Growth morphology of zinc tris(thiourea) sulphate crystals

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Abstract. The growth morphology of crystals of zinc tris(thiourea) sulphate (ZTS) is investigated experimentally, and computed using the Hartman–Perdok approach. Attachment energies of the observed habit faces are calculated for determining their relative morphological importance. A computer code is developed for carrying out these calculations. A special procedure is adopted for computing the cohesive energy of a slice of the structure parallel to any rational crystallographic plane. For estimating the cohesive energies, formal charges on the experimentally determined atomic positions in the molecules of ZTS are calculated by *ab initio* molecular-orbital computations, with wave functions obtained by the Hartree–Fock procedure. Fairly good agreement with the observed crystal morphology is obtained for a model of growth mechanism in which ZTS is assumed to exist in solution as zinc tris(thiourea) ions and sulphate ions.

1. Introduction

Zinc tris(thiourea) sulphate (ZTS), $Zn[CS(NH_2)_2]_3SO_4$, is a metalorganic nonlinear-optical crystal which can be grown fairly easily in large sizes from aqueous solution. Its growth and characterization have been reported in a number of recent publications [1–5]. In this paper we report a calculation of its theoretical growth morphology, using the Hartman–Perdok formalism [6–8]. A crystal-growth experiment is also reported, whereby the experimental morphology was ascertained unambiguously, for comparison with the computed morphology.

The processes involved during the growth of a crystal are highly complex, involving many-body interactions. Moreover, the sophisticated techniques currently available for computing cohesive energies cannot be used for crystals having too large a number of atoms in the unit cell. This is because of the prohibitive requirements on computer time and memory. For such crystals the Hartman–Perdok approach, though approximate, offers a workable and useful solution.

The usefulness of attempts at computing and predicting growth morphologies of crystals arises for the following reason. Crystals grown under a specific set of conditions (temper-

ature, pressure, chemical composition, impurities, pH value, etc.) tend to have a specific morphology (in a statistical sense). What this means is that if one were to measure the relative areas of the various habit faces for a substantial number of fairly large crystals of a given species, the ratios of these numbers (areas) are likely to be quite unique, with only a small scatter around the average ratios. This set of numbers is indeed a valuable clue Nature gives us about the mechanism it adopted for the growth of that crystal. The clue is not only valuable qualitatively, it is also very substantial quantitatively because a crystal usually has a fairly large number of habit faces. A theory or model which can predict this entire set of numbers correctly (within the statistical variations) provides a good insight into what really happens in the interfacial layer between the growing crystal and the mother nutrient. Even more importantly, success in this venture gives insight into how one should *choose* the growth parameters to achieve a desired result.

In §2 we describe the basic theoretical methodology used in the present work. Section 3 gives some details of the computer code developed by us for this work, and §4 describes the verification of this code. The experiment carried out for obtaining the main features of the experimental morphology is described in §5. In §6 the theoretical results for the growth morphology of ZTS crystals are presented.

2. The methodology

In the Hartman–Perdok analysis, one computes the *attachment energy*, E_{att}, for the various likely habit faces. This is the energy released (per mol) when a 'slice' of the crystal structure, parallel to a crystallographic plane (hkl), and of a suitably chosen thickness, attaches itself to the crystal.

The term 'slice' has a carefully defined meaning [6–8]. Unlike a crystallographic plane specified by Miller indices hkl, it has a non-zero thickness. It is a portion of the crystal structure, parallel to (hkl), infinite in two dimensions, and having a finite thickness in the third dimension. A chemical requirement for the selection of its thickness is that it should have the smallest stoichiometric average thickness (usually equal to, or a multiple of, or a submultiple of the interplanar spacing d_{hkl}). This means that the slice must be composed of an integral number of formula units; i.e. the proportion of the chemical species in it must be the same as in the bulk crystal. Another requirement, called the 'flatness condition', is that all differences in lattice translations between atoms related by symmetry operations must be parallel to (hkl). The reason for imposing this condition is that if some translation differences oblique to (hkl) were to be admitted, the slice would lose its orientational uniqueness and would become more 'rough' than it actually is during the real growth conditions.

The 'morphological importance' (MI) of a habit face is postulated in the Hartman–Perdok theory to be inversely proportional to E_{att}. The logic behind this approach, which is in line with the well-known Wulff theorem in the theory of crystal morphology, is as follows.

