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THE USE OF MOMENTS OF MOMENTUM TO ACCOUNT FOR CRYSTAL HABITS

by

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ABSTRACT

A 3-step theory of crystal growth is proposed which involves first an association of molecules or ions in solution to form an impinging growth unit, then second the orientation of this unit prior to its impact on the surface of a crystal, and finally the attachment of this unit to the crystal face. From this theory the habit of a crystal is dependent upon the moments of momentum of the impinging growth unit. The results of sample calculations are presented for sodium chloride, succinic acid, sucrose, and chromium boride. The faces predicted by this proposed theory are compared with those predicted by other, energy-based calculations and with those experimentally observed.

The proposed theory suggests alternative strategies for crystallization and habit modification which may be of technological importance.

Listings of the two computer programs that were used are provided in Appendix B.

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INTRODUCTION

Crystal habits are economically important as well as being scientifically useful for understanding the crystallization process. In commerce, many high volume solids such as sodium chloride and sucrose are sold in crystalline form. In electroplating, the success of a metallic deposit often depends upon the crystal form of that deposit. In the electronic high technology fields, the properties of semiconductors such as silicon and gallium arsenide are dependent upon crystal purity and habit. In medicine, the crystal habit and in vivo growth of crystals such as urea and weddellite are important in diseases such as gout and kidney stones. Since the properties of materials often depend upon crystal structures, an understanding of the crystallization process itself and the various factors that influence this process are important.

There have been a number of proposals made for understanding the crystallization process and the resulting crystal habit. An early, empirical method presented by J.D.H. Donnay and D. Harker (1) simply observes that crystal faces are usually the ones that have large interplanar spacings in the unit cells. The area of importance of a crystal face is proportional to the reciprocal of the interplanar spacing of each face as is summarized in relationship 1 below.

$$A_{hkl} \propto 1/d_{hkl} \tag{1}$$

Other more sophisticated methods of accounting for crystal habits have been developed based on Gibbs' principle that the crystal habit is the one with a minimum in surface energy (2,3). Typical of these is the molecular theory of crystal growth which determines the importance of crystal faces from minima in free energies. Thermodynamics, molecular dynamics, Monte Carlo calculations, computer simulations, and graph theory (topology) with and without kinks, steps, and surface roughening have all been used to estimate crystal habits and growth (4-18). The Periodic Bond Chain (PBC) method of P. Hartman and W. G. Perdok (19,20) is typical of this type of calculation. Most of these methods assume that molecules are adsorbed from solution onto a crystal face and that the habit regulating event is the incorporation of the adsorbed species into the crystal. Such methods have been used to calculate equilibrium crystal habits in such compounds as sucrose, chromium boride, succinic acid, biphenyl, and weddellite (21-27). These methods focus attention on the bonding in a crystal or microcrystallite as the most important factor governing crystal growth. Much of what happens in crystal growth, however, occurs in solution during diffusion to the growing crystal.

PROPOSED THEORY

A 3-step, kinetically based theory of crystal growth is proposed to offer an alternative to the existing thermodynamically and statistically based ones. The first step is the association of molecules and ions in solution to form an impinging growth unit. The largest size of this unit is the crystallographic unit cell; but the actual impinging growth unit is expected to be smaller than this, since in most unit cells atoms and ions are shared among several adjacent unit cells. The formulation of this growth unit is a function of the degree of saturation, which in turn is dependent upon solvent, temperature, and ionic strength of the solution. Any proposed growth unit must, of course, be a chemically reasonable association of ions or molecules that can geometrically build up the entire structure. Intermolecular forces can enhance the association process that originiates in the solution. This association step is assumed to be a rapid process which quickly attains equilibrium as indicated in figure 1 and the following seven equations.

Step #1: Association

$$nA + mB \underset{k_{-1}}{\overset{k_1}{\Longleftrightarrow}} AnBm\ (\text{random}) \qquad (2)$$

If the association quickly attains equilibrium, the previous equilibrium approximation can be made for the reaction in equation 2 above, and the following six equations can be obtained:

$$k_{-1}[A_nB_m\ (\text{random})] = k_1[A]^n[B]^m \qquad (3)$$

$$[A_nB_m\ (\text{random})] = (k_1/k\text{-}1)\ [A]^n[B]^m \qquad (4)$$

where

$$k_1 = A_1 \exp\ (-\ \Delta G^{\neq}_1)/kT \qquad (5)$$

and

$$k_{-1} = A_{-1} \exp\ (-\ \Delta G^{\neq}_{-1})/kT$$

thus

$$(k_1/k_{-1}) = (A_1/A_{-1}) \exp\ [-(\ \Delta G^{\neq}_1\ -\ \Delta G^{\neq}_{-1})/kT] \qquad (6)$$

From this it follows that

$$[A_nB_m\ (\text{random})] = (A_1/A_{-1}) \exp\ [(-E_a)/kT]\ [A]^n[B]^m \qquad (7)$$

where

$$E_a = [\ \Delta G^{\neq}_1 - \Delta G^{\neq}_{-1}] \qquad (8)$$

The concentration of the impinging growth unit is thus given by equation 7 and is a function of the solute concentration, the temperature, the activation energies, and other factors such as molecular geometry which are summarized in the pre-exponential factors, A_1 and A_{-1}. The unit formed, A_nB_m, is randomly oriented in the solution unless the geometry or conditions of crystallization impose a preferred orientation. Such an imposition may occur in gel growth and in MOCVD systems which have streaming reactant solutions in which solute concentrations are inhomogeneous.

There is some experimental evidence that these impinging units exist in solution. The existence of large molecular associations is accepted for colloids, and there is evidence that aggregations occur on smaller scales as reported by J. J. Burton (28,29), M. Hoare and P. Pal (30-32), and D. Bonchev, O. Mekenyan, and H. Fritsche (33).

Two simplifying assumptions are made at this point in the proposed theory. It is assumed that growth units do not change during or after attachment to the growing crystal face, and as such they have the same molecular arrangement in solution immediately prior to impact that they have within the crystal after incorporation. It is further assumed that only one type of impinging growth unit occurs in a given solution.

Step #2: Orientation

This randomly oriented unit must migrate from the bulk of the solution to the face of the growing crystal; and while migrating, this unit must acquire the correct orientation so that upon impact with the crystal it can attach. This second, orienting step is assumed to be the rate determining one.

$$A_nB_m \text{ (random)} \underset{k_{-2}}{\overset{k_2}{\Longleftrightarrow}} A_nB_m \text{ (oriented)} \tag{9}$$

The following equations are a consequence of the above reaction step:

$$k_2[A_nB_m \text{ (random)}] = k_{-2} [A_nB_m \text{ (oriented)}]_{hkl} \tag{10}$$

$$[A_nB_m \text{ (oriented)}]_{hkl} = (k_2/k_{-2}) [A_nB_m \text{ (random)}] \tag{11}$$

$$[A_nB_m \text{ (oriented)}]_{hkl} = (k_2/k_{-2}) (A_1/A_{-1}) \exp (-E_a/kT) [A]^n[B]^m \tag{12}$$

The rate of growth-unit disorientation depends upon the moments of momentum of the migrating, impinging growth unit. It is assumed that

$$k_{-2} = c/J_{hkl} \tag{13}$$

where c is a constant of proportionality and J_{hkl} is the moment of momentum of the impinging growth unit about the axis through the center of mass perpendicular to the hkl-plane. The larger this moment of momentum the less easily the impinging growth unit will be moved away from the hkl-orientation needed for the proper impact, and thus the faster will be the growth of the corresponding face. Each hkl-direction and each molecular association has a different rate constant for disorientation, k_{-2}. In equation 13, however, it is assumed that this difference in rate constants is due only to the difference in moments of momentum about each hkl-axis. Thus, the constant of proportionality, c, in this equation is the same for each orientation. As a consequence, equation 12 can be rewritten.

$$[A_nB_m \text{ (oriented)}]_{hkl} = (k_2/c) (A_1/A_{-1}) \exp (-E_a/kT)(J_{hkl}) [A]^n[B]^m \tag{14}$$

From equation 14, the concentration of the correctly oriented, impinging growth unit is dependent upon its angular momentum. When this moment of momentum is small, the concentration of the impinging growth unit having the correct orientation for subsequent attachment and growth also will be small. Crystal faces that grow slowly are the ones that are observed ultimately to be the main facets of the crystal habit, since fast growing faces grow themselves out of existence. Thus, axes having the smallest moments of momentum in the impinging growth unit will be the same ones observed as facets in the resulting crystal.

Step #3: Attachment

The third step of this theory is the actual attachment of the correctly oriented impinging growth unit onto the growing face.

$$A_nB_m \text{ (oriented) } \overset{k_3}{\underset{k_{-3}}{\Longleftrightarrow}} A_nB_m \text{ (attached)} \qquad (15)$$

The energies of the intermolecular bonds formed in the crystal are larger than the association or orientation energies of the growth unit in solution; and the rates of this third step have been assumed to be faster than the preceeding two steps, since the second step was considered to be the rate determining one. During crystal growth, a crystal can grow only as fast as correctly oriented material arrives at the growing surface, and all material is incorporated into a crystal upon reaching a growing surface. During dissolution of a crystal, however, the situation is different. The energy of attachment in this third step may be the rate determining one during dissolutions, since the bonds holding the units into the crystal must first be broken before material can be carried away from the surface.

