theory during the last two decades, *ab initio* methods are able to calculate many physical properties with unprecedented accuracy. Methfessel and collaborators [4] studied the trends in surface energy, work function and relaxation for the whole series of bcc and fcc 4*d* transition metals, using a full-potential (FP) version of the linear muffin-tin orbital (LMTO) method in conjunction with the local density approximation (LDA) to the exchange-correlation potential. In the same spirit Skriver and co-workers have used a LMTO technique to calculate the surface energy and the work function of most of

the elemental metals [5]. Recently, Vitos and collaborators using their full-charge Green's function LMTO technique in the atomic sphere approximation (ASA) in conjunction with the generalized gradient approximation (GGA) elaborated a very useful database that contains the low-index surface energies for 60 metals in the periodic table [6]. Later the authors fitted a pair potential model to their calculated surface energies by taking interactions up to the third or fourth neighbours into account and used the resulting interaction energies to estimate the energy needed for the creation of steps and kinks on the low-index surfaces [7]. Also many semi-empirical [8] and tight-binding [9] studies exist.

In this contribution we show, using precise *ab initio* techniques, that irrespective of the orientation, the surface energies of Cu, Ag, and Au are simply proportional to the number of broken bonds between a surface atom and its nearest neighbours; for all surface orientations, except the (111) and (100), one has to take into account in the total number of broken bonds also the nearest bonds lost by the subsurface atoms. We demonstrate this in calculations for the low-index surfaces (111), (100), and (110) as well as for four vicinal surfaces. The resulting anisotropy ratios, *i.e.* the ratio of the surface energy for a given surface orientation with respect to the (111) surface energy, practically always agree with the "ideal" broken-bond ratios, *i.e.* the number of broken bonds between nearest neighbours for this surface with respect to the (111) surface. This finding implies that i) for the noble-metal surfaces the interaction between an atom and its second and further neighbours is very small and, that ii) the charge rearrangement caused by the bond breaking does not significantly change the effective bond strength, in the sense that the cutting of the next bond requires the same energy. Therefore, the energy needed to break a bond does not depend on the orientation, so that for each noble metal the surface energy for only one orientation is needed. We show that highly accurate calculations are compulsory to obtain these results.

To perform the calculations, we have used both the full-potential screened Korringa-Kohn-Rostoker (FKKR) method [10], and the full-potential linearized augmented plane wave (FLAPW) method [11] as implemented in the FLEUR code in conjunction with LDA. All calculations have been performed using the experimental lattice parameters: 3.61 Å for Cu, 4.09 Å for Ag, and 4.08 Å for Au. For the FKKR an angular momentum cut-off of $\ell_{\max} = 3$ for the wave functions and of $\ell_{\max} = 6$ for the multipole expansion of the charge density and the potential has been used. To calculate the charge density, we integrated the Green's function along a contour on the complex energy plane, which extends from the bottom of the valence band up to the Fermi level [12]. Due to the smooth behaviour of the Green's functions for complex energies, only few energy points are needed; 27 points have been used. A very large number of $\boldsymbol{k}_\parallel$ points in the irreducible part of the two-dimensional Brillouin zone (2D-IBZ) have been used for the decisive complex energies close to the Fermi level (~ 300 points for the (111) and up to ~ 800 points for the (110) surface). The surface energy γ for a N-layer slab embedded in semi-infinite vacuum is given by $\gamma = (E_{\mathrm{s}} - N E_{\mathrm{b}})/2$, where E_{s} is the total energy of the slab and E_{b} is the energy per atom in the bulk crystal; note that for fcc crystals N is also the number of inequivalent atoms in the slab. To be consistent for all the cases we used as E_{b} the energy per atom of the central layer of the slab. We have converged the number of metal layers so that the surface energies are converged within 0.01 eV; we used 12 layers for the (111), 14 for the (100), and 18 for the (110) surface. In FLAPW we calculated the surface energies from the total energies of two films of different thickness: for the (111) surface 13- and 11-layer films were used, for the (100) orientation 15 and 13 layers and for the (110) surfaces 19- and 17-layer films were calculated. A basis set of 80–90 augmented plane waves per atom and 425, 325, and 408 $\boldsymbol{k}_\parallel$ points were used in the 2D-IBZ of the (111), (100), and (110) surface, respectively.

In table I we collect the scalar-relativistically calculated surface energies within both FKKR

Table I – *Scalar-relativistic surface energies for the three noble metals using both* FKKR *and* FLAPW *compared with previous* LMTO *results from ref.* [6]. *All results are given in* eV/(surface atom).