The total cohesive energy per mol (E_{cr}) of a crystal can be taken as composed of two parts:

$$E_{cr} = E_{slice} + E_{att}. \tag{2.1}$$

Here E_{slice} is the cohesive energy per mol of any slice (hkl). If the atoms of the slice are tightly bound within the slice, i.e. if E_{slice} is large, then the energy (E_{att}) released when

this slice binds to the rest of the crystal would be small, and vice versa. If E_{att} is small, there is a larger chance that a growth unit, after being attached to the growing crystal, will get blown away (detached) by thermal fluctuations. Such a habit face will therefore grow more slowly compared to a face for which E_{att} is larger. And it is the slowest growing faces which determine the final morphology. Fast-growing faces disappear rather early in the growth process, and do not show up in their final morphology.

A limitation of the original Hartman–Perdok formalism is that it predicts the same growth rates for opposite pairs of habit faces hkl and $\bar{h}\bar{k}\bar{l}$. These growth rates can differ, not for structural, but rather for *environmental* reasons. For example, the polarity of the face may determine phenomena such as solvation, as also the identity and orientation of the groups of atoms which may tend to attach to such a face during the growth of the crystal. Including the solid–fluid interactions in the calculations is a highly nontrivial task.

To determine E_{att} in eq. (2.1), we have to compute E_{cr} and E_{slice}. For computing these cohesive energies for ZTS, we first used information about the crystal structure [9,10] for computing the formal charges on each atomic site by *ab initio* molecular orbital calculations.

Bond distances and angles for a molecule of ZTS (figure 1) are not the same in solution and in the crystalline state. The changes that occur in the intermolecular bonding affect the charge distribution within the molecule. The final distribution of the electron cloud is exactly what is determined by an X-ray diffraction experiment. Therefore, for calculating the formal electron charge assignable to each atom in the molecule, we imposed the constraint that the interatomic distances be kept fixed at their experimentally determined crystal-structure values during the *ab initio* molecular orbital calculations.
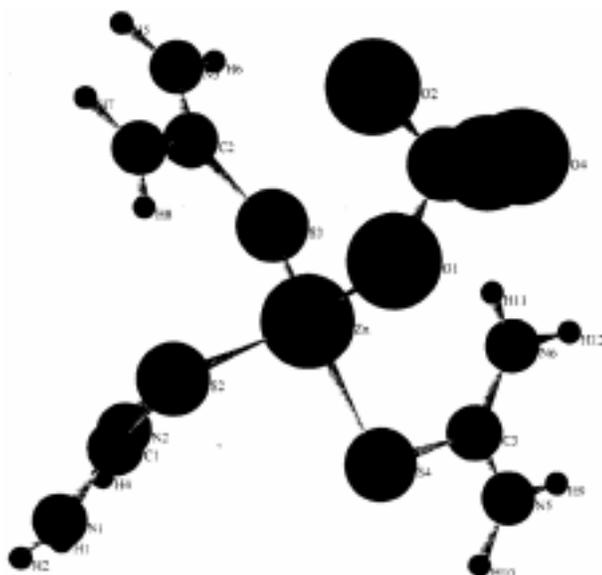

Figure 1. A molecule of ZTS. The labels used for atoms in table 1 are those indicated here.

These calculations were performed using the Gaussian 94 set of programs [11]. The wave function for the fixed geometry of the molecule was calculated by the Hartree–Fock procedure using the 6-311G(d) basis set. With this wave function, the electrostatic potential-derived charges were generated according to the Merz–Singh–Kollman scheme [12,13]. The formal charges at atomic sites, derived from the electrostatic potential at the HF/6-311G(d) level, are given in table 1.