As a consequence of reaction 15, the following two kinetic equations can be obtained.

$$[A_nB_m\ (\text{attached})]_{hkl} = (k_3/k_{-3})\ [A_nB_m\ (\text{oriented})]_{hkl} \tag{16}$$

$$[A_nB_m(\text{attached})]_{hkl} = (k_3/k_{-3})(k_2/c)(A_1/A_{-1})\ \exp(-E_a/kT)(J_{hkl})[A]^n[B]^m \tag{17}$$

The ratio of the rate constants, k_3/k_{-3}, for the attachment step is dependent upon the strength and energy of that attachment, which is a function of the number and strength of the bonds holding the unit to the growing face. This ratio is a function of the particular hkl-face being considered. Although ratios of rates for the forward and reverse reactions of different faces are not necessarily equal, it greatly simplifies the subsequent calculations if one assumes that these k_3/k_{-3} ratios for the different hkl-faces are approximately equal. Because of this approximation this theory will be used to order crystal faces only among those faces which the Periodic Bond Chain (PBC), Burton, Cabrera, and Frank (BCF), or other energy-based theories have indicated are faces in which there are strong intermolecular forces of attraction to hold the added units to the crystal and are thus faces for which one may assume that the orientation step is rate determining. If all possible impinging unit orientations were considered, rather than just limiting the calculations to those orientations with favorable energies for attachment, one could easily obtain misleading results. Some high order planes may be found which have favorable moments of momenta indicating that the concentration of these orientations are small and that the corresponding faces should be dominant in the crystal. However, it does little good to find planes of favorable momenta if upon impacting on the crystal surface the energies do not favor attachment. In such cases the principal assumption of this proposed theory has been violated, and the orientation step (step #2) is no longer the rate determining one.

The rate of growth of a face, R_{hkl}, is proportional to the concentration of the attached, correctly oriented impinging growth units.

$$R_{hkl} = k_4 \, [A_nB_m \text{ (attached)}]_{hkl} \tag{18}$$

$$R_{hkl} = (k_4)\,(k_3/k_{-3})\,(k_2/k)\,(A_1/A_{-1}) \exp(-E_a/kT)\,(J_{hkl})\,[A]^n[B]^m \tag{19}$$

$$R_{hkl} = K \exp(-E'_a/kT)\,(J_{hkl})\,[A]^n[B]^m \tag{20}$$

The above three equations have a constant of proportionality, k_4, which is needed primarily to convert from units suitable for concentrations to those suitable for rate of growth. The differences in rates of attachment among the various hkl-faces have been considered above in the discussion of step #3. Consequently, k_4 is not dependent upon the hkl-direction being considered.

Since slowly growing crystal faces are the ones that ultimately have the greatest areas, the area of a particular face, A_{hkl}, is proportional to R_{hkl}^{-1}, and

$$A_{hkl}/A_{hkl}' = R_{hkl}'/R_{hkl} \tag{21}$$

where the primed factors are those for the most prominent hkl-face.

Thus, by equation 21, the ratio of areas of crystal faces should be proportional to the inverse ratio of the rate of growth and thus inversely proportional to the moments of momentum about the axes in the impinging growth units. A ratio parameter, Γ_{hkl}, is defined in equation 22.

$$\Gamma_{hkl} = A_{hkl}/A_{hkl}' = J'_{hkl}/J_{hkl} \qquad (22)$$

SAMPLE CALCULATIONS

By equation 22 the relative surface areas of crystal faces could be calculated from the moments of momentum of the impinging growth units. The calculation involves a computation of the moments of momentum about axes for several expected impinging growth units. These growth units should be reasonable molecular associations derived from the crystallographic unit cell. The same set of possible crystal faces considered by other theories will be considered in this paper. The moments of momentum will be used to rank the planes in order of expected importance for each model. A summary table is presented for each of the four compounds used as examples in this paper. The tables give the J-values, Γ-values, the order of the most prominent faces predicted by other theories of crystal growth as well as the experimentally observed order.

The calculations were performed using two programs written in BASIC and run on an IBM-PC computer. Listings of the programs is given in Appendix B. The first program calculates the direction cosines of the vectors through the center of mass about which the moments of inertia are computed for each hkl-plane of the assumed growth unit, and the second program calculates the moments of momentum using equation 23. A derivation of equation 23 is given in Appendix A.

$$J_{hkl} = (MU)\ \Sigma_{i=1}^{n}(M_l)[(x_i)^2 + (2/5)(r_i)^2] \qquad (23)$$

Since literature summaries of observed crystal habits list only the most prominent crystal faces in a qualitative manner, quantitative analysis was not possible. The tables summarize the experimentally observed order of facet prominence as reported in the literature. Plus marks are used in the tables to indicate the extent of predominance if such information is available from the literature.

The calculated values of the moments of momentum were obtained from equation 23 with the value of the multiplier factors, MU, selected to scale each calculation to the same number of atoms or ions as found in the unit cell. The values of Γ_{hkl} were calculated by dividing each moment of momentum into the smallest value calculated for that trial impinging unit, as indicated by equation 22.

Sodium Chloride, NaCl:

Table 1 summarizes the results for the calculations of the moments of momentum for several impinging growth units for the sodium chloride structure. The impinging growth units are illustrated and labeled in figure 2. The crystal structure is the rock salt one with a = 0.563 nm (34).

From this table and accompanying figure, the impinging unit that likely associates in solution prior to impact and growth consists of the simple association of Na^+ and Cl^- ions into $(NaCl)_1$ units. As the degree of association increases (100) and (111) are more likely faces to appear. The associated growth unit consisting of 2 Na^+ and 2 Cl^- ions arranged in a plane as $(NaCl)_2$ is the structure used for model B in table 1 and illustrated in figure 2. Model D consists of exactly half the unit cell with an even greater degree of association and favors the (111) faces.

The moments of momentum for a few higher order faces were also calculated in Table 1. These terms all have large moments of momentum, which is in agreement with the observation that higher order faces are not common in crystals.

A. Julig and B. Deprick have observed that the (110) faces appear and become more predominant as the degree of supersaturation increases in aqueous sodium chloride solutions containing glycine (35). As the degree of supersaturation increases one would anticipate a greater degree of association, and this theory predicts that (110) faces should become more likely, as the degree of association increases from model A to model B in table 1. Julig and Deprick also observed that (110) faces become less likely at any degree of supersaturation as the pH of the solution deviated from the isoelectric point of glycine. Buffers and electrostatic charges in solution can alter the degree of association and thus the resulting habit.

Sodium chloride has been subjected to extensive studies to ascertain the effects of various additives on the resulting crystal habits (36). These studies conclude that selective adsorption of the additive onto crystal faces is the *modus operandi*. This could still be the mechanism under the theory proposed in this paper; but the proposed theory would allow for two further mechanisms for crystal habit modification. Altered habits could result from the attachment of the additive to the associated impinging growth unit while it is in solution. Such an attachment would alter the moments of inertia of this unit; or, the additive substance could alter the solution properties enough to cause a change in the size and shape of the impinging growth unit thus also altering its moments of momentum and thereby the resulting crystal habit.

The work of J. D. Birchall and R. J. Davey (36) on the effects of polysaccharides on the crystallization of sodium chloride suggests that the polymer adsorbs on the crystal surfaces and on the heterogeneous nucleation sites in solution. The theory presented in this paper suggests that the role of polymers in altering the rheological properties of solution should be considered also, especially since they conclude that "the polysaccharides are most active in influencing nucleation and growth when in chain extended configurations." This is just the configuration in which polymer solutions have the most altered rheological properties.

Succinic Acid, $C_4H_6O_4$:

J. S. Broadley, D. W. J. Cruickshank, J. D. Morrison, J. M. Robertson (FRS), and H. M. M. Shearer reported the refined crystal structure of β-succinic acid in 1959 (37). Using their data, the moments of momentum and the Γ_{hkl}-values for β-succinic acid were calculated by the programs described in this report. The results are summarized in Table 2, and the various impinging growth units considered are illustrated in Figure 3. Impinging units B, C, and E, consisting of molecules oriented along the c-axis, agree with the experimental observation that (001) is the most prominent face (24). These are reasonable molecular associations, since the c-axis is also the direction for hydrogen bonding in succinic acid. Model D has (010) predicted as its most favored face.

The PBC analysis done according to the calculation method of Hartman and Perdock by R. J. Davey, J. W. Mullin, and M. J. L. Whiting (24) indicated that (110) should be the most pronounced face, but as they noted this is not in agreement with the observation that (001) is observed to be the most prominent face. The proposed theory of this paper using model C predicts that (001) should be the face with the largest area and that the next face should be the (1,1,-1). The third most favored face in this model should be (110). This ordering of faces is in better agreement with the experimentally observed order of (001)>>(010)>(11-1)>(110) than is the ordering predicted by the PBC method.

Impinging unit B emphasizes the ionic intermolecular forces at the ends of the molecule parallel to the c-axis. A review of the gamma values for this model in Table 2 indicate that this model may overemphasize the (001) face in the anticipated crystal habit. Nevertheless, Davey, Mullin, and Whiting (24) observed that the crystals of succinic acid become needle-like when grown out of isopropanol. This solvent has a smaller dipole moment than water, and perhaps the theory of this paper would suggest that isopropanol encourages the formation of another, competing impinging growth unit such as B, which is expected to favor more greatly the formation of the (001) face.

Sucrose, $C_{12}H_{22}O_{11}$:

Using the crystal structure of sucrose reported by George M. Brown and Henri A. Levy (38), the values for J_{hkl} and Γ_{hkl} were computed and summarized in Table 3 and figure 4.

