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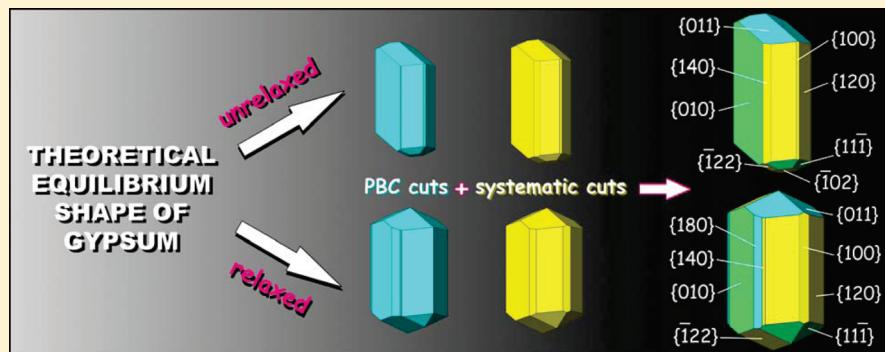
# Theoretical Equilibrium Morphology of Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). 2. The Stepped Faces of the Main [001] Zone

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## ABSTRACT:



The athermal equilibrium shape (ES) of gypsum crystal is calculated, in a vacuum, in the zone interval of the stepped  $\{1k0\}$  forms ( $3 \leq k \leq 8$ ). The surface profiles are obtained by applying either the Hartman—Perdok method of the periodic bond chains (PBC) or the method of systematic cuts (SC) generated under the only conditions of stoichiometry, electroneutrality, and annihilation of the dipole moment perpendicular to each  $d_{1k0}$  slice. The specific surface energy values  $\gamma_{1k0}$  have been calculated, both for ideal and relaxed surface profiles, using a semiempirical potential function proposed by Adam. From calculations, it follows that the ES in the [001] zone is characterized not only by the well-known  $\{120\}$  and  $\{010\}$  flat forms and by the stepped  $\{100\}$  pinacoid but also by the  $\{140\}$  and  $\{180\}$  stepped forms. Further, following the PBC method, the stepped  $\{130\}$  and  $\{170\}$  forms also should enter the ES. Finally, an unambiguous analogy arises between our results and the systematic presence of the  $\{1k0\}$  faces on the giant crystals found in the Naica mine, whose growth occurs very near the equilibrium.

## 1. INTRODUCTION

In a recent work,<sup>1</sup> it has been shown that the theoretical equilibrium shape of gypsum is deeply modified with respect to the historical ones calculated by Simon and Bienfait<sup>2a,b</sup> and by Heijnen and Hartman.<sup>3</sup> As a matter of fact

- The  $\{120\}$  prism now competes with the traditionally dominant  $\{010\}$  pinacoid and then the equilibrium shape changes from tabular  $\{010\}$  to prismatic [001];
- The  $\{011\}$  and  $\{\bar{1}11\}$  prisms maintain their morphological importance;
- New stepped forms,  $\{100\}$  and  $\{\bar{1}22\}$ , along with the kinked  $\{\bar{1}02\}$  pinacoid, compose the equilibrium shape as well.

These relevant changes are due to the following reasons:

- The quality of the force field used: we adopted in our calculation the semiempirical potential functions calibrated by Adam<sup>4</sup> on selected properties of gypsum, instead of the Coulomb potentials based on a set of formal charges, used in pioneering works<sup>2,3</sup> on equilibrium and growth morphology of gypsum.
- The values of the athermal specific surface energies ( $\gamma_{hkl}$ ) were calculated by two different methods of choosing the surface configurations of the  $\{hkl\}$  forms:

- Following the first, surface profiles were drawn respecting the rigorous constraints imposed by the PBC generation (Hartman—Perdok method<sup>5</sup>) and the consequent character of the  $\{hkl\}$  forms;
- Following the second way (called onward the method of systematic cuts, SC), that is, cutting the bulk with crystallographic planes of suitable orientation, the surface profiles were generated under the only conditions of the electroneutrality, conservation of the stoichiometric ratio, and the annihilation of the dipole moment perpendicular to each  $d_{hkl}$  slice.

Energies of both unrelaxed and relaxed surface profiles, for every  $\{hkl\}$  forms, were reported for the sake of comparison and discussion.

Further, we showed that PBC and SC methods do complement each other in predicting surface profiles, by increasing the number of surface configurations for a given  $\{hkl\}$  form, which is of great importance in the quest for the global minimum of the

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surface energy and when dealing with either solvent or impurity adsorption. In fact, one cannot forget that surface adsorption can change the relative stability of the different configurations of the same face, and surface profiles favored in a vacuum could not form the most stable interface in the presence of the adsorbed phase.

In this paper, we will deepen our investigation on the theoretical equilibrium morphology of gypsum by analyzing the development of the forms lying on the  $\{001\}$  zone, that is, the main structural and morphological zone of the crystal, when the reference frame is that by De Jong and Bouman,<sup>20</sup>  $\{010\}$  and  $\{120\}$ , which are the main F forms, will no longer be considered since they have already been evaluated in detail in our just mentioned paper. The stepped  $\{100\}$  form will be extensively treated in a forthcoming paper on the structure and genetic mechanisms of the 100 most frequently observed growth twin.

Here we will deal with the  $\{1k0\}$  forms occurring in between the  $\{120\}$  and the  $\{010\}$  forms. This kind of face is very peculiar since it, although stepped, appears in 14% of the natural gypsum crystals, as we deduced from the Goldschmidt Atlas,<sup>6</sup> and also occurs in the giant crystals grown very close to the equilibrium<sup>7,8</sup> in the Naica mine.