γ (eV)	Cu			Ag			Au		
	FKKR	FLAPW	LMTO	FKKR	FLAPW	LMTO	FKKR	FLAPW	LMTO
(111)	0.67	0.62	0.71	0.57	0.51	0.55	0.62	0.50	0.61
(100)	0.87	0.81	0.91	0.73	0.65	0.65	0.84	0.68	0.90
(110)	1.33	1.25	1.32	1.11	1.00	0.95	1.28	1.01	1.32

and FLAPW and we compare them with the values obtained by the LMTO in ref. [6]. For Cu and Ag, the absolute values calculated with all three methods agree nicely. For Au both FKKR and LMTO predict that the surface energies are very close to the Cu values, whereas FLAPW predicts similar surface energies for Au and Ag in agreement with previous FLAPW results, 0.66 eV for Ag(100) and 0.67 eV for Au(100) [13]. A pseudopotential technique, on the other hand, shows the FKKR behavior: $\gamma = 0.58$ eV for Ag(100) and 0.70 eV for Au(100) [14].

As central result we present in fig. 1 the anisotropy ratios. We remark that both FKKR and FLAPW calculations produce practically the same anisotropy ratios for all the noble metals, while previous LMTO [6] and FP-LMTO [4] calculations gave anisotropy ratios that deviate considerably from the present results, especially for Ag. Notably, both FKKR and FLAPW give results that are very close to 4/3 for the $\gamma_{(100)}/\gamma_{(111)}$ ratio and close to 6/3 for the $\gamma_{(110)}/\gamma_{(111)}$ ratio. These are exactly the ratios between the number of first-neighbour broken bonds for these surfaces. This finding can lead to two independent conclusions. Firstly, the broken bonds between a surface or a subsurface atom and its second and further neighbours give a negligible contribution to the surface energy. Secondly, the energy needed to break a bond is the same for any surface orientation. This is surprising, since one expects that breaking a bond in a surface leads to a rearrangement of the electronic charge resulting in a strengthening of the remaining bonds, so that one needs more energy to break them. But as we see from our data and will discuss below this bond strengthening, due to the reduction of
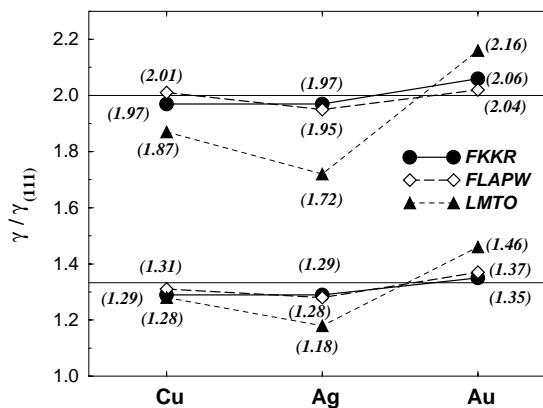

Fig. 1 – The anisotropy ratios for the three noble metals, $\gamma_{(100)}/\gamma_{(111)}$ and $\gamma_{(110)}/\gamma_{(111)}$, using both FKKR and FLAPW. The LMTO results are from ref. [6]. FP-LMTO calculations [4] for Ag produced similar results to those in ref. [6]. Surface energies are calculated in eV/(surface atom). The two straight solid lines represent the ideal first-neighbour broken-bond ratios: 4/3 for (100) and 6/3 = 2 for (110).

TABLE II – FKKR *scalar-relativistic surface energies given in* eV*/(surface atom) for the seven more close-packed surfaces together with the anisotropy ratios in parenthesis. d is the distance between two successive layers and a the lattice constant.* BB *is the number of first-neighbour broken bonds.*

	Cu	Ag	Au	d/a	BB
(111)	0.675	0.566	0.623	0.5774	3
(100)	(1.29) 0.874	(1.29) 0.728	(1.35) 0.842	0.5000	4
(110)	(1.97) 1.327	(1.97) 1.113	(2.06) 1.284	0.3535	6
(311)	(2.32) 1.564	(2.31) 1.309	(2.36) 1.468	0.3015	7
(331)	(2.99) 2.016	(2.97) 1.680	(3.05) 1.900	0.2294	9
(210)	(3.32) 2.240	(3.29) 1.864	(3.45) 2.149	0.2236	10
(211)	(3.34) 2.255	(3.32) 1.877	(3.39) 2.110	0.2041	10