D. Aquilano, M. Franchini-Angela, M. Rubbo, G. Mantovani, and G. Vaccari (21) observed the disagreement between the rates of growth predicted by a PBC analysis which they did using the methods of Hartman and Perdok and the experimental data for sucrose. From Table 3, impinging growth unit B agrees with the reported observation that the prominent face of sucrose is the (001) face. It is interesting to note that both the PBC calculation of Aquilano et al. and the BCF calculation of Saska and Myerson assign a low value to the (001) face, yet this is an experimentally observed one. Saska and Myerson conclude that "The agreement of the calculated growth form with observed habits is fairly good and the reduction of the growth velocity in the c-axis direction [which is likely due to the preferential water adsorption on the (001) face] would result in an excellent agreement with the observed forms." [Page 554 of (22)]. The moment of momentum calculations predict the most prominent face and some of the other experimentally observed ones for sucrose without recourse to adsorption of water onto one of the faces.

Chromium Boride, CrB:

Using the data cited by R. Hamar and S. Hamar-Thibault (23), the moments of momentum for the faces for which they calculated the energies with a PBC calculation are summarized for several impinging growth units in Table 4. Various impinging growth units considered in these calculations are illustrated in Figure 5.

From this table, impinging growth unit B agrees best with the observed crystal structure predicting not only that the faces (010) and (130) should be most pronounced but that they should both be about equal in surface area. This seems to be the observed order of preferred faces as reported by Hamar and Harmar-Thibault (23). Unit B in figure 5 has the two chromium and the two boron atoms arranged in a pseudotetrahedron.

DISCUSSION AND CONCLUSIONS

A 3-step theory of crystal growth has been presented in this report. The steps of association, orientation, and attachment occur in that order during crystallization with the orientation step being the rate determining one. From this, a working hypothesis results by which the relative areas of facets of crystals can be predicted from the calculated moments of momentum of the associated, impinging growth unit using the Γ_{hkl} of equation 22.

The qualitative results of the moment of momentum calculations for several impinging growth units in the crystal structures of sodium chloride, succinic acid, sucrose, and chromium boride are compared with the observed order of importance of crystal faces. From this comparison, it is possible to select a chemically reasonable impinging growth unit that agrees with the observations. This theory allows for events occurring in solution to contribute to regulating crystal growth. Crystal habits may not be only a consequence of the thermodynamics of the solid.

This proposed theory also provides alternative explanations for the mode of action of modifiers of crystal habits. Additive substances can adsorb onto the face of growing crystals as advocated by existing theories of crystal growth, but two additional modes are possible in the theory of this paper. The additives can adsorb onto the associated, impinging growth unit while it is still in solution and in this way modify the moments of momenta of this unit and thereby the resulting crystal habit. The additives can also modify the properties of the solution such as its viscosic or electrolytic properties to induce the formation of an altered impinging unit which will have different moments of momenta and an altered crystal habit.

The results of calculations on four crystals have been summarized in tables and figures. The results of this theory are as good as the predictions made by other methods. The method easily allows for the possibility of quantitative comparisons and more detailed refinements of the structures of impinging growth-units when relative crystal face areas are available from experiments.

The modified model of crystal growth encouraged by this theory also suggests technological improvements in methods of crystal growth. Crystals of preferred orientations may be obtained if one is able to encourage the formation of appropriate associated, impinging growth-units in solution prior to crystallization. Such considerations may affect the growth of simple and compound semiconductors allowing desired crystal orientations to be more easily obtained. For example, large-area crystalline silicon from the catalytic decomposition of silicon compounds may be more easily obtained by selecting the decomposing compound or the gas flow conditions to encourage the formation of appropriate impinging growth-units. Similar considerations may assist in the growth of single crystals of GaAs in MOCVD systems and in epitaxial semiconductor growth studies.

The theory as presented assumes the existence of a unique impinging growth unit. In solutions there may be a statistical distribution of several impinging growth units. Also, the energies of attachment may alter the molecular arrangements within the growth units upon attachment. Thus, the molecules in the impinging growth unit need not have the same molecular arrangement as the final solid. Consideration of these two additional factors may improve quantitative agreement between predicted and observed crystal habits.

TABLE OF SYMBOLS

[A] and [B]	molar concentration of species A and B
A_i	pre-exponential factor in the rate constant expression
A_{hkl}	surface area of the hkl-face in a crystal
c	a constant of proportionality between the rate constant for disorientation and the moment of momentum
d_{hkl}	distance between hkl-planes in the crystal unit cell
E_a	activation energy for formation of impinging unit
$\Delta G_i^{\neq}$ and $\Delta G_{-1}^{\neq}$	free energy of activation for forward and reverse chemical reactions respectively
J_{hkl}	moment of momentum for molecular model rotated about an axis through the center of mass and perpendicular to the hkl-face
k	Boltzman's constant
k_i	kinetic rate constants for forward chemical reactions
k_{-1}	kinetic rate constants for reverse chemical reactions
K	a constant equal to $(k_4)(k_d/k_{-3})(k_2/c)(A_1/A_{-1})$
M_i	mass of atom i
MU	normalization factor for each model
r_i	covalent or ionic radius of atom i
R_{hkl}	rate of growth of the hkl-face
T	absolute temperature
x_i	perpendicular distance from the hkl axis of rotation to atom i
Γ_{hkl}	ratio of the area of an hkl-face to the area of the largest or most prominent face.

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APPENDIX 1: The Calculation of the Moment of Momentum

The moment of momentum for a collection of n particles is defined in physics texts (40) to be

$$\bar{J} = \sum_{i=1}^{n} \bar{x}_i \times m_i \bar{v}_i \tag{A1}$$

where x_i is the perpendicular vector from the i-th particle to the axis of rotation.

Since

$$\bar{v}_i = \bar{\omega} \times \bar{x}_i , \tag{A2}$$

it follows that

$$\bar{J} = \Sigma_i [m_i \, \bar{x}_i \times (\bar{\omega} \times x_i)] \tag{A3}$$

which contains a triple cross product made up of moments and products of inertia, which are terms having the forms given below:

$$I_{i,x} = \sum_i m_i \, (y_i^2 + z_i^2) \tag{A4}$$

and

$$P_{xy} = \Sigma_i \, m_i \, x_i \, y_i$$

In the case of an associated impinging unit, it is assumed to be a rigid collection of spherical atoms, each one of which has a uniform density. The contribution that each spherical atom makes to the total moment is small compared to that contributed by the rotation of these same atoms about the axis of rotation. This is because the distance from the axis of rotation, x_i, is large compared to the radius of each atom, r_i; and these distances enter the calculation squared. The contribution of each individual atom to the moment is given by

$$2/5\ m_i r_i^2 \tag{A5}$$

where m_i is the atomic mass of the i-th atom (40).

The contribution of each atom to the moment is the sum of its atomic component plus that arising by virtue of the rotation of this atom about the axis of rotation normal to the hkl-plane. The total moment for each atom is thus

$$J_{hkl,i} = m_i x_i^2 + 2/5 m_i\ r_i^2, \tag{A6}$$

where r_i is the atomic radius and x_i is the perpendicular distance from the i-th atom to the axis of rotation.

The total moment for the hkl-plane is the sum over all the atoms in the model being considered, or

$$J_{hkl} = \Sigma_i m_i [x_i^2 + 2/5 r_i^2] \tag{A7}$$

Since each model may have a different number of atoms, it is convenient to introduce a scale factor, MU, which scales the total moments to the number of atoms found in the crystallographic unit cell. This does not change the relative order or crystal faces within a model but does facilitate comparisons among models. As an example, if a model has four molecules while the crystallographic unit cell has only two, then the scale factor MU is 1/2. Thus,

$$J_{hkl} = (MU) \ \Sigma^{n}_{i-1}(M_1)[(x_i)^2 + (2/5)(r_i)^2] \qquad \text{(A8)}$$

Equation A8 is the same as equation 23 used in this report.

APPENDIX 2: Computer Program Listings Used for the Calculation of the Moments of Momenta

This appendix contains the listings of the computer programs used to calculate the moments of momenta described in this report. The first program computes the direction cosines to the normals of the selected crystallographic planes, and it computes the areas of those planes. The flow diagram for this program is given in figure 6.

The second program listed in this appendix uses the direction cosines computed for each crystallographic plane and the atomic positions of the model being considered to compute the moments of momenta. Lines beyond 2000 must be changed by the user for each space group and model. Use of this section eliminates the need to enter atomic parameters for atoms related by symmetry to the atoms of the first molecule entered. The flow diagram for this program is given in figure 7.