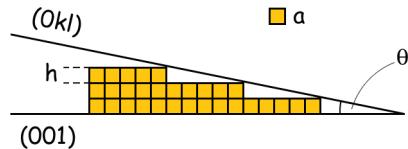
At last, there is an intriguing reason to study the extended sequence of  $\{1k0\}$  forms of gypsum, that is, to determine if they might enter or not in the equilibrium shape of the crystal. As a matter of fact, Hartman<sup>9</sup> stated that for nonionic crystals the equilibrium shape may also exhibit S and K faces while the equilibrium shape of ionic crystals shows no S faces. Recently, we showed that this statement is not so general and it can be violated for a crystal with ionic bonds such as calcite ( $\text{CaCO}_3$ ), where both the kinked  $\{0001\}$ <sup>10</sup> and the stepped  $\{10\bar{1}0\}$ <sup>11</sup> forms enter the athermal equilibrium shape, as a consequence of the relaxation of their surface profiles. Here we will show that, using a more performing potential and duly considering surface relaxation, the  $\{140\}$  and  $\{180\}$  forms can compose the equilibrium shape of gypsum.

## 2. EVALUATING THE SURFACE ENERGY FROM THE SURFACE PROFILES OF STEPPED FACES

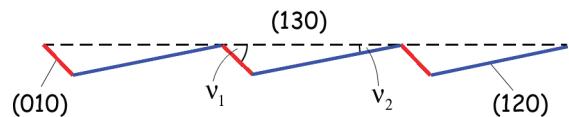
The equilibrium shape of a crystal only depends on the ratios among the specific surface free energies ( $\gamma_{hkl}$ ) of the different  $\{hkl\}$  forms of the crystal as it follows from the Gibbs-Wulff's theorem.<sup>12</sup> A face having F character hardly shows a unique surface configuration, as was demonstrated by Hartman<sup>13</sup> in general terms and by ourselves, in the case of gypsum.<sup>1</sup> Hence, one is concerned to find the lowest among the possible  $\gamma_{hkl}$  values in order to determine the polyhedron of minimum surface energy. The same consideration applies even more so to a S face, since all its possible surface profiles can be built by domains having the profiles of the two F faces adjacent to it.

On the basis of this idea, several approximate approaches were proposed to evaluate the specific energy of a surface profile which deviates from that of an ideal F face.

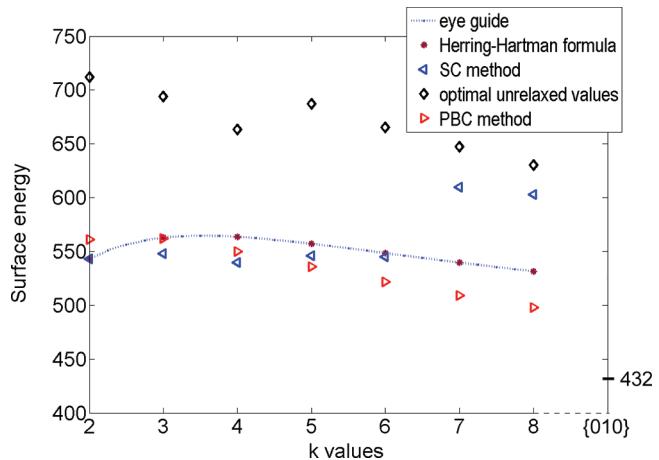
**2.1. Vicinal Faces.** This term usually indicates<sup>14</sup> a face with less than about  $10^\circ$  deviation from a F face. A good example may be represented by a face growing by spiral mechanism where the Burgers' vectors generate either monomolecular steps or high macrosteps. This kind of face may be well described by the terrace–ledge–kink (TLK) model. Figure 1 represents the schematic structure of a  $\{0kl\}$  vicinal face, with the reference  $\{001\}$  ideal face viewed along the  $[100]$  direction.



**Figure 1.** Profile of a  $\{0kl\}$  vicinal face viewed along the  $[100]$  direction. The angle formed with the reference  $\{001\}$  F face is  $\theta$ , while  $p = \tan \theta$  is the slope of the vicinal face. The height of the step running along the  $[100]$  direction is  $h = (ma) \tan \theta$ , where  $(ma)$  represents the length of the terrace.



**Figure 2.** Surface profile of the S face (130) of gypsum crystal. The simplest model consists of alternating elements of the F faces (120) and (010).



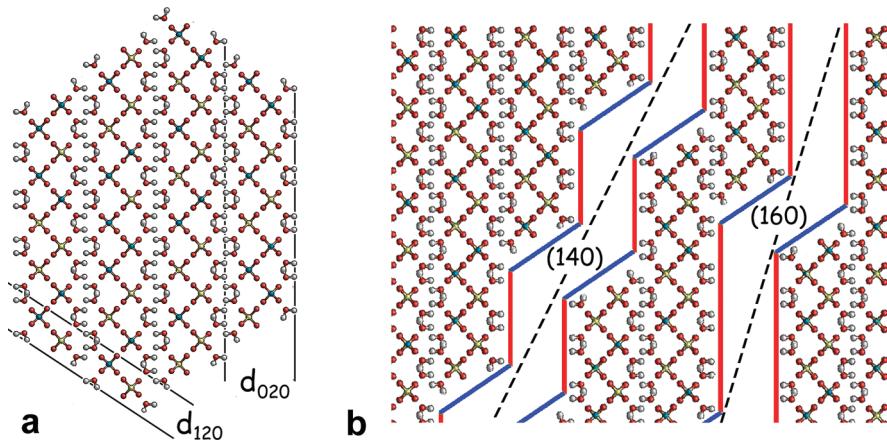
**Figure 3.** Surface energy of the S faces (1k0) of gypsum crystal. The dotted curve is calculated by eqs 2 and 3. The reference frame is that by De Jong and Bouman.<sup>20</sup>

If we know  $\rho_{[100]}$ , the specific edge free energy of the step  $[100]$ , and  $\gamma_{001}$ , the specific surface free energy of the  $\{001\}$  face, the relationship introduced by Yamada<sup>15</sup> allows one to obtain an approximation of the surface energy of a vicinal face:

$$\gamma(\theta) = \gamma_{001} \cos \theta + \left( \frac{\rho_{[100]}}{h} \sin \theta \right) \quad (1)$$

From purely geometrical considerations, one can imagine that the surface energy  $\gamma(\theta)$  due to the slope is made by two contributions:

- The *main* contribution can be thought of as the projection of the  $\gamma_{001}$  on the direction representing the vicinal face;
- The *smaller* contribution is due to the projection on the same direction of the surface energy of the step (i.e., the edge energy  $\rho_{[100]}$  divided by the thickness,  $h$ , of the step). In that regard, it is worth remembering that the  $(\rho/h)$  value can hardly coincide with the  $\gamma_\infty$  value of the corresponding infinite face.