neighbours, is negligible for the noble metals. To examine whether this finding also holds for the vicinal surfaces we used the FKKR method and calculated the surface energies and the anisotropy ratios for the next four more close-packed surfaces (see table II). The number of layers used in the calculations is 21 for the (113), 30 for the (331) and the (210), and finally 32 for the (112) surface. For all these surfaces the anisotropy ratios are close to the ratios given by the broken first-neighbour bonds. Au shows slightly larger deviations from these ideal ratios compared to Ag and Cu, which attends 3.6% in the case of the (210) surface. So the free energy $\gamma_{(hkl)}$ in eV/(surface atom) needed to create any surface with a Miller index (hkl) reduces just to the product of $\gamma_{(111)}$ and the ratio of the first-neighbour broken bonds, $N_{(hkl)}$, and $N_{(111)} = 3$:

$$\gamma_{(hkl)} = \frac{N_{(hkl)}}{3}\gamma_{(111)}. \tag{1}$$

$N_{(hkl)}$ can be easily obtained for any fcc surface [15]:

$$N_{(hkl)} = \begin{cases} 2h + k, & h, k, l \text{ odd}, \\ 4h + 2k, & \text{otherwise}, \end{cases} \qquad h \geq k \geq l. \tag{2}$$

Given the disagreement of our anisotropy ratios with the published results of [4,6], we have performed extensive tests regarding the accuracy and consistency of our calculations. With the FKKR method we have performed calculations also for the somewhat smaller LDA lattice constants. Moreover, we have used both the full-potential KKR code as well as the KKR code with ASA potentials and full-charge density. While the absolute values of the surface energies change, the anisotropy ratios are extremely stable. With the FLAPW code we have performed additional calculations with the GGA and have estimated the effect of spin-orbit coupling for Au. Whereas the latter tends to increase the absolute values of the surface energies, GGA lowers the absolute values, but again we obtained anisotropy ratios in very good agreement with the broken-bond rule.

In the course of these checks we identified the most probable reason for the failure of previous calculations. In fig. 2 we present the convergence of the surface energy of Ag with respect to the square root of the number of $\boldsymbol{k}_\parallel$-points used to perform integrations in the full first Brillouin zone, as for this system the difference between our present results and the ones in refs. [4] and [6] is the largest. The (111) surface energy is very sensitive to the number of $\boldsymbol{k}_\parallel$-points, while this is not the case for the (100) surface; the (110) surface behaves similarly to the (100) surface. This sensitivity might arise from a surface state centered at the $\bar{\Gamma}$ point, which all three noble metals possess and which requires a very dense $\boldsymbol{k}_\parallel$-grid to account for it. This is in line with the observation that the largest deviations are obtained for Ag, for which

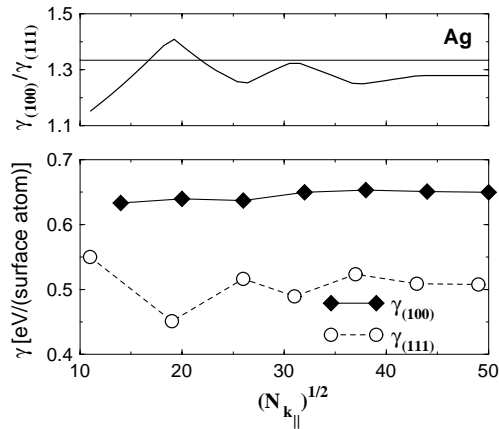Fig. 2 – Convergence of the surface energies $\gamma(111)$ and $\gamma(100)$ with the square root of the number of $\boldsymbol{k}_\parallel$-points in the full first 2D Brillouin zone using the FLAPW method. The upper panel shows the resulting anisotropy ratio $\gamma_{(100)}/\gamma_{(111)}$ together with the ideal value of 4/3.

this surface state is closest to the Fermi level. In the upper panel of fig. 2 we show the ratio between the (100) and the (111) surface energies, which follows the oscillations of the $\gamma_{(111)}$ energy. In refs. [4] and [6] the square root of the number of $\boldsymbol{k}_\parallel$-points in the full Brillouin zone used is about 9 and 13, respectively. For these numbers of $\boldsymbol{k}_\parallel$-points the FLAPW method gives a ratio which is 1.15–1.20, very close to the ratio of 1.18 obtained by both LMTO methods. Thus the non-convergence of the surface energies with the number of $\boldsymbol{k}_\parallel$-points is the reason for the differences seen in fig. 1.