Program I: COMPUTABO SUPERFICIES

This program computes the direction cosines of the normals to selected crystallographic planes and calculates the areas of those planes.

```
100 REM PROGRAM=COMPUTABO SUPERFICIES by P.G. Barber, (c) 1984
110 REM Keysville, Virginia 23947
120 REM
130 DIM H(3),K(3),L(3),R(3,3),RP(3)
140 REM                                      *********data entry
150 PI=3.14159/180
160 INPUT "Do you wish the results printed (Y/N): ";Y$
170 INPUT "Enter unit cell lengths, a,b,&c: ";A,B,C
180 INPUT "Enter unit cell angles, alpha, beta, & gamma: ";AA,BA,CA
190 IF Y$="Y", THEN LPRINT "Unit Cell Parameters = "A;B;C;AA;BA;CA
200 AA=AA*PI:BA=BA*PI:CA=CA*PI
210 INPUT "Do you wish to enter coordinates of the points (Y/N): ";Z$
220 IF Z$<>"Y" THEN 270
230 INPUT "Enter coords of first point, h1,k1,l1: ";H(1),K(1),L(1)
240 INPUT "Enter coords of second point, h2,k2,l2:";H(2),K(2),L(2)
250 INPUT "Enter coords of third point, h3,k3,l3: ";H(3),K(3),L(3)
260 GOTO 410
270 INPUT "Enter Miller indices [hkl] of plane: ";HX,KX,LX
280 IF Y$="Y" THEN LPRINT "************************************---":LPRINT "   [hk
l] = "HX;KX;LX
290 FOR I=1 TO 3
300 H(I)=0!:K(I)=0!:L(I)=0!:NEXT I
310 IF LX<>0 THEN 370
320 IF HX<>0 THEN 350
330 IF KX=0 THEN PRINT "ERROR!! [hkl] all zero!!":GOTO 270 ELSE K(1)=1/KX:H(2)=1
:K(2)=1/KX:K(3)=1/KX:L(3)=1
340 GOTO 410
350 IF KX<>0 THEN H(1)=1/HX:K(2)=1/KX:H(3)=1/HX:L(3)=1 ELSE H(1)=1/HX:H(2)=1/HX:
K(2)=1:H(3)=1/HX:L(3)=1
360 GOTO 410
370 IF HX=0 GOTO 400
380 IF KX=0 THEN H(1)=1/HX:H(2)=1/HX:K(2)=1:L(3)=1/LX ELSE H(1)=1/HX:K(2)=1/KX:L
(3)=1/LX
390 GOTO 410
400 IF KX<>0 THEN H(1)=1:K(1)=1/KX:K(2)=1/KX:L(3)=1/LX ELSE L(1)=1/LX:K(2)=1:L(2
)=1/LX:H(3)=1:L(3)=1/LX
410 FOR I=1 TO 3
420 REM LPRINT H(I),K(I),L(I)
430 H(I)=H(I)*A:K(I)=K(I)*B*SIN(CA):L(I)=L(I)*C
440 AT=L(I)*COS(BA)
450 BT=L(I)*COS(AA)
460 CPS=AT*AT+BT*BT+2*AT*BT*COS(CA)
470 L   =SQR(L(I)*L(I)-CPS)
480 IF L(I)<0 THEN L(I)=-L ELSE L(I)=L
490 REM LPRINT H(I),K(I),L(I)
500 NEXT I
510 REM                                      *********calculate vectors
520 FOR I=2 TO 3
530 R(I,1)=H(I)-H(1):R(I,2)=K(I)-K(1):R(I,3)=L(I)-L(1)
540 NEXT I
550 R(1,1)=R(3,1):R(1,2)=R(3,2):R(1,3)=R(3,3)
560 REM                                      *********A x B=area
570 RP(1)=R(2,2)*R(1,3)-R(1,2)*R(2,3)
580 RP(2)=R(1,1)*R(2,3)-R(2,1)*R(1,3)
590 RP(3)=R(2,1)*R(1,2)-R(1,1)*R(2,2)
600 IF HX=0 OR IF KX=0 OR IF LX=0 THEN 620
610 FOR I=1 TO 3:RP(I)=RP(I)/2:NEXT I
620 AR=SQR(RP(1)*RP(1)+RP(2)*RP(2)+RP(3)*RP(3))
630 REM                                      *********print results
640 IF Z$<>"Y" THEN 680
650 INPUT "Is superficies triangular (Y/N): ";X$
```

```
660 IF X$="Y", THEN AR=.5*AR
670 GOTO 720
680 AR=.5*AR
690 IF HX=0 THEN AR=2*AR : GOTO 720
700 IF KX=0 THEN AR=2*AR : GOTO 720
710 IF LX=0 THEN AR=2*AR
720 PRINT
730 PRINT "Area of face bounded by points: "
740 FOR I=1 TO 3
750 PRINT H(I),K(I),L(I)
760 NEXT I
770 PRINT "                     is "AR" square Angstroms"
780 PRINT
790 PRINT "The vector perpendicular to the face is "
800 FOR I=1 TO 3:RP(I)=RP(I)/AR:NEXT I
810 PRINT "     N= "RP(1)"i + "RP(2)"j + "RP(3)"k"
820 PRINT
830 IF Y$<>"Y", GOTO 900
840 LPRINT :LPRINT "Area of face bounded by points: "
850 FOR I=1 TO 3:LPRINT H(I),K(I),L(I):NEXT I
860 LPRINT "                    is "AR" square Angstroms."
870 LPRINT :LPRINT "The vector perpendicular to the face is "
880 LPRINT "    N= "RP(1)"i + "RP(2)"j + "RP(3)"k"
890 LPRINT
900 INPUT "Another superficiei calculation (Y/N): ";X$
910 IF X$="Y", THEN 210
920 END
```