**Figure 4.** (a) The unrelaxed profiles of the F faces (120) and (010) of gypsum built by the PBC method. (b) The simplest way to compose the stepped profiles of the faces (140) and (160), starting from elementary segments of the (120) and (010) faces.

Hence, the Yamada approximation can be successfully applied when the \$\theta\$ angle is so small that the vicinal face preserves the F character of its reference ideal face. This is not the case of the \$\{1k0\}\$ forms of gypsum where the slope of the S face closest to the (120) F face, that is, the (130) face, reaches \$12^\circ\$, while that of the S face closest to the (010) F face, that is, the (1.10.0) face, is \$17^\circ\$.

**2.2. A Stepped Face Lying in between Two F Faces.** 2.2.1. *The Hartman's and Herring's Approximations.* Let us consider, as a useful example, the case of the (130) face of gypsum. This is certainly a S face, since within a slice of thickness \$d\_{130}\$ there are no bonds between the [001] PBCs. According to Hartman & Perdok criterion,<sup>16</sup> the profile of the (130) face can be imagined as composed by alternating elements of the F faces (120) and (010), as represented in Figure 2.

The total surface free energy of the (130) face, following Hartman,<sup>9</sup> reads:

$$A_{130}\gamma_{130} = A_{120}\gamma_{120} + A_{010}\gamma_{010} + A_{130}\Delta\gamma_{130} \quad (2a)$$

or

$$\gamma_{130} = \left[ \gamma_{120} \frac{A_{120}}{A_{130}} + \gamma_{010} \frac{A_{010}}{A_{130}} \right] + \Delta\gamma_{130} \quad (2b)$$

This means that the \$\gamma\$ value of a S face can be represented by a linear combination of the \$\gamma\$ values of the two reference F faces, plus an a priori unknown correction term \$\Delta\gamma\_{130}\$ which depends on the interactions between the [001] chains. Here, \$A\_{hkl}\$ represents the mesh area of the \$(hkl)\$ faces. From Figure 2 it follows that

$$A_{120} \sin(\nu_1 + \nu_2) = A_{120} \sin \nu_1 \quad \text{and}$$

$$A_{010} \sin(\nu_1 + \nu_2) = A_{130} \sin \nu_2$$

and then

$$\gamma_{130} = \gamma_{120} \frac{\sin \nu_1}{\sin(\nu_1 + \nu_2)} + \gamma_{010} \frac{\sin \nu_2}{\sin(\nu_1 + \nu_2)} + \Delta\gamma_{130} \quad (2c)$$

In expression 2c of the specific surface energy of the S face the sign of the correction term is very important because only if \$\Delta\gamma\_{130} < 0\$, then (130) can enter the crystal equilibrium shape.<sup>9</sup>

Following Herring, Bennema,<sup>17</sup> investigating under which circumstances it is possible to decrease the free energy of an initial flat surface by rearranging the surface into hills and valleys, expressed the specific surface energy \$\gamma(S)\$ of a S face (made by hills and valleys) as

a linear combination of the specific surface energies of the two flat equilibrium faces (\$F\_1\$ and \$F\_2\$) generating the S face:

$$\gamma(S) = f(F_1) \times \gamma(F_1) + f(F_2) \times \gamma(F_2) \quad (3a)$$

Here, \$\gamma\_i\$ and \$f\_i\$ are considered components of vectors in the direct and reciprocal space respectively and the \$a\$-dimensional coefficients \$f(F\_1)\$ and \$f(F\_2)\$ represent the "...areas of the flat \$F\_1\$ and \$F\_2\$ faces, in the hill and valley structure, per unit projected area in the plane of the macroscopic S surface". \$f(F\_1)\$ and \$f(F\_2)\$ are easily traced back to the ratios between equidistance or areas, or sine ratios as in eq 2c.

Expressing the module of the reciprocal vectors in terms of the lattice constants, we obtained the expressions of the coefficients \$f(010)\$ and \$f(120)\$ in a parametric form, suitable to describe \$\gamma\_{1k0}\$ of gypsum. These values, reported in eq 3b, are used, along with the surface energy of (010) and (120), to draw the dotted spline interpolant in Figure 3. The reciprocal unit vector \$(\tau^\*)\$ normal to \$(1k0)\$, is expressed in terms of the unit vectors normal to (010) and (120):

$$\tau_{1k0}^* = \frac{(k-2) \times a_0 \sin \beta}{\sqrt{b_0^2 + k^2 a_0^2 \sin^2 \beta}} \tau_{010}^* + \sqrt{\frac{b_0^2 + 4a_0^2 \sin^2 \beta}{b_0^2 + k^2 a_0^2 \sin^2 \beta}} \tau_{120}^* \quad (3b)$$

**2.2.2. The Direct Calculation of the Surface Energy from the Profiles of \$(1k0)\$ Stepped Faces.** Both eqs 2 and 3 are based on an intrinsic approximation. As a matter of fact, both \$\gamma\_{120}\$ and \$\gamma\_{010}\$ values are related to infinite surfaces, since one usually does calculate a surface energy value (\$\gamma\_\infty\$) by applying the 2D periodic boundary conditions to the related surface profile. Unfortunately, in the above-mentioned models of stepped profiles, the surfaces of both (120) and (010) faces look like infinite strips along the [001] direction, and hence they are more similar to the ledges of infinite steps than to infinite faces. \$\Delta\gamma\$ is the measure of this approximation and it can be assessed by minimization of the surface energies of the \$1k0\$ slabs.