The crystal structure of ZTS involves extensive hydrogen bonding. In keeping with the current trend, the contribution of this bonding to the cohesive energy was computed by us through the Coulomb interaction term. The total expression for the interaction potential between two atoms $A_i(\mathbf{r}_i)$ and $A_j(\mathbf{r}_j)$, with formal charges q_i and q_j was taken as

$$V = V_1 + V_2, \tag{2.2}$$

$$V_1 = \frac{q_i q_j}{4\pi\epsilon_0 r}, \tag{2.3}$$

$$V_2 = V_m\left[-2\left(r^*/r\right)^6 + \left(r^*/r\right)^{12}\right]. \tag{2.4}$$

Here $r = |\mathbf{r}_i - \mathbf{r}_j|$; ϵ_0 is the dielectric permittivity of free space; and r^* is the interatomic distance at which $V = V_m$ ($r^* = (r_i^* + r_j^*)/2$); usually, r^* is taken as twice the van der Waals radius. $V_m = \sqrt{(V_{mi} \times V_{mj})}$. Table 2 shows the values taken by us for r_i^* and V_m.

Table 1. Formal charges (in units of the electron charge) associated with various atoms in a molecule of ZTS.

Zn	S1	S2	S3	S4	O1
1.529	1.660	−0.513	−0.665	−0.744	−0.939
O2	O3	O4	N1	N2	N3
−0.795	−0.835	−0.808	−0.784	−0.763	−0.768
N4	N5	N6	C1	C2	C3
−0.789	−0.895	−0.744	0.599	0.690	0.769
H1	H2	H3	H4	H5	H6
0.424	0.423	0.235	0.442	0.401	0.427
H7	H8	H9	H10	H11	H12
0.440	0.335	0.435	0.433	0.383	0.417

Table 2. Values of r_i^* and V_{mi} taken by us for the various atomic species in ZTS [14, 15].

Atom i	$r_i^*(\text{Å})$	V_{mi} (kcal/mol)
Zn	2.78	0.350
S	4.15	0.223
O	3.21	0.228
N	3.93	0.167
C	4.35	0.039
H	1.0	0.01

For computing the various cohesive energies correctly, it is important to identify the growth units in the aqueous solution. For example, the entire ZTS molecule may remain undissociated in solution, in which case it constitutes the growth unit. Alternatively, and more probably, it may split into ZT and sulphate ions, in which case there are two types of growth units, namely ZT and S (S for sulphate). We confirmed the existence of sulphate ions in the solution by conducting the following simple experiment. A few drops of an aqueous solution of $BaCl_2$ were added to the solution of ZTS. A white precipitate of $BaSO_4$ formed immediately, indicating the presence of free sulphate ions in the solution.

3. Further computational details

A Fortran-90 computer code called LATTICE was developed for carrying out the various calculations.

Bulk energy

For calculating the bulk cohesive energy E_{cr}, a central unit cell is chosen as the 'reference cell', and the potential at each atomic site in this cell, due to two-body interactions with all atoms in a 'super cell' around the central cell, is computed using eq. (2.2). A progressively larger super cell is tried, till an increase in the size of this cell makes no significant difference to the computed value of E_{cr}.

The convergence of the Ewald sum is achieved by always choosing the unit cell in such a way that it is charge-neutral [16,17]:

$$\sum_i q_i = 0. \tag{3.1}$$

Here q_i is the charge on the ith atom in the unit cell, and the summation runs over all atoms of the unit cell.

Slice energy

Calculation of E_{slice} presents some special problems, which have hardly been discussed in the open literature. A serious problem one encounters is that, for an arbitrarily chosen plane with Miller indices h, k, l, one cannot always identify periodicity in two directions in this plane. In other words, one cannot always define a 2-dimensional unit cell for the atomic structure of a slice of the crystal parallel to this plane.

One must also choose the thickness, t_{hkl}, of the slice in such a way that stoichiometry is maintained.

A third aspect is that of a possible non-zero component of the dipole moment of the chosen slice thickness in a direction along the plane normal. If it is non-zero, a correction E_{corr} must be applied to E_{att} in eq. (2.1). We calculate E_{corr} as follows [16,17]:

$$E_{\text{corr}} = -2\pi p_{hkl}^2 / V_p, \tag{3.2}$$

$$p_{hkl} = d_{hkl} \sum_i q_i (hx_i + ky_i + lz_i). \tag{3.3}$$

Here p_{hkl} is the component of the dipole moment along the plane normal; d_{hkl} is the 'd-spacing' for the family of crystallographic planes (hkl); V_p is the volume of the primitive unit cell; and (x_i, y_i, z_i) are the fractional coordinates of the ith atom in the unit cell.

In what follows, we shall assume that the correction E_{corr} has been applied to the attachment energy, and that E_{att} stands for the *corrected* attachment energy.