Program II: MOMENTA MOMENTORUM

This program computes the moments of momentum for a collection of atoms about normals to selected crystallographic planes.

```
100 REM PROGRAM = MOMENTA MOMENTORUM by P. G. Barber
110 REM (c) Keysville, VA 23947, March 1984
120 REM ************************* Set-up and input data, limited to <=200 atoms**

130 ND=200
140 DIM H(ND),K(ND),L(ND),D(ND),M(ND),MU(ND),R1(ND),R2(ND),R3(ND)
150 DIM RR(ND),RN(ND),IN(ND),AW(ND),AR(ND),S$(ND),A$(ND)
160 PI=180/3.14159
170 PRINT "PROGRAM: Momenta Inertiae by P.G. Barber, (c)1984"
180 INPUT "Enter Y if you wish to print the results: ";Y$
190 INPUT "Enter D if you wish disc input of structure: ";Y1$
200 IF Y1$="D", THEN GOSUB 1150
210 INPUT "Enter title";T$
220 INPUT "Enter unit cell lengths, a,b,&c:";A,B,C
230 INPUT "Enter unit cell angles, alpha,beta,&gamma:";AA,BB,CC
240 INPUT "Enter number of atoms:";N
250 INPUT "Enter number of types of atoms:";NT
260 FOR I=1 TO NT
270 PRINT "For atom type # "I:INPUT " Enter atomic symbol,atomic weight, and ato
mic radius";S$(I),AW(I),AR(I):NEXT I
280 CLS:PRINT:PRINT
290 PRINT "################################################"
300 PRINT USING "         \                              \";T$
310 PRINT "################################################"
320 PRINT "A= "A"     B= "B"     C= "C
330 PRINT "alpha= "AA"    beta= "BB"    gamma= "CC
340 PRINT "Number of atoms= "N
350 FOR I=1 TO NT:PRINT "Atom # "I" is "AS$(I)" with wt ="AW(I)" and radius ="AR
(I):NEXT I
360 INPUT "Are these values correct (Y/N)?";X$
370 IF X$<>"Y", GOTO 210
380 IF Y$="Y", THEN GOSUB 940
390 AA=AA/PI:BA=BB/PI:CA=CC/PI
400 IF Y1$="D", THEN GOSUB 1400
410 FOR I=1 TO N
420 PRINT "Enter [hkl] for atom #"I;:INPUT HT,KT,LT
430 H(I)=HT*A:K(I)=KT*B:L(I)=LT*C
440 PRINT "Enter type number for atom # "I;:INPUT J
450 PRINT "Enter multiplier of atom #"I;:INPUT MU(I)
460 M(I)=AW(J):D(I)=AR(J):A$(I)=S$(J)
470 PRINT :PRINT
480 PRINT "                     *** atom #"I" is  "A$(I)"  ***"
490 PRINT "[hkl]= "HT,KT,LT
500 PRINT "mass= "M(I)" g/mole"
510 PRINT "multiplier= "MU(I)
520 PRINT "atomic radius= "D(I)" Angstroms"
530 PRINT
540 INPUT "Are these values correct (Y/N)?";X$
550 IF X$<>"Y" GOTO 420
560 IF Y$="Y", THEN GOSUB 1050
570 NEXT I
580 INPUT "Enter Y if you wish to store data as file: ";Y2$
590 IF Y2$="Y", THEN GOSUB 1400
600 INPUT "Enter the {hkl} vector:";Q1,Q2,Q3
610 INPUT "Enter [hkl] for origin:";HT,KT,LT
620 H(0)=HT*A:K(0)=KT*B:L(0)=LT*C
630 INPUT "Enter [hkl] for terminum:";HT2,KT2,LT2
640 H2=HT2*A:K2=KT2*B:L2=LT2*C
650 PRINT "For vector {hkl} = ";Q1,Q2,Q3
660 PRINT "Axis is from [hkl]= "HT,KT,LT
670 PRINT "          to [hkl]= "HT2,KT2,LT2
680 INPUT "Are these coordinates correct (Y/N)?";X$
```

```
690 IF X$<>"Y",GOTO 610
700 IF Y$="Y", THEN GOSUB 1010
710 REM ************************ Calculation ***********************************

720 IT=0!:IP1=0:IP2=0:IP3=0
730 R1(0)=H2-H(0):R2(0)=K2-K(0):R3(0)=L2-L(0)
740 DR=SQR(R1(0)*R1(0)+R2(0)*R2(0)+R3(0)*R3(0)+2*R1(0)*R2(0)*COS(CA)+2*R1(0)*R3(
0)*COS(BA)+2*R2(0)*R3(0)*COS(AA))
750 R1(0)=R1(0)/DR:R2(0)=R2(0)/DR:R3(0)=R3(0)/DR
760 FOR I=1 TO N
770 R1(I)=H(I)-H(0):R2(I)=K(I)-K(0):R3(I)=L(I)-L(0)
780 RR(I)=R1(I)*R1(I)+R2(I)*R2(I)+R3(I)*R3(I)+2*R1(I)*R2(I)*COS(CA)+2*R2(I)*R3(I
)*COS(AA)+2*R1(I)*R3(I)*COS(BA)
790 RN(I)=R1(I)*R1(0)+R2(I)*R2(0)+R3(I)*R3(0)+R2(I)*R1(0)*COS(CA)+R3(I)*R1(0)*CO
S(BA)+R1(I)*R2(I)*COS(CA)+R3(I)*R2(0)*COS(AA)+R1(I)*R3(0)*COS(BA)+R2(I)*R3(0)*CO
S(AA)
800 IN(I)=MU(I)*M(I)*(.4*D(I)*D(I)+RR(I)-RN(I)*RN(I))
810 IT=IT+IN(I)
820 P1=MU(I)*M(I)*R1(I)*R2(I):P2=MU(I)*M(I)*R2(I)*R3(I):P3=MU(I)*M(I)*R1(I)*R3(I
)
830 IP1=IP1+P1:IP2=IP2+P2:IP3=IP3+P3
840 REM LPRINT I,RR(I),RN(I),P1,P2,P3
850 REM LPRINT R1(I),R2(I),R3(I),DR
860 NEXT I
870 PRINT T$,"I= ";IT
880 PRINT "P(xy) =  ";IP1; "P(yz) =  ";IP2; "P(xz) =  ";IP3
890 IF Y$="Y", THEN GOSUB 1110
900 INPUT "Do you wish another calculation of I (Y/N):";Z1$
910 IF Z1$="Y" THEN GOTO 600
920 GOTO 1460
930 REM ****************************** Print Out Initial Input Data ************

940 LPRINT "###############################################"
950 LPRINT USING "          \                              \";T$
960 LPRINT "###############################################"
970 LPRINT "A= "A"     B= "B"     C= "C
980 LPRINT "alpha= "AA"    beta= "BB"     gamma= "CC
990 FOR I=1 TO NT:LPRINT "Atom # "I" is "AS$(I)" with wt ="AW(I)" and radius ="A
R(I):NEXT I
1000 RETURN
1010 LPRINT :LPRINT "   XXXXXXX  MOMENT OF INERTIA ABOUT {hkl}="Q1;Q2;Q3"   XXXX
XXX"
1020 LPRINT USING "Axis from [hkl]=+#.#### +#.#### +#.#### to [hkl]=+#.#### +#.#
### +#.####";HT,KT,LT,HT2,KT2,LT2
1030 LPRINT "                   is"
1040 RETURN
1050 LPRINT "                   ****  atom #"I"  ****"
1060 LPRINT "[hkl]= "HT,KT,LT
1070 LPRINT "mass= "M(I)" g/mole"
1080 LPRINT "multiplier= "MU(I)
1090 LPRINT "atomic radius= "D(I)" Angstroms"
1100 RETURN
1110 LPRINT ;;; "I = "IT:LPRINT "P(xy)=";IP1;"P(yz)=";IP2;"P(xz)=";IP3
1120 REM LPRINT "I of atom #"I" = "IN(I)
1130 RETURN
1140 REM *********************** Disc Input of Data ****************************

1150 INPUT "Enter data file name: ";F$
1160 OPEN F$ FOR INPUT AS #1
1170 INPUT #1, T$:INPUT #1,A,B,C,AA,BA,CA,N,NT
1180 FOR I=1 TO N:INPUT #1,H(I),K(I),L(I),M(I),MU(I),D(I),A$(I):NEXT I
```

```
1190 REM *******************To Subroutine to expand with sym. related atoms****
1200 REM GOSUB 2000
1210 IF Y$<>"Y",THEN GOTO 1370
1220 REM *********************** Disc Input Print Out ************************

1230 LPRINT :LPRINT "#########################################################"
1240 LPRINT USING "          \                              \";T$
1250 LPRINT "#########################################################":LPRINT
1260 LPRINT "Disc entry of data from data file #: "F$
1270 LPRINT "a = "A"b = "B"c = "C
1280 LPRINT "alpha = "(AA*PI)" beta = "(BA*PI)" gamma = "(CA*PI)
1290 LPRINT N" atoms entered in structure."
1300 LPRINT "*** atom # ***            [hkl]        mass       mu    D(A)"
1310 V$=" ### \   \ +##.#### +##.#### +##.####   ###.###  #.##  #.##"
1320 INPUT "Enter multiplier factor:";P
1330 FOR I=1 TO N:MU(I)=MU(I)*P:NEXT I
1340 FOR I=1 TO N
1350 LPRINT USING V$;I,A$(I),H(I)/A,K(I)/B,L(I)/C,M(I),MU(I),D(I)
1360 NEXT I
1370 RETURN 600
1380 FOR I=1 TO N:MU(I)=MU(I)*P:NEXT I
1390 RETURN 610
1400 INPUT "Enter data disc file name: ";F1$
1410 OPEN F1$ FOR OUTPUT AS #2
1420 PRINT #2,T$:PRINT #2,A,B,C,AA,BA,CA,N,NT
1430 FOR I=1 TO N:PRINT #2,H(I),K(I),L(I),M(I),MU(I),D(I),A$(I):NEXT I
1440 CLOSE#2
1450 RETURN
1460 END
2000 REM *******************Subroutine expands input data set*******************

2010 REM *******************Change as needed for space group or model**********
2020 H(N+1)=H(1)+A/2:K(N+1)=K(1):L(N+1)=L(1)+C/2:H(N+2)=H(2)+A/2:K(N+2)=K(2):L(N
+2)=L(2)-C/2
2030 N=2*N
2040 H(N+1)=H(1):K(N+1)=K(1):L(N+1)=L(1)+C:H(N+2)=H(2)+A/2:K(N+2)=K(2):L(N+2)=L(
2)+C/2
2050 N=N+2
2060 H(N+1)=H(1)+A:K(N+1)=K(1):L(N+1)=L(1)+C:H(N+2)=H(2)+A:K(N+2)=K(2):L(N+2)=L(
2):H(N+3)=H(1)+A:K(N+3)=K(1):L(N+3)=L(1)
2070 N=N+3
2080 FOR I=10 TO 18
2090 H(I)=H(I-9)     :K(I)=K(I-9)+B/2:L(I)=L(I-9)
2100 M(I)=M(I-8):MU(I)=MU(I-8):D(I)=D(I-8):A$(I)=A$(I-8)
2110 NEXT I
2120 N=N+9
2130 FOR I=19 TO 27
2140 H(I)=H(I-18):K(I)=K(I-18)+B:L(I)=L(I-18):M(I)=M(I-18):MU(I)=MU(I-18):D(I)=D
(I-18):A$(I)=A$(I-18)
2150 NEXT I
2160 N=N+9
2170 FOR I=3 TO 27 STEP 2
2180 M(I)=M(1):MU(I)=MU(1):D(I)=D(1):A$(I)=A$(1)
2190 M(I+1)=M(2):MU(I+1)=MU(2):D(I+1)=D(2):A$(I+1)=A$(2)
2200 NEXT I
2210 GOTO 2330
2220 REM *************************** Subroutine to select ions*****************
2230 H(1)=H(3):K(1)=K(3):L(1)=L(3):M(1)=M(3):MU(1)=MU(3):D(1)=D(3):A$(1)=A$(3)
2240 H(2)=H(4):K(2)=K(4):L(2)=L(4):M(2)=M(4):MU(2)=MU(4):D(2)=D(3):A$(2)=A$(4)
2250 H(3)=H(10):K(3)=K(10):L(3)=L(10):M(3)=M(10):MU(3)=MU(10):D(3)=D(10):A$(3)=A
$(10)
```

```
2260 H(4)=H(11):K(4)=K(11):L(4)=L(11):M(4)=M(11):MU(4)=MU(11):D(4)=D(11):A$(4)=A
$(11)
2270 H(5)=H(16):K(5)=K(16):L(5)=L(16):M(5)=M(16):MU(5)=MU(16):D(5)=D(16):A$(5)=A
$(16)
2280 H(6)=H(17):K(6)=K(17):L(6)=L(17):M(6)=M(17):MU(6)=MU(17):D(6)=D(17):A$(6)=A
$(17)
2290 H(7)=H(21):K(7)=K(21):L(7)=L(21):M(7)=M(21):MU(7)=MU(21):D(7)=D(21):A$(7)=A
$(21)
2300 H(8)=H(24):K(8)=K(24):L(8)=L(24):M(8)=M(24):MU(8)=MU(24):D(8)=D(24):A$(8)=A
$(24)
2310 H(9)=H(12):K(9)=K(12):L(9)=L(12):M(9)=M(12):MU(9)=MU(12):D(9)=D(12):A$(9)=A
$(12)
2320 N=9
2330 RETURN
```

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Table 1
Summary of Calculations for Sodium Chloride

	MODEL A		MODEL B		MODEL C		MODEL C		EXPERIMENTALLY OBSERVED
hkl	J_{hkl}	Γ_{hkl}	J_{hkl}	Γ_{hkl}	J_{hkl}	Γ_{hkl}	J_{hkl}	Γ_{hkl}	
100	661	0.33	682	0.86	1403	1.00	1523	0.78	
010	661	0.33	1145	0.51	2593	0.54	1523	0.78	{100}
001	219	1.00	682	0.86	1403	1.00	1681	0.71	
110	661	0.33	914	0.64	1998	0.70	1523	0.78	[SOMETIMES {111} WITH ADDITIVES PRESENT]
101	440	0.50	583	1.00	1403	1.00	1311	0.91	
011	440	0.50	914	0.64	1998	0.70	1311	0.91	
111	514	0.43	771	0.76	1800	0.78	1187	1.00	
201	573	0.38	603	0.97	1403	1.00	1322	0.90	
210	661	0.33	775	0.75	1641	0.85	1523	0.78	
102	307	0.71	603	0.97	1403	1.00	1417	0.84	
211	587	0.37	693	0.84	1601	0.88	1258	0.94	
112	366	0.60	654	0.84	1601	0.88	1240	0.96	
301	617	0.36	623	0.94	1403	1.00	1364	0.87	
310	661	0.33	728	0.80	1522	0.92	1523	0.78	
311	621	0.35	670	0.87	1511	0.93	1326	0.90	
321	630	0.35	772	0.76	1743	0.80	1326	0.90	
PREDICTED PROMINENT FACE	{100}		{110}		{NONE}		{111}		