### 3. THE SPECIFIC SURFACE ENERGIES OF THE \$\{1k0\}\$ STEPPED FORMS OF GYPSUM

Atomistic modeling of the surface structures were performed using the empirical potential functions developed by Adam to explore the crystallographic and crystal-chemical properties of hydrated \$\text{CaSO}\_4\$ materials. The functions represent Coulomb and short-range interactions, the polarizability of the oxygen of water and a

Table 1. Specific Surface Energies ( $\text{erg cm}^{-2}$ ) of the Stepped  $\{1k0\}$  Forms and of the Two Reference F Forms  $\{120\}$  and  $\{010\}$ <sup>a</sup>

Form $\{hkl\}$	Growth mode	$U_{\text{PBC}}$ unrelaxed	$R_{\text{PBC}}$ relaxed	$\Delta_{UR}$ (%)	$U_{\text{SCM}}$ unrelaxed	$R_{\text{SCM}}$ relaxed	$\Delta_{UR}$ (%)
$\{120\}$	F	(a) 735	561	-23.67	712	543	-23.73
		(b) 763	621	-18.61	763	579	-18.68
					822	621	-18.61
						561	-31.75
						694	-15.57
$\{130\}$	S				888	702	-26.49
					694	548	-21.04
		730	562	-23.01	714	563	-18.88
					740	581	-18.63
						555	-25.00
$\{140\}$	S				768	612	-17.30
						616	-19.79
		709	550	-22.43	663	540	-18.55
					759	587	-22.66
						629	-17.13
$\{150\}$	S					648	-32.64
						799	-16.94
						776	-19.83
					683	546	-20.06
		(a) 689	538	-21.92	683	557	-18.45
$\{160\}$	S	(b) 687	536	-21.98	721	577	-19.97
					762	618	-18.90
					693	545	-21.36
					694	566	-18.44
		665	522	-21.50	730	553	-24.25
$\{170\}$	S					617	-15.48
						757	-20.74
						830	-19.28
					775	610	-21.29
		(a) 647	511	-21.02	788	630	-18.71
$\{180\}$	S	(b) 647	510	-21.17	791	637	-19.16
		(c) 647	509	-21.33	818	633	-19.97
						653	-20.17
						659	-19.44
					753	613	-18.59
$\{010\}$	F				759	603	-20.55
					807	625	-22.55
		630	498	-20.95		650	-19.45
						645	-22.94
		(a) 463	432	-6.69	463	432	-6.69
		(b) 1123	965	-14.07	796	503	-36.80
						752	-5.52
						965	-14.07
					1123		

<sup>a</sup> In the third and fourth column, the energy values are related to unrelaxed and relaxed surface profiles, respectively, obtained by the PBC theory. In the sixth and seventh column, the energy values of surfaces obtained through the systematic cuts (SC) method. In the seventh column, arrows relate the energies of complementary configurations of the same  $1k0$  cut relaxing in a different way to the energy of the unrelaxed surface.

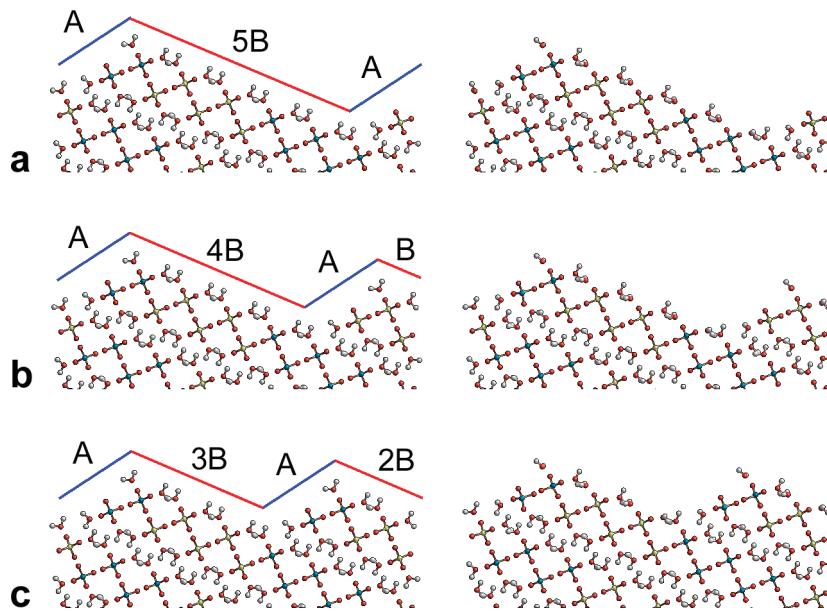
three body force within  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{O}$ . The potential was calibrated fitting unit cell parameters, bond lengths, and angles, and selected IR frequencies of known anhydrous phases and of gypsum. We refer to the work by Adam for a detailed description of the model.

The computer programs we used to manipulate the crystal structure and perform the energy minimization are GDIS<sup>18</sup> and GULP,<sup>19</sup> respectively.