We have developed a special procedure for tackling the problem of a possible absence of 2-dimensional periodicity for a given slice parallel to a habit face. We exploit the periodicity of the bulk structure for singling out repeat units (entire molecules) which lie within the slice, and which are labelled in terms of indices (i, j, k) of a unit cell of the bulk crystal. A computer code called SLICE was written for calculating E_{slice}, as also p_{hkl}.

We first perform a coordinate transformation, so that a plane (hkl) becomes $(00l)$. Let us denote by $H(h_{ij})$ the matrix which effects this transformation. Under this transformation a point (x, y, z) changes to, say, (x', y', z').

The coordinates of an atom belonging to the slice, as also to the cell (i, j, k) of the bulk crystal, are given by

$$x'(i, j, k) = x'(1, 1, 1) + a(i - 1)\left[h_{11} - \frac{h_{13}h_{31}}{h_{33}}\right]$$

$$+ b(j - 1)\left[h_{12} - \frac{h_{13}h_{32}}{h_{33}}\right], \tag{3.4}$$

$$y'(i, j, k) = y'(1, 1, 1) + a(i - 1)\left[h_{21} - \frac{h_{23}h_{31}}{h_{33}}\right]$$

$$+ b(j - 1)\left[h_{22} - \frac{h_{23}h_{32}}{h_{33}}\right], \tag{3.5}$$

$$z'(i, j, k) = z'(1, 1, 1). \tag{3.6}$$

Here a, b, c are the lattice parameters of the crystal (ZTS has the point-group symmetry $mm2$).

In the computer code, an atom is taken as belonging to the slice if it satisfies the following condition:

$$c(k - 1) = -\frac{h_{31}}{h_{33}}a(i - 1) - \frac{h_{32}}{h_{33}}b(j - 1). \tag{3.7}$$

Only those values of i and j in eqs (3.4) and (3.5) are accepted for which k, determined by eq. (3.7), is an integer.

Our use of the periodicity of the bulk crystal for tackling the possible lack of 2-dimensional periodicity for a general slice has the additional advantage that it helps ensure that the slice maintains stoichiometry. This is an important consideration in the Hartman–Perdok scheme.

4. Validation of the computer code

We checked the newly developed computer code for reliability by testing it for a large number of crystals for which morphology data are available in the literature. We present here the comparison for one such crystal, namely β-succinic acid [18].

Table 3 gives a comparison of the calculated bulk cohesive energy, E_{cr}. Table 4 shows some results for a slice of the crystal parallel to (100). The slice is chosen to have a thickness $t_{100} = d_{100} = 5.516$ Å. The agreement is quite good.

5. Experimental

Using ultra-pure water, a slightly supersaturated solution of ZTS was prepared. The growth morphology of a crystal can be a weak or strong function of temperature. This is partly because the coordinates of atoms, as also the interactions among them, change with temperature. Therefore, we carried out the test growth of ZTS crystals at a specific temperature. Since the atomic coordinates used by us for computing cohesive energies were determined at room temperature, we chose the growth temperature for our experiment as 28 °C. A seed crystal was dipped in the supersaturated solution, and it was left to grow by slow evaporation of the solvent. Figure 2 shows the crystal after three weeks of growth. Its morphology indicates the polar nature of the point group determined by the crystal structure.

Table 3. Calculation of E_{cr} (kcal/mol). Comparison of our results with those of Clydesdale *et al* [18].

	Our results	Results of ref. [18]
Coulomb term	−13.25	−13.26
Short-range term	−18.93	−17.58
Total ($= E_{cr}$)	−32.18	−30.84

Table 4. Calculation of E_{slice} (kcal/mol) for the (100) face of β-succinic acid, and comparison with the results of Clydesdale *et al* [18].