Table 2
Summary of Calculations for -Succinic Acid

hkl	MODEL A Jhkl	MODEL A Γhkl	MODEL B Jhkl	MODEL B Γhkl	MODEL C Jhkl	MODEL C Γhkl	MODEL D Jhkl	MODEL D Γhkl	MODEL E Jhkl	MODEL E Γhkl	MODEL F Jhkl	MODEL F Γhkl	PBC Calcn[24]	Experimentally aqueous	Observed[24] isopropanol
1 1 0	1032	1.00	3458	0.07	3512	0.44	2586	0.54	5064	0.66	3662	0.81	(1)	(4)+	
0 1 0	1448	0.71	4333	0.06	4701	0.33	1408	1.00	4660	0.72	5314	0.56	(2)	(2)+	(2)+
0 0 1	1536	0.67	242	1.00	1540	1.00	3359	0.42	3359	1.00	3702	0.80	(3)	(1)+++	(1)+++
0 2-1	1068	0.97	3149	0.08	3270	0.47	2084	0.68	4286	0.78	3652	0.81	(4)		
1 1-1	1108	0.93	1435	0.17	1963	0.78	3076	0.46	3929	0.85	2956	1.00	(5)	(3)+	
1 0 0	1892	0.55	2494	0.10	3598	0.43	3733	0.38	5439	0.62	5439	0.54	n.a.		
PREDICTED PROMINENT FACE	{110}		{001}		{001}		{010}		{001}		{11-1}		{110}	{001}	{001}

Table 3
Summary of Calculations for Sucrose

hkl	MODEL A		MODEL B		MODEL C		MODEL D		MODEL E		PBC[21]	BCF[22]		Experimentally Observed	
	Jhkl	Γhkl	Jhkl	Γhkl	Jhkl	Γhkl	Jhkl	Γhkl	Jhkl	Γhkl				ref. 21	ref. 22
1 1 0	3492	0.32	5840	0.49	777	0.94	3126	0.36	3241	0.37	(2)++	(2)	(1)		(2)++
1 0 0/2 0 0	2971	0.37	5259	0.54	1114	0.66	3402	0.33	2089	0.57	(3)+	(1)	(2)	(1)++	(3)++
1-1 1	1113	1.00	2924	0.97	1433	0.51	3269	0.34	2695	0.44		(3,4)	(3)		
1 1 1	3311	0.34	5122	0.56	732	1.00	2543	0.44	3221	0.37		(3,4)	(4)		(6)
-11 1	3344	0.33	4681	0.61	1117	0.66	2454	0.46	1198	1.00	(4)	(5)			
0 0 1	2848	0.39	2848	1.00	1125	0.65	1125	1.00	2844	0.42		(10)		(2)	(1)++
1 0 1	1919	0.58	3355	0.85	1156	0.63	2592	0.43	3274	0.37		(8)			(7)
0 1 1	3504	0.32	4678	0.61	875	0.84	2049	0.55	2042	0.59	(7)	(6)			
1 1-1	3240	0.34	4577	0.62	1019	0.72	2356	0.48	3017	0.40	(5)	(7)			
0-1 1	2025	0.55	3199	0.89	1250	0.59	2423	0.46	3266	0.37	(6)	(9)		(4)	
1 0-1	3536	0.31	4446	0.64	1096	0.67	2007	0.56	1971	0.61		(11)		(5)	(5)+
0 1 0	2679	0.42	5088	0.56	998	0.73	3406	0.33	2454	0.49					
1-1 0	2159	0.52	4507	0.63	1334	0.55	3682	0.31	1302	0.92	(1)++			(3)	(4)+
PREDICTED PROMINENT FACE	{1-11}		{001}		{111}		{001}		{-111}		{1-10}	{100},	{110}	{100}	{001}

Table 4
Summary of Calculations on Chromium Boride

	MODEL A		MODEL B		MODEL C		MODEL D		MODEL E			
hkl	Jhkl	Γhkl	Jhkl	Γhkl	Jhkl	Γhkl	Jhkl	Γhkl	Jhkl	Γhkl	PBC[23]	Experimentally Observed
0 1 0	127	1.00	358	1.00	401	0.68	266	0.56	816	0.34	1.000 (1)	(1)++
1 1 0	223	0.57	452	0.79	371	0.73	411	0.36	460	0.60	1.446	
0 2 1	166	0.77	515	0.70	359	0.76	498	0.30	762	0.36	1.595	
1 1 1	255	0.50	577	0.62	272	1.00	750	0.20	599	0.46	1.372 (3)	(3)+
1 3 0	147	0.86	376	0.95	363	0.75	148	1.00	389	0.70	1.263 (2)	(2)++
0 4 1	139	0.91	412	0.87	370	0.74	334	0.44	697	0.39	1.421	
1 3 1	162	0.78	475	0.75	309	0.88	265	0.56	274	1.00	1.400	
1 0 0/2 0 0	319	0.40	546	0.66	498	0.55	1290	0.11	1882	0.15	1.395 (4)	
0 0 1/0 0 2	319	0.40	506	0.71	501	0.54	1429	0.10	2301	0.12	1.509	
0 1 1/0 2 2	223	0.57	592	0.60	374	0.73	847	0.17	1120	0.24	1.553	
1 0 1	319	0.40	526	0.68	363	0.75	1359	0.11	1818	0.15	n.a.	
PREDICTED PROMINENT FACE	{010}		{010}		{111}		{130}		{131}		{010}	{010}

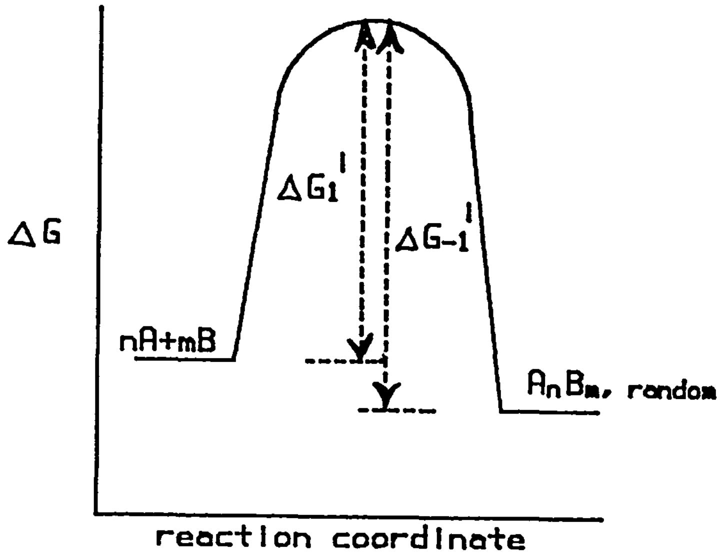
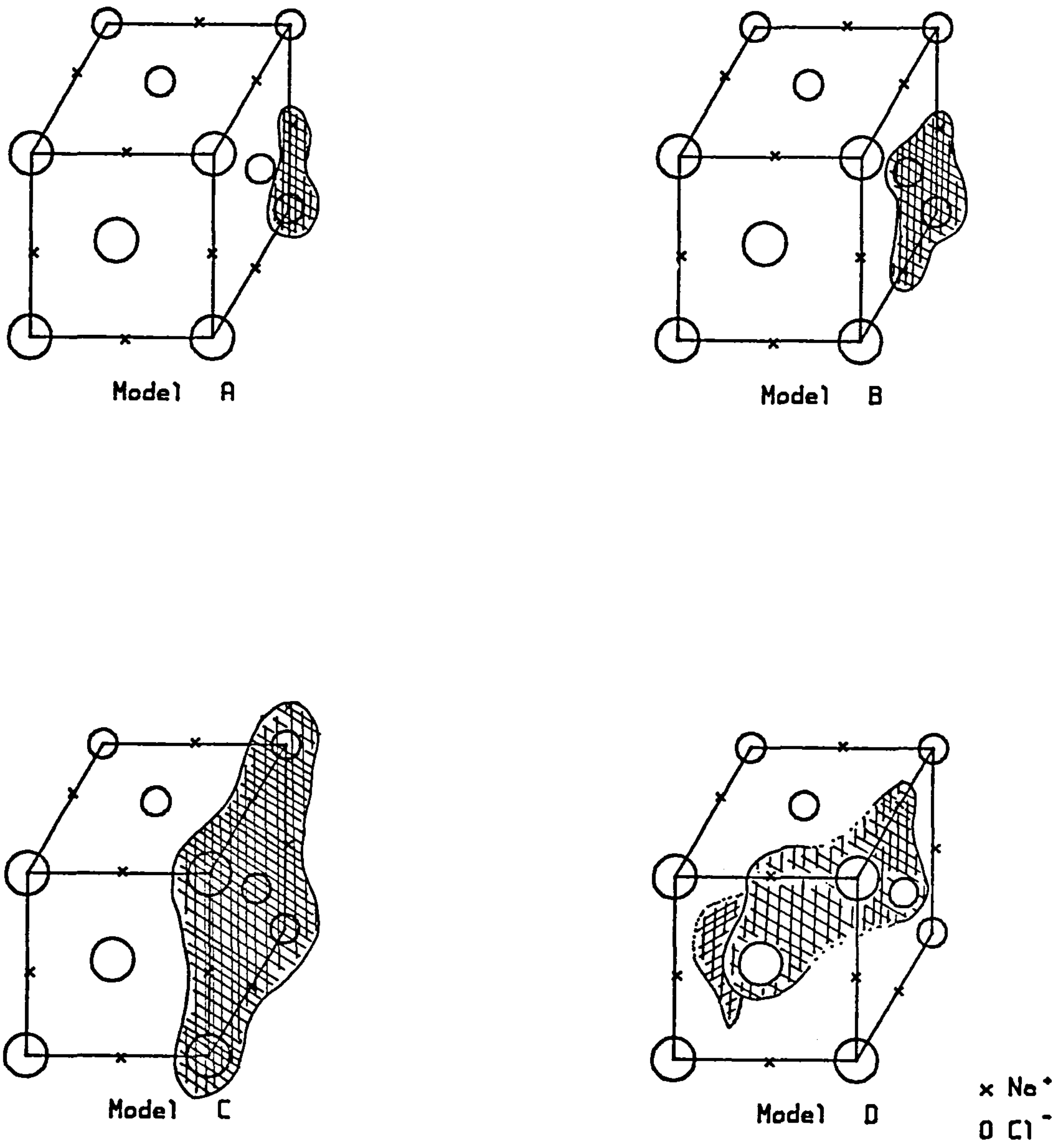