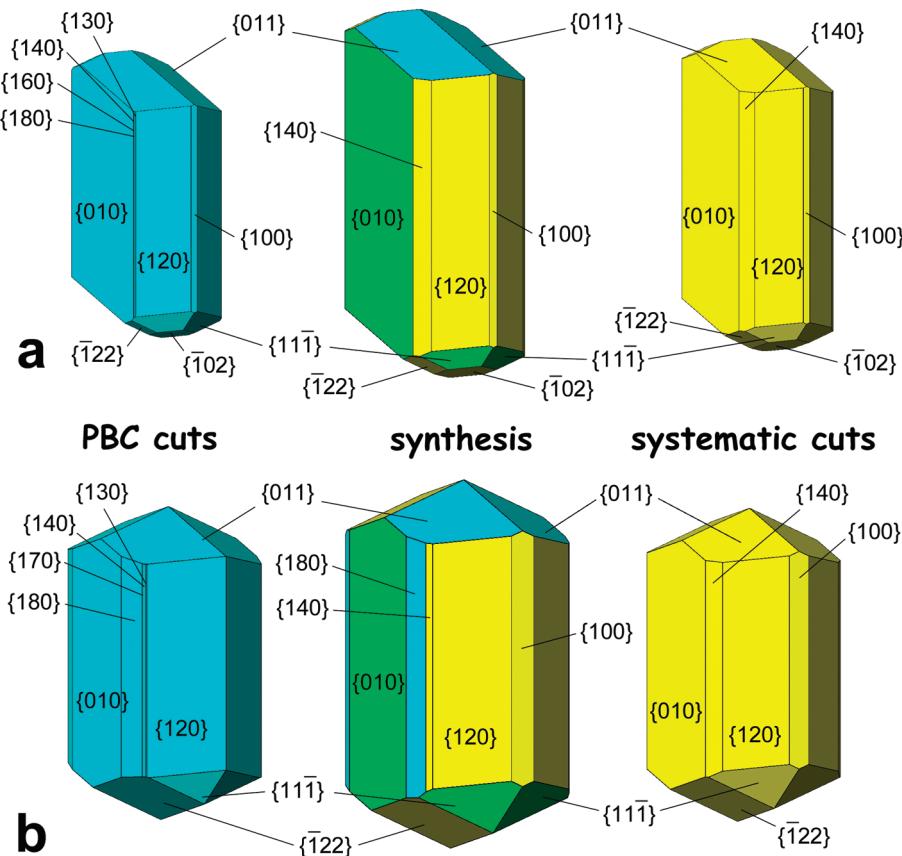
Figure 4 shows the way we choose to draw the profiles of the  $\{1k0\}$  faces. We started from repeatable segments of the  $\{120\}$  and  $\{010\}$  surface profiles obtained by the PBC method, while

the repeatable thicknesses  $d_{020}$  and  $d_{120}$  we adopted fulfil the systematic extinction rules (Figure 4a). Figure 4b illustrates, as an example, the simplest way to compose the stepped profiles of the faces  $\{140\}$  and  $\{160\}$ . The  $\{140\}$  profile is made by alternating the *minimum repeatable segments*  $|^{1/2}[2\bar{1}0]|$  and  $[[100] \sin \beta]$  of the faces  $\{120\}$  and  $\{010\}$ , respectively. The segments, for the  $\{160\}$  profile, become  $|^{1/2}[2\bar{1}0]|$  and  $2 \times [[100] \sin \beta]$ , respectively.

The specific surface energies of the  $\{1k0\}$  forms lying in between the two reference F forms,  $\{120\}$  and  $\{010\}$ , are reported in Table 1. We did not consider the remaining stepped form  $\{110\}$ , lying in



**Figure 5.** Unrelaxed (left side) and relaxed (right side) stepped profiles of the {170} form obtained from the PBC analysis. The (a, b, c) profiles correspond to different configurations, all having the common slope of the {170} form. A and B label the surface domain of kind (120) or (020). See also Figure 4.



**Figure 6.** Athermal equilibrium shape of gypsum crystal. (a) The three “unrelaxed” shapes are obtained from PBC (left side) and from SC (right side) methods. A synthesis is drawn using the minimum  $\gamma$  values obtained from both methods (center). (b) The corresponding “relaxed” shapes.

between the stepped {100} pinacoid and the {120} prism, as the {110} prism has never been observed.

All  $\gamma$  values referred to surface profiles obtained by either the PBC or the SC methods. The decrease of  $\gamma$  caused by the surface

relaxation is also indicated, as  $\Delta_{UR}$  (%). The SC method allows one to generate two complementary profiles when the interface resulting from the cut is situated neither on the symmetry centers nor on the glide planes. Hence, different relaxations affect the two complementary profiles and, consequently, two  $\gamma$  values will be reported in correspondence of the same unrelaxed surface energy.

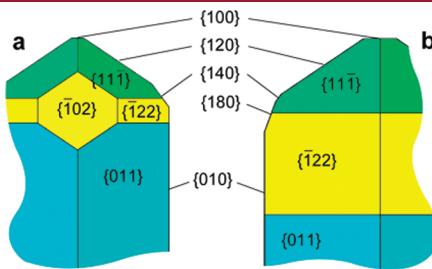
Table 1 allows one:

- to compare the two methods we used (PBC and SC) to build the surface profiles, on the basis of the calculated  $\gamma$  values of the  $\{1k0\}$  forms;
- to appreciate the novelty that some  $\{1k0\}$  stepped forms can belong to the equilibrium shape of the gypsum crystal, as can be seen in Figures 6 and 7.

From Table 2, one can see that  $\gamma_{min}^{relaxed}$  behaves as a monotonous decreasing function of the dihedral angle formed between the  $\{120\}$  and the  $\{010\}$  forms in the case the initial surfaces are generated by the PBC method.

Instead,  $\gamma_{min}^{relaxed}$  calculated by the SC method has a mean value of  $544.4 \text{ erg cm}^{-2}$ , with a negligible dispersion of  $\pm 0.7\%$ , in the case of the forms from  $\{120\}$  to  $\{160\}$ , the lower value corresponding to  $\{140\}$ . Further,  $\gamma_{min}^{relaxed}$  jumps to values much larger than  $\gamma_{min}^{relaxed}$  ( $\{120\}$ ) in the case of the forms  $\{170\}$  and  $\{180\}$ .

Then, the two methods work better in different domains, although the values they produce are rather close for those stepped forms near to the  $\{120\}$  form; the SC method fails as the forms approach  $\{010\}$ , the most stable flat form of the crystal. All



**Figure 7.** Detailed [001] projection of the (a) unrelaxed and (b) relaxed equilibrium shapes (see Figure 6, synthesis).