In the following we discuss the range of validity and the limits of the broken-bond rule. Firstly, we note that we obtain similar anisotropy results for the anisotropy ratios of the Rh, Ir, Pd, and Pt surfaces, although with slightly larger deviations (about ±3–5%) from the ideal ratios [16]. On the other hand, the broken-bond rule seems to contradict basic knowledge about the electronic structure, since the binding energy does not in general scale linearly with the coordination number C. In fact, tight-binding models with nearest-neighbour interaction show that the binding energies, being determined mainly by the bandwidth, scale as $\sqrt{C}$ [17], leaving no room for a pairwise decomposition of the total energy. Nevertheless, in the region of high coordination numbers the square root can be linearised, *i.e.* $\sqrt{C} - \sqrt{C_0} \simeq \frac{1}{2}\frac{C-C_0}{\sqrt{C_0}}$, where C_0 is the bulk coordination. In this linear approximation the bond relaxation is neglected and the surface anisotropy energy scales with the number $C_0 - C$ of broken bonds. While these tight-binding models give a simple explanation of the calculated anisotropy ratios of the fcc transition metals [16], they cannot be applied to noble or *sp* metals. Nevertheless very extensive *ab initio* calculations by Robertson *et al.* for Al [18] and Methfessel *et al.* for Ag [4], both studying a variety of systems with widely different geometries and coordinations, show that the coordination dependence of the total energy is on the average well described by $\sqrt{C}$, so that also here the same arguments as above can be applied. Robertson *et al.* [18] have also shown that for Al a pair-potential model can describe well the cohesive energy over a wide range of structures, using an effective coordination number, C_{eff}, defined as the sum of the influence of the neighbours. For the noble metals our results indicate that C_{eff} is practically the number of nearest neighbours. Thus the broken-bond rule for the surfaces of the noble models is not in contradiction to the accepted understanding of the electronic structure. However the accuracy with which this simple rule describes the surface anisotropy

of these metals, even for rough surfaces, is a very unexpected and welcome feature.

Finally we studied the effect of lattice relaxations on the calculated surface energies using the FLAPW and allowing the three first layers to relax. Although the calculated surface energies change, the effect on the anisotropy ratios is much smaller. For Cu, relaxations reduce γ by 0.8%, 0.7% and 2.6% for the (111), (100) and (110) surfaces, respectively. The (100)/(111) anisotropy ratio stayed unchanged by the relaxations while the relaxed (110)/(111) ratio was 1.98 compared to the value of 2.01 for the unrelaxed structure. For Ag, the surface energy was reduced by 0.1%, 0.7% and 1.8% for the three low-index surfaces, respectively. The new anisotropy ratios are 1.27 and 1.93, slightly smaller than the original values of 1.28 and 1.95. Finally for Au, relaxations reduce the surface energies by 0.2% and 0.8% for the (111) and (100) surfaces and the anisotropy ratio becomes 1.35, slightly smaller than the value, 1.37, for the unrelaxed structure. The Au(110) surface shows a large relaxation; the distance between the first and the second layer (Δd_{12}) is reduced by 13.8%, the Δd_{23} is expanded by 6.9% and finally the Δd_{34} is also reduced by 3.2%. The surface energy is reduced by 6.5% and the anisotropy ratio is now 1.89 compared to the 2.04 for the unrelaxed structure, but remains close to the broken-bond rule value of 2.0. So even large relaxations have a rather small impact on the calculated anisotropy ratios which are reasonably described by the broken-bond rule.

Several experiments at high temperatures have been carried out mainly on gold crystallites [19] to determine the γ-anisotropy, but their interpretation is difficult. Entropy terms, describing the lower vibrational frequencies of the atoms at the surface as compared to the bulk, the formation of kinks and finally the creation of holes and pillboxes at the low-index surfaces, have to be added to the total free energy. Also at such high temperatures the surface-melting faceting [20], *i.e.* the break-down of a vicinal surface in a dry and a melted one, plays a predominant role. Recently, Bonzel and Edmundts [21] have shown that analyzing the equilibrium shape of crystallites at various temperatures by scanning tunneling microscopy can yield absolute values of the surface and step energies *vs.* temperature, but this technique has not been applied yet. The easy calculation of the surface energies for the noble metals as a product of the $\gamma_{(111)}$ and the number of first-neighbour broken bonds can be used to develop more complicated models describing the above phenomena. There are also other important applications in materials science like the growth and stability of a thin film or the growth of a crystal surface where the knowledge of the absolute values and the anisotropy of the surface energies is crucial. Here we should also note that, although for the fcc metals the broken-bond rule is well obeyed, the tiny deviations from these ideal values are important for the stability of the (110) surface, being reconstructed for Au, but not for Cu and Ag [22].

In this letter we have shown for different surface orientations that the surface energies of the noble metals accurately scale with the number of the broken nearest-neighbour bonds, so that the calculated anisotropy ratios always agree well with the ideal broken-bond ratios. We have demonstrated this in FKKR and FLAPW calculations for seven low-index and vicinal surfaces of Cu, Ag and Au. We believe that the simplicity of these results is of great interest for a variety of problems in materials science like step, kink, and alloy formation, crystal growth, surface-melting faceting or the shape of small crystallites on a catalyst.

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