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Crystal structure and crystal growth: I. The influence of internal structure on morphology: a discussion

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In his paper on the influence of internal structure on morphology, Dowty (1976) discusses the periodic-bond-chain (PBC) method. Unfortunately a few concepts have been presented incorrectly, and the application therefore gives wrong results. Furthermore, it can be shown that the concept of template fraction as introduced by Dowty is closely akin with the concept of attachment energy in the PBC method.

Dowty gives three theoretical and practical shortcomings of the PBC method. First, he states that the periodic-bond-chains in even moderately complex structures have complicated structures with various kinks and excrescences, and that this obscures the division of faces into *F, S,* and *K* types. Indeed, in complicated structures PBC's are complicated, but the criteria for the categories *F, S,* and *K* are sufficiently clear to distinguish them. We have applied the PBC method to complicated structures such as olivine ('t Hart, 1975), feldspar (Woensdregt, 1975) and mica (Hartman, unpublished), thus showing that Dowty's second argument, namely that the method is extremely difficult to apply without avoiding subjectivity and error, need not be true. The example of barite (Hartman and Perdok, 1955) is a poor one, since during the last 20 years my ideas have evolved considerably. The third argument, namely that if the PBC method is correct it would be difficult to see why the Donnay-Harker (DH) method should be successful in so many cases, does not hold. On the contrary, the results of the PBC method often agree with those of the DH method, and moreover, we understand why the DH method sometimes fails (Hartman and Perdok, 1956; Hartman, 1968a, 1968b).

It is important to point out that Dowty's Figures 1b and 1c do not represent *S* and *K* faces respectively. Both are *F* faces, because the uppermost surfaces are parallel to the crystal face. The differences between these faces and the *F* face in Figure 1a lies in the high degree of roughness, and the so-called *S* face is simply a rough *F* face with a high bonding anisotropy (*cf.* van Dijk *et al.*, 1974). The surface of an *S* face in the block model used by Dowty should end with sharp edges, so that the profile is stepped irregularly like that of a staircase on a nature trail in a hilly landscape. The surface of a *K* face should end with corners, so that the surface geometry would be one of parallel pyramids of different heights.

For quantitative results the PBC method uses the concept of attachment energy, E_{att}, defined as the interaction energy per molecule released when a new slice with thickness d_{hkl} is attached to the crystal face (hkl). Dowty introduces the template fraction defined as "the fraction of the total bond energy in a growth layer attaching that layer to the substrate." In his examples Dowty takes a slice of indefinite thickness. Herein the bond energy is equal to the lattice energy E_{cr}. The template fraction is then $T = E_{\mathrm{s}}/E_{\mathrm{er}}$, where $E_{\mathrm{s}} = \Sigma i E_{\mathrm{i}}$ with E_{i} the interaction energy per molecule of a slide d_{hkl} with the i'th underlying slice. E_{s} is the surface energy per molecule. The attachment energy $E_{\mathrm{att}} = \Sigma E_{\mathrm{i}}$. In current crystal-growth theories the growth layers are assumed to be slices of thickness d_{hkl}. In that case the template fraction simply becomes $T = E_{\mathrm{att}}/E_{\mathrm{cr}}$. As to the calculation of the attachment energy, Dowty refers to the paper on barite (Hartman and Perdok, 1955) where indeed we did not express E_{att} in units of energy per molecule. It is most unfortunate that Dowty used for the calculation of the HP values a method that might be considered as a sin of youth.

Dowty calculates his template fraction by taking into account first-order bonds only, a method that can be used very well for covalent bonding, reasonably well for Van der Waals bonding, but not for ionic bonding. Therefore barite and NaCl are among the worst examples to be chosen. For these a point-charge model as used by Stranski (1928) for NaCl is essential. Stranski's calculations show that E_{s}, and therefore the template fraction, for a planar (111) surface of NaCl amounts to infinity. We have applied a point-charge model, using the Madelung method described by Hartman (1973) to calculate E_{att}. Computer programs were developed by Mr. C. F. Woensdregt and by Dr. C. S. Strom in our Institute for energy calculations, as well as for making projections of several unit-cells of crystal structures in any desired direction. Thus far results have been obtained for rutile and trirutile (Felius, 1976), fluorite, corundum, quartz, anatase, calcite, olivine, feldspar, and 1M mica, to be published in the near future. Gypsum was treated by Simon and Bienfat (1965) in a slightly different way.

In a positive vein it must be said that Dowty's method will correctly assign the surface of least bonding, a surface also sought by the PBC method, provided this surface is a plane. According to our experience, complicated structures tend to have undulatory surfaces. A second point is that Dowty is correct in saying that we chose an incorrect surface for (011) of barite. According to our present views his surface is correct.

To summarize, Dowty's template fraction method can be used in a limited number of cases, as he correctly points out. The use of the term template fraction is superfluous because it is related to the attachment energy or to the surface energy in a very simple way, and because in current theories on crystal growth of flat faces the attachment energy, but not the template fraction, plays a role that permits easy correlation with the growth rate.

Dowty has presented the PBC method incorrectly and he has calculated the attachment energy using an incorrect and out-of-date method.

Finally, it is my conviction that any improvement in Dowty's method will bring it into closer harmony with the PBC method, so that the results will be exactly the same.

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