**Table 2.** The  $\{1k0\}$  Stepped Forms along with the Reference  $\{120\}$  and  $\{010\}$  F Forms<sup>a</sup>

$\{1k0\}$ form and character	$\{120\}$ F	$\{130\}$ S	$\{140\}$ S	$\{150\}$ S	$\{160\}$ S	$\{170\}$ S	$\{180\}$ S	$\{010\}$ F
dihedral angle (deg) formed with the $\{010\}$ form	55.79	44.43	36.33	30.46	26.11	22.79	20.18	0
$\gamma_{min}^{relaxed}$ (PBC method, $\text{erg cm}^{-2}$ )	561	562	550	536	522	509	498	432
$\gamma_{min}^{relaxed}$ (SC method, $\text{erg cm}^{-2}$ )	543	548	540	546	545	610	603	432
$\Delta\gamma_{min}^{relaxed}$ (%)	+3.21	+2.49	+1.82	+1.86	-4.40	-19.8	-21.08	0

<sup>a</sup> The minimum values of the specific surface energy ( $\gamma_{min}$ ), obtained either by the PBC or SC method, are reported. To test the sensitivity of the two methods in building the profiles of minimum energy, the difference (%) between these values  $\Delta\gamma_{min}^{relaxed} = (\gamma_{min}^{\text{PBC}} - \gamma_{min}^{\text{SC}}) / \gamma_{min}^{\text{PBC}}$  is also given.

**Table 3. Evaluation of the Correction Term  $\Delta\gamma_{1k0}$  (Absolute Value and Weight %)**

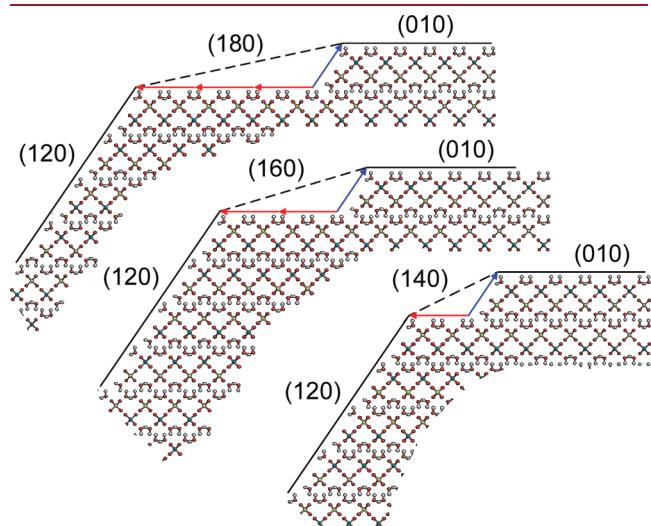
index of the form	$\{120\}$	$\{130\}$	$\{140\}$	$\{150\}$	$\{160\}$	$\{170\}$	$\{180\}$	$\{010\}$
number ( $n$ ) of elementary segments corresponding to the $n \times A_{120}$ areas	2	1	2	1	2	1		
number ( $n$ ) of elementary segments corresponding to the $n \times A_{010}$ areas	1	1	3	2	5	3		
$\gamma_{1k0}$ value [ $\text{erg cm}^{-2}$ ] in Hartman's-Herring's formula	543	564.6	565.1	558.4	549.6	540.7	532.4	432
minimum $\gamma_{1k0}$ value [ $\text{erg cm}^{-2}$ ] from either PBC or SC method	543	548 <sub>(SC)</sub>	540 <sub>(SC)</sub>	536 <sub>(PBC)</sub>	522 <sub>(PBC)</sub>	509 <sub>(PBC)</sub>	498 <sub>(PBC)</sub>	432
$\Delta\gamma_{1k0}$ [ $\text{erg cm}^{-2}$ ] from Hartman's equation (2)	0	-16.7	-22.9	-21.8	-26.9	-30.9	-33.6	0
$\Delta\gamma_{1k0}$ (%) weight with respect to the minimum $\gamma_{1k0}$ value, from Hartman's equation (2)		-3.05	-4.24	-4.07	-5.15	-6.07	-6.74	

this is illustrated in the fifth row of Table 2, where the values of  $\Delta\gamma_{min}^{relaxed} = (\gamma_{min}^{\text{PBC}} - \gamma_{min}^{\text{SC}}) / \gamma_{min}^{\text{PBC}}$  are collected.

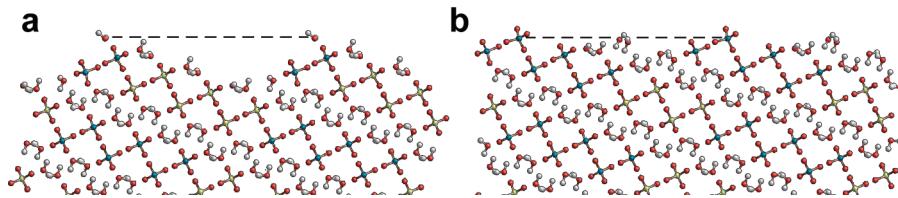
Both  $\gamma_{min}^{\text{unrelaxed}}$  and  $\gamma_{min}^{\text{relaxed}}$  values were used to draw the athermal equilibrium shape of gypsum calculated by the Gibbs-Wulff's theorem<sup>12</sup> (Figures 6 and 7).

A critical comparison between PBC and SC methods, concerning the  $\{1k0\}$  forms close to the  $\{010\}$  pinacoid, can be found in the conclusions.