Figure 1: Reaction Coordinate Diagram for the Association Step



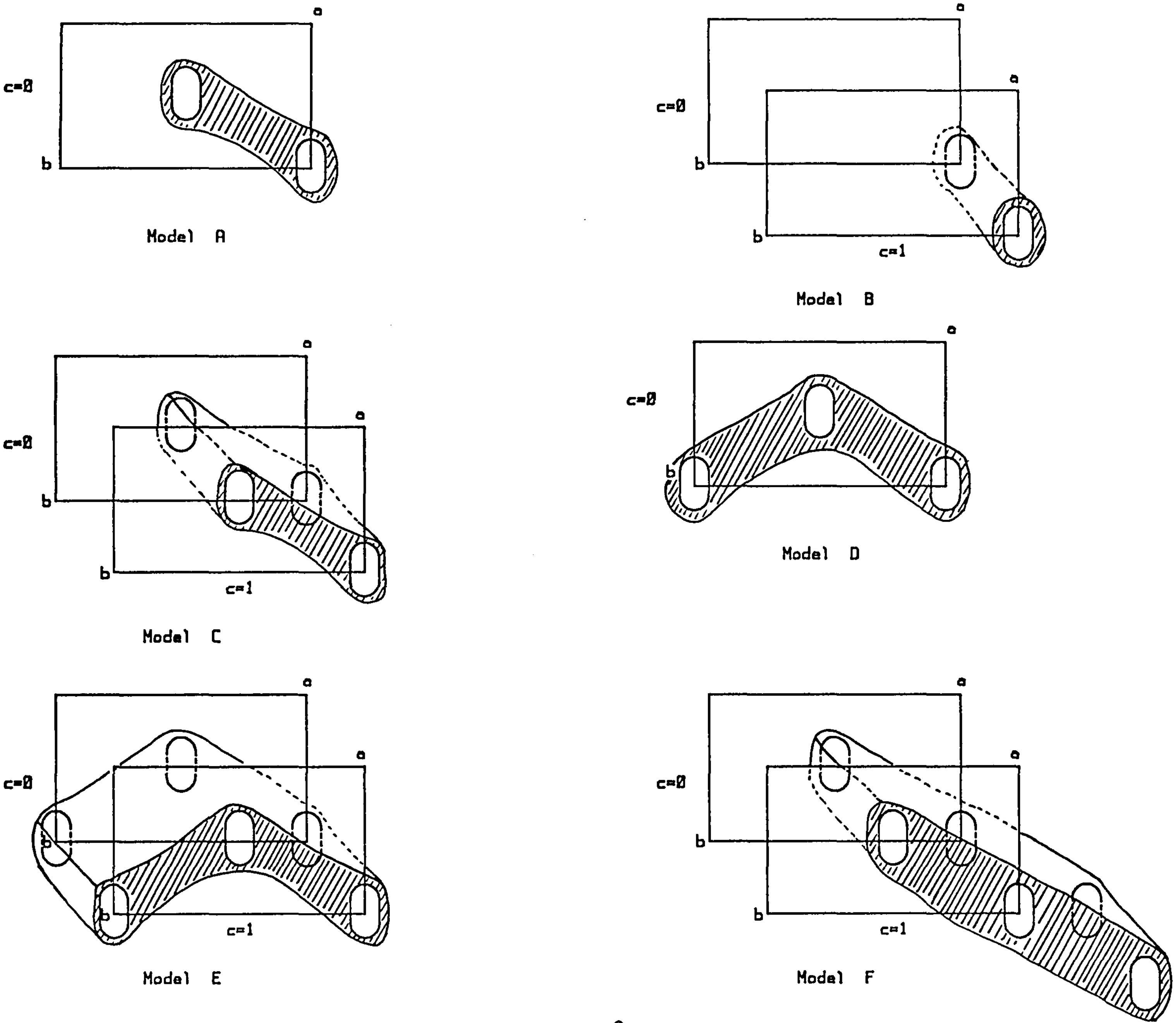
Model A

Model B

Model C

Model D

Figure 2: Trial Structures Used for Sodium Chloride



Model A

Model B

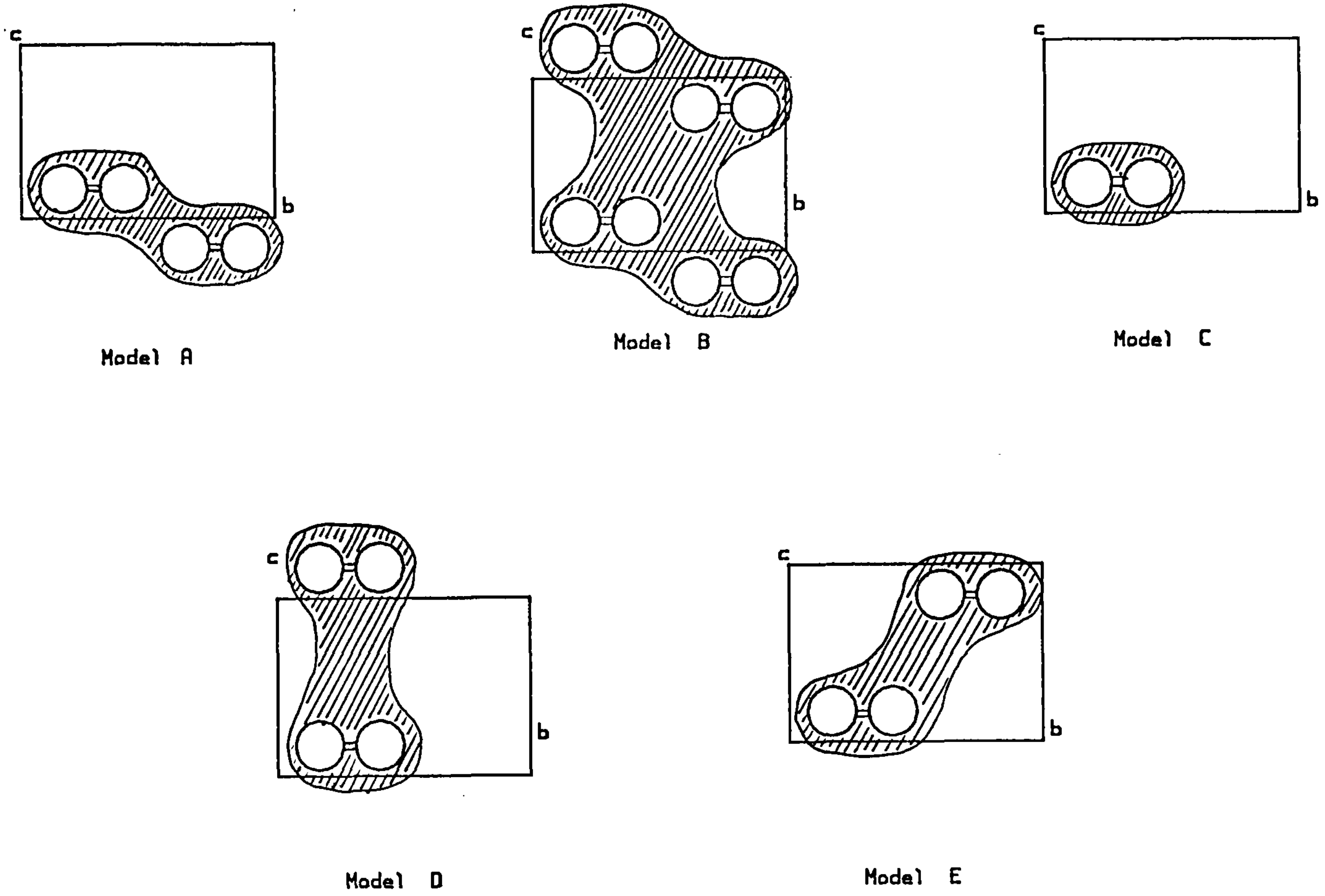
Model C

Model D

Model E

Model F

Figure 3: Trial Structures Used for β-Succinic Acid



Model A

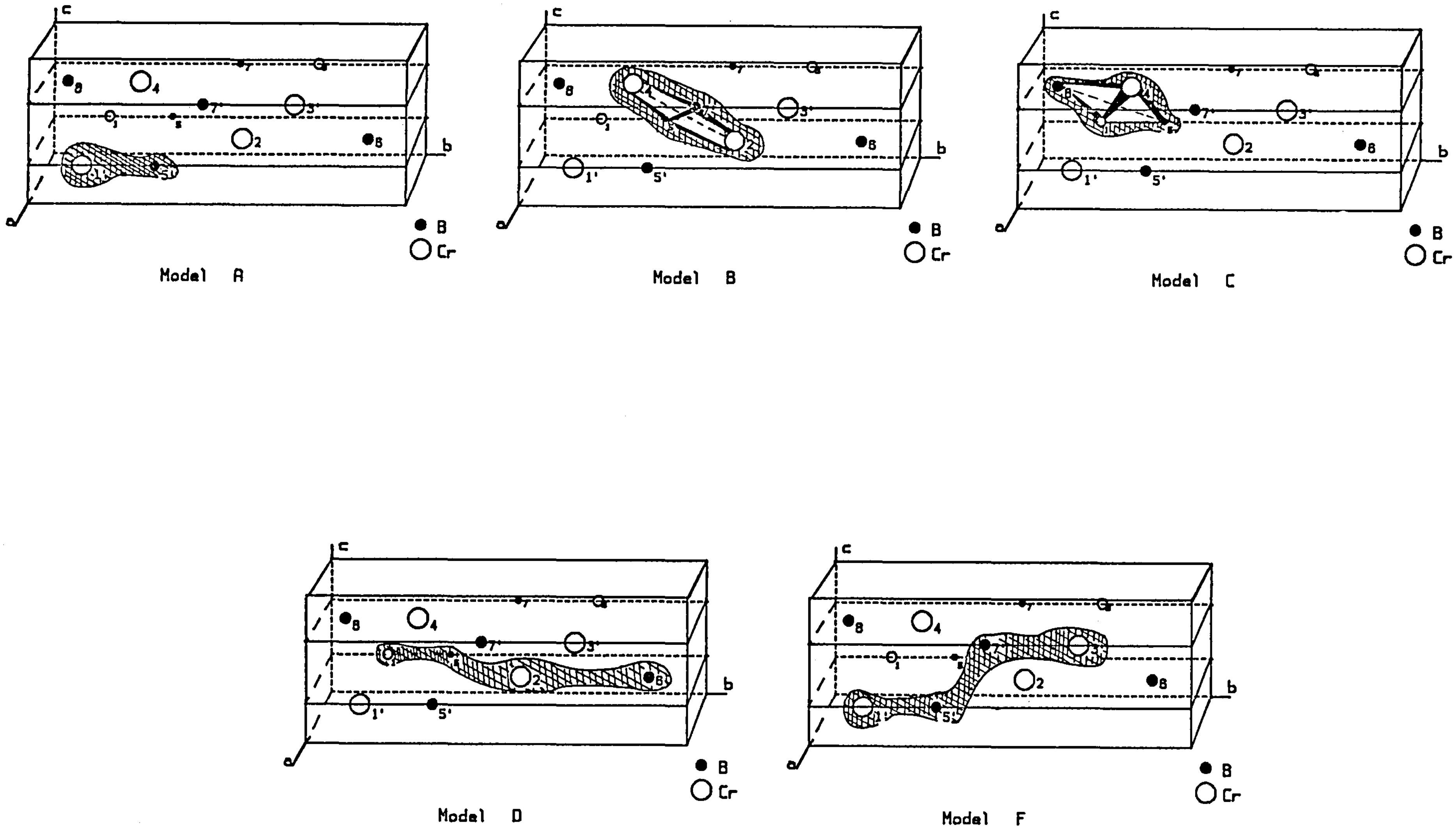
Model B

Model C