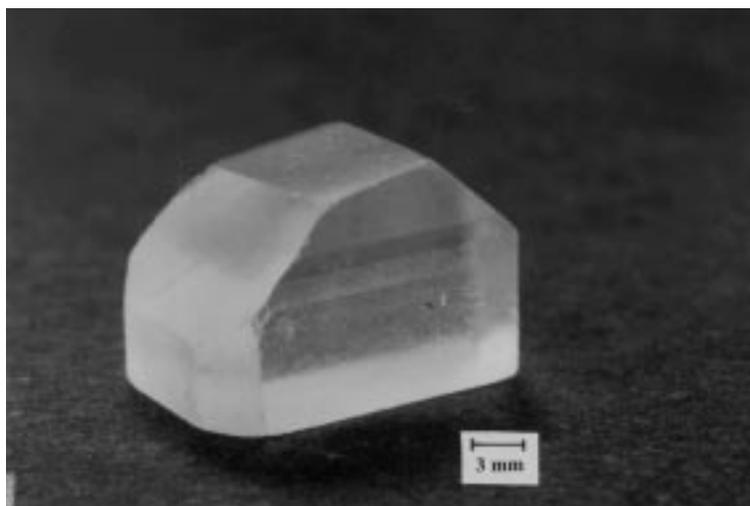|	Our results	Results of ref. [18]
$E_{Coulomb}$	0.368	0.366
$E_{shortrange}$	−10.424	−10.239
E_{slice}	−10.055	−9.874
E_{att}	−22.125	−20.967

Figure 2. Photograph showing the experimental growth morphology of a crystal of ZTS.

Table 5. Cohesive energy E_{slice}, and attachment energy E_{att}, for the various habit faces of ZTS.

Face index (hkl)	E_{slice} (kcal/mol)	E_{att} (kcal/mol)
1 0 0	−337.46	−119.75
1 1 0	−243.08	−214.13
0 1 0	−240.88	−216.32
0 1 2	−279.03	−178.17
0 0 1	−253.18	−204.02
2 0 1	−278.36	−178.84

6. Theoretical results

Cohesive energy E_{cr} was calculated for ZTS. It was assumed that ZTS exists in aqueous solution as ZT and sulphate ions. The calculated value of E_{cr} is −457.2 kcal/mol.

The cohesive energy for the various habit faces was also calculated, and, using eq. (2.1), the attachment energy E_{att} was deduced. Table 5 shows the results.

Figure 3 shows the computed growth morphology of ZTS, which was drawn by taking the distance of each habit face as proportional to E_{att}. The agreement with experiment is quite satisfactory, in the sense that the broad features of the observed morphology are reproduced. Admittedly, one reason why we are able to reproduce even the*polar* nature of the morphology is that only those faces were included in the computed morphology which are observed experimentally.
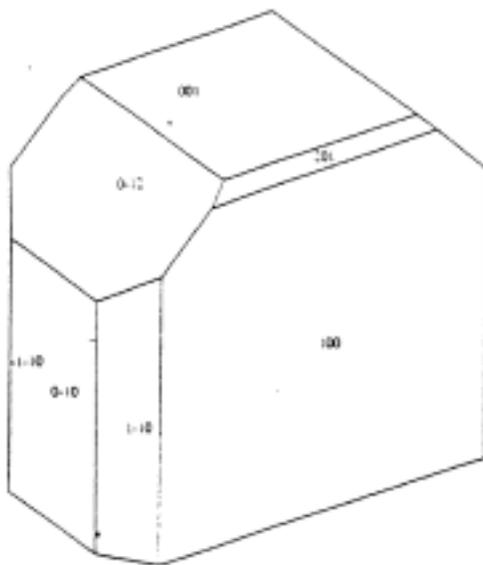
Figure 3. Theoretical growth morphology of ZTS.

7. Conclusion

The growth morphology of ZTS crystals, grown from aqueous solution at natural pH, can be explained in terms of the Hartman–Perdok formalism, taking the inverse of the attachment energy as a measure of the morphological importance of a habit face.

Our work also shows that the basic mechanism of growth of a ZTS crystal involves ZT and sulphate ions as the growth units.

A sophisticated computer code was developed for carrying out these calculations.

In the work reported here we have avoided reference to the PBC (periodic bond chain) analysis [7] of the crystal structure. This is a rather complex problem for the present case, work on which is in progress in our laboratory. Details will be published in due course. The work reported here shows that one can reproduce the main features of the observed morphology of ZTS without recourse to PBC analysis. Preliminary PBC analysis shows that some of the morphologically important faces of ZTS are actually 'S-faces', rather than 'F-faces'. Their high morphological importance must therefore be explained in terms of appropriate site-blocking mechanisms.

Acknowledgements

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