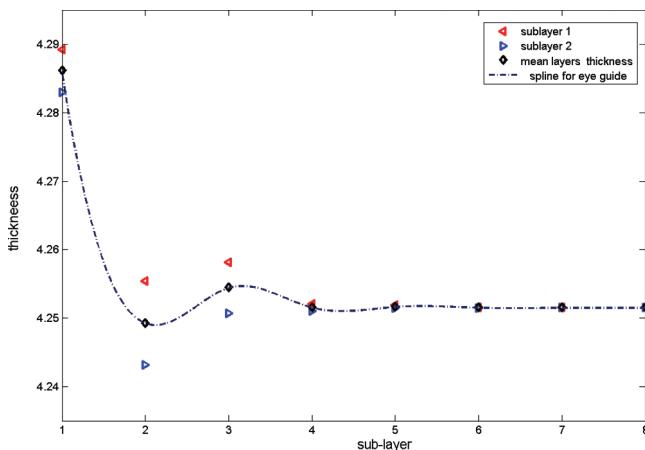
The theoretical ES of gypsum has been discussed as a whole in our preceding paper.<sup>1</sup> Thus, here we will confine our attention to elucidate why some stepped  $\{1k0\}$  forms can belong to the ES. According to the surface profiles obtained from the PBC analysis, the  $\{130\}$ ,  $\{140\}$ , and  $\{180\}$  forms enter the ES for either unrelaxed or relaxed surfaces. The  $\{160\}$  form enters the unrelaxed ES, while  $\{170\}$  enters the relaxed one. The  $\{150\}$  form never belongs to the ES.



**Figure 8.** The composition of stepped  $\{1k0\}$  surface profiles for even  $k$  values. Arrows indicate the length of the segments representing the elementary  $A_{120}$  (in blue) and  $A_{010}$  (in red) areas. Dashed lines indicate the areas corresponding to the  $\{1k0\}$  forms.



**Figure 9.** The relaxed surface profiles of the stepped {180} form of gypsum, as it follows from the combination of segments of {010} and {120} forms. The sketched segments indicate the repeat period on the (180) surface projected along the [001] direction. (a) The profile constructed by PBCs. (b) The lowest energy profile among those obtained by systematic cuts.



**Figure 10.** Deviation, from the bulk distance, between equivalent Ca layers measured along the perpendicular to the (120) surface.

As anticipated in the analysis of Table 2, the results of using only the SC method would be much more restrictive, since only the {140} form belongs to the ES (either unrelaxed or relaxed).

This is obviously due to the lower surface energy of the face (120) calculated from the initial surface structure generated with this method. Summing up the results of both methods, the {140} form can appear on the athermal ES even neglecting surface relaxation, while the {180} form can only appear on the athermal relaxed ES.

#### 4. EVALUATING THE HARTMAN'S CORRECTION TERM

Following Hartman, the sign of  $\Delta\gamma_{1k0}$ , gives indication of the stability of the {1k0} form.

Let us now represent the surface energy of the {1k0} form, through the Hartman's formula 2b, in the following way:

$$\gamma_{1k0} = \left[ \frac{A_{120}\gamma_{120} + A_{010}\gamma_{010}}{A_{1k0}} \right] + \Delta\gamma_{1k0} \quad (4)$$

Previously<sup>1</sup> we estimated both  $\gamma_{120}$  and  $\gamma_{010}$ , for infinite (120) and (010) surfaces, and found their lowest values. Then, the term in square brackets in (4) is known as well as  $\gamma_{1k0}$  (see Table 1).

We would like also to recollect that the elementary areas  $A_{120}$  and  $A_{010}$  are the module of the vector product of the vector [001] times the vectors  $1/2[2\bar{1}0]$  and [100], respectively.

Further, we want to look at the Hartman's formula stressing that the elementary areas  $A_{120}$  and  $A_{010}$  areas have to be multiplied by the number of segments needed to obtain the desired (1k0) profile (see Figures 4 and 5) and the consistent mesh area; only in this way the correct area ratios, equal to the ratios between equidistance or sinus functions, are obtained.

As a matter of fact, the "composition" of each even profile we calculated is indicated in Table 3 and illustrated in Figure 8.

From Table 3 it comes out that:

- (i) All  $\Delta\gamma_{1k0}$  values are negative, which implies that, according to Hartman,<sup>9</sup> all the {1k0} forms could enter the equilibrium shape of the gypsum crystal.
- (ii) At variance with the current opinion that only the S faces of molecular or covalent crystals can belong to the equilibrium shape, gypsum represents the second case of crystal where ionic interactions are strong and several S forms enter the equilibrium shape. The calcite crystal is the first case, as the {10\bar{1}0} stepped prism and the {0001} kinked pinacoid belong to the athermal equilibrium shape due to the high relaxation energy.<sup>10,11</sup>

#### 5. CONCLUSIONS

The ES of gypsum shows not only flat faces but also the {140} and {180} stepped forms contrary to the usually accepted opinion. Following the PBC method also the stepped {130} and {170} forms should belong to the ES.

The PBC method allows one to describe  $\gamma_{min}^{(1k0)}$  as a function monotonically decreasing from {130} to {180}, what is accomplished building the {1k0} with increasing proportion of the lowest energy form, the pinacoid {010}, and decreasing proportion of the less stable {120} prism.

In this regard, it is worth spending a short consideration on the reason why the reliability of the CS method fails as the stepped {1k0} forms approach the flat {010} pinacoid.

Comparing the profiles of the {180} form obtained by applying either the PBC or the SC method, one can observe that on the two surfaces the unsaturated bonds are differently distributed (see Figure 9).

The initial surface structure generated by the PBC analysis preserves the water molecules on crystallographic sites and the energy minimization produces their reorientation; on the contrary, the initial surface generated by a cut is such that the water molecules are concentrated in the middle of the repeat period and, as a consequence, a higher number of  $\text{Ca}-\text{O}_{(\text{water})}$  and  $\text{Ca}-\text{O}_{(\text{sulfate})}$  unsaturated bonds are exposed. The coordination of these water molecules changes upon minimization, but they are not moved to more stable positions.

Conversely, the initial surface obtained with the SC method are more solvated and closer to a deeper energy minimum in the case of the forms {120}, {130}, {140}.

In any case, the changes of coordination on the surface are accompanied by atomic movements on several layers close to the surface. These long-range effects cannot be described and foreseen by a linear combination of energies and are accounted for and included in the Hartman correction term.

As an example the deviation from the bulk distance between equivalent Ca layer measured along the  $\langle 120 \rangle$  normal are reported in Figure 10. The collective movements of the atoms in the cells closer to the surface will determine the expansion of the crystal at the surface and the shifts of the surface layers with respect to the bulk.

Our finding on the theoretical ES of gypsum involves the following considerations:

- (i) Recollecting the results obtained in our preceding paper,<sup>1</sup> the ES is “dominated” by four F forms,  $\{010\}$ ,  $\{120\}$ ,  $\{011\}$  and  $\{11\bar{1}\}$ , and “smoothed” by four S forms,  $\{100\}$ ,  $\{\bar{1}22\}$ ,  $\{140\}$ ,  $\{180\}$ , and by the K form  $\{\bar{1}02\}$ . Taking also into account that the K- $\{0001\}$ <sup>10</sup> and the S- $\{10\bar{1}0\}$ <sup>11</sup> forms enter the athermal-relaxed equilibrium shape of calcite, another ionic crystal, we think that it would be reasonable to change our mind about the morphology of ionic crystals at equilibrium. In other words, the contribution of the surface relaxation is often not negligible but rather important in the case of the S and K faces.
- (ii) The correction term  $\Delta\gamma_{1k0}$  introduced by Hartman is not negligible, even if its value is in between 3 and 7% of the optimal  $\gamma_{1k0}$  values.
- (iii) There is a striking analogy between our finding and the systematic presence on the giant crystals found in the Naica mine of “...the  $\{1k0\}$  faces which are striated and composed of alternating bundles of  $\{120\}$ ,  $\{140\}$ , and  $\{160\}$  faces making an overall orientation close to  $\{140\}$ ...”<sup>7,8</sup> It is worth remembering that the limited number of crystals along with their exceptional size give evidence of the very low supersaturation regime which ruled both gypsum nucleation and crystal growth. This means that, when the growth occurs very near the equilibrium, the  $[001]$  zone of gypsum exhibits the  $\{1k0\}$  faceting that we investigated theoretically in the present work.

One could reasonably object that the  $\{1k0\}$  faceting of Naica crystals occurs in solution at a mean growth temperature of 58 °C, while our calculation simulates the nonrealistic vacuum condition at 0 K. Nevertheless, one should remember that

- (a) The entropic contribution due to the temperature further decreases the surface energy value, especially for those  $\{1k0\}$  profiles where the weight percent of the  $\{120\}$  segments dominates.
- (b) Water adsorption affects the  $\{120\}$  segments more than the  $\{010\}$  ones, owing to the higher density of sites ( $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ ) available for strong solvent interaction on the  $\{120\}$  surfaces.<sup>21</sup> This determines, once again, a reduction of the surface energy of the  $\{1k0\}$  forms with respect to the fully hydrated  $\{010\}$  (see Figure 4) and, consequently, it is likely that the  $\{1k0\}$  stepped forms contribute to the equilibrium shape of the critical nucleus and of the macroscopic crystal in aqueous solution.

- (2) (a) Simon, B.; Bienfait, M. *Acta Crystallogr.* **1965**, *19*, 750–756.  
(b) Simon, B. Thèse, Université d’Aix-Marseille, 1968.
- (3) Heijnen, W. M. M.; Hartman, P. *J. Cryst. Growth* **1991**, *108*, 290–300.
- (4) Adam, C. D. *J. Solid State Chem.* **2003**, *174*, 141–151.
- (5) Hartman, P. In *Crystal Growth: An Introduction*; Hartman, P., Ed.; North Holland Publishing Co.: Amsterdam, 1973; pp 367–402.
- (6) Goldschmidt, V. *Atlas der Kristallformen*; Universitätverlag, Ed.: Heidelberg, Germany, 1923–1931; Vol. 1–9.
- (7) García-Ruiz, J. M.; Villasuso, R.; Ayora, C.; Canals, A.; Otálora, F. *Geology* **2007**, *35* (4), 327–330.
- (8) Forti, P.; Sanna, L. *Episodes* **2010**, *33* (1), 23–32.
- (9) Hartman, P. *Acta Crystallogr.* **1958**, *11*, 459–464.
- (10) Bruno, M.; Massaro, F. R.; Prencipe, M.; Aquilano, D. *CrysEngComm* **2010**, *12* (11), 3626–3633.
- (11) Massaro, F. R.; Bruno, M.; Aquilano, D. *Cryst. Growth Des.* **2010**, *10*, 4096–4100.
- (12) Kern, R. In *Morphology of Crystals. Part A*; Sunagawa, I., Ed.; Terra Scientific Publishing Co.: Tokyo, 1987; pp 77–206.
- (13) Hartman, P.; Heijnen, W. M. M. *J. Cryst. Growth* **1983**, *63*, 261–264.
- (14) Mutaftschiev, B. *The Atomistic Nature of Crystal Growth*; Springer Series in Material Science: Berlin, 2001; p 368.
- (15) (a) Yamada, M. *Physik. Zeit.* **1923**, *24*, 364. (b) Yamada, M. *Physik. Zeit.* **1924**, *25*, 52. (c) Yamada, M. *Physik. Zeit.* **1924**, *25*, 289.
- (16) Hartman, P.; Perdok, W. G. *Acta Crystallogr.* **1955**, *8*, 525–529.
- (17) Bennema, P. In *Crystal Growth: An Introduction*; Hartman, P., Ed.; North Holland Publishing Co.: Amsterdam, 1973; pp 343–366.
- (18) GDIS (the acronym is not given by the authors of the code) is a GTK based program for the display and manipulation of isolated molecules and periodic assemblies. GTK (GIMP Tool Kit) is a highly usable, feature rich toolkit for creating graphical user interfaces.
- (19) Gale, J. D. *J. Chem. Soc. Faraday Trans.* **1997**, *93* (4), 629–637.
- (20) De Jong, W. F.; Bouman, J. Z. *Kristallogr.* **1938**, *100*, 275–276.
- (21) Van der Voort, E.; Hartman, P. *J. Cryst. Growth* **1991**, *112*, 445–450.

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## REFERENCES

- (1) Massaro, F. R.; Rubbo, M.; Aquilano, D. *Cryst. Growth Des.* **2010**, *10*, 2870–2878.