Model D

Model E

Figure 4: Trial Structures Used for Sucrose



Model A

Model B

Model C

Model D

Model F

Figure 5: Trial Structures Used for Chromium Boride

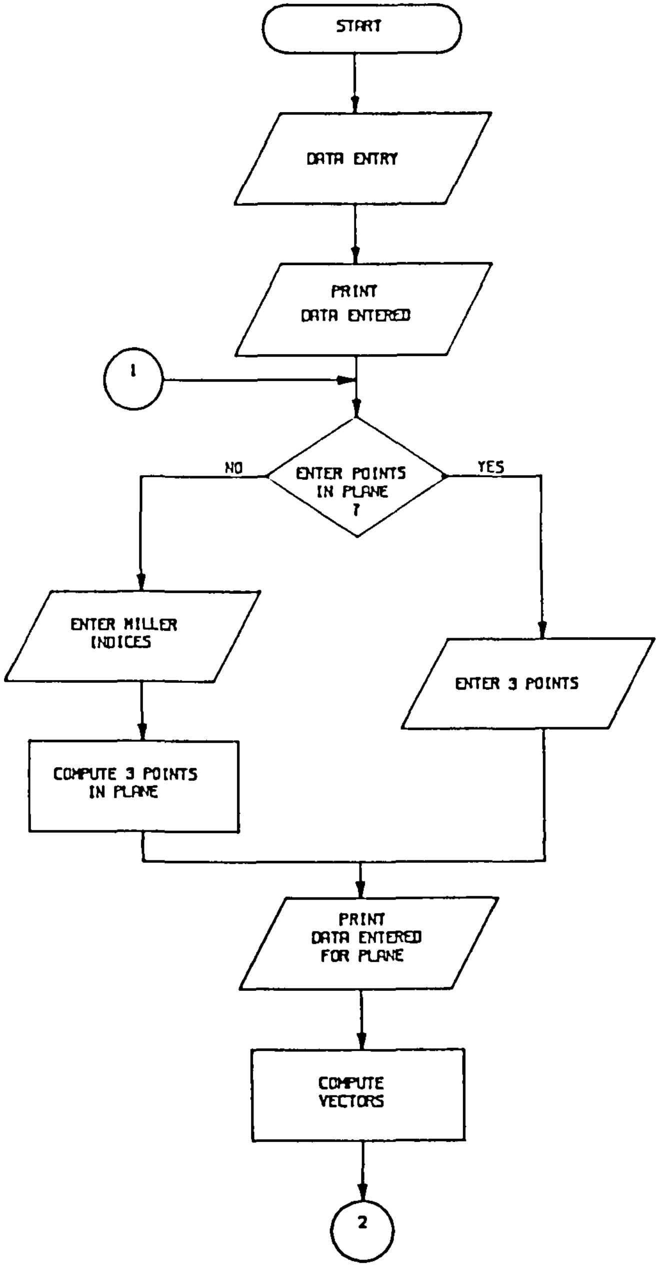


Figure 6: flowchart for program Computabo Superficies, page 1

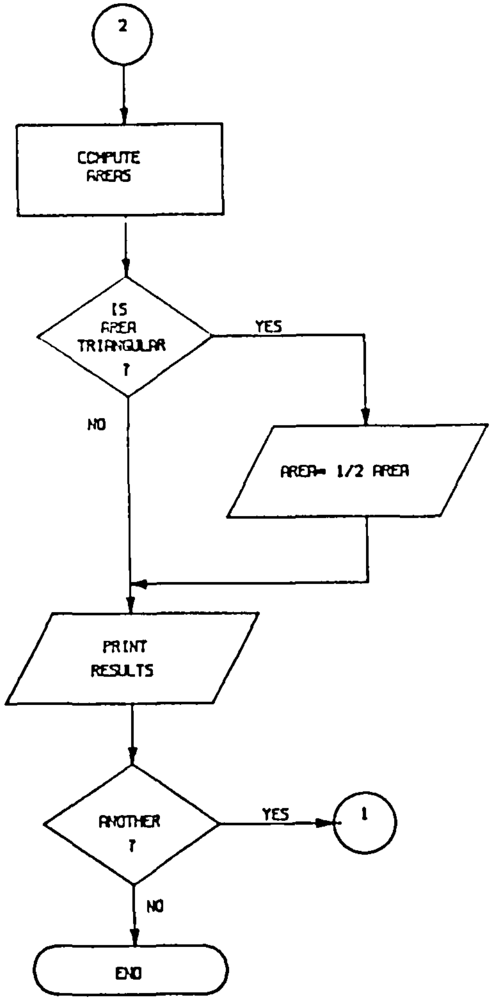
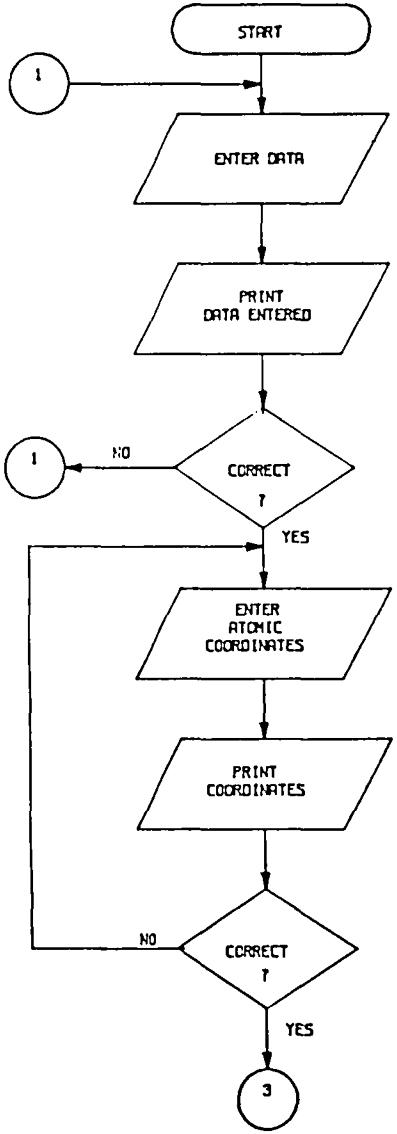


Figure 6: flowchart for program Computabo Superficies, page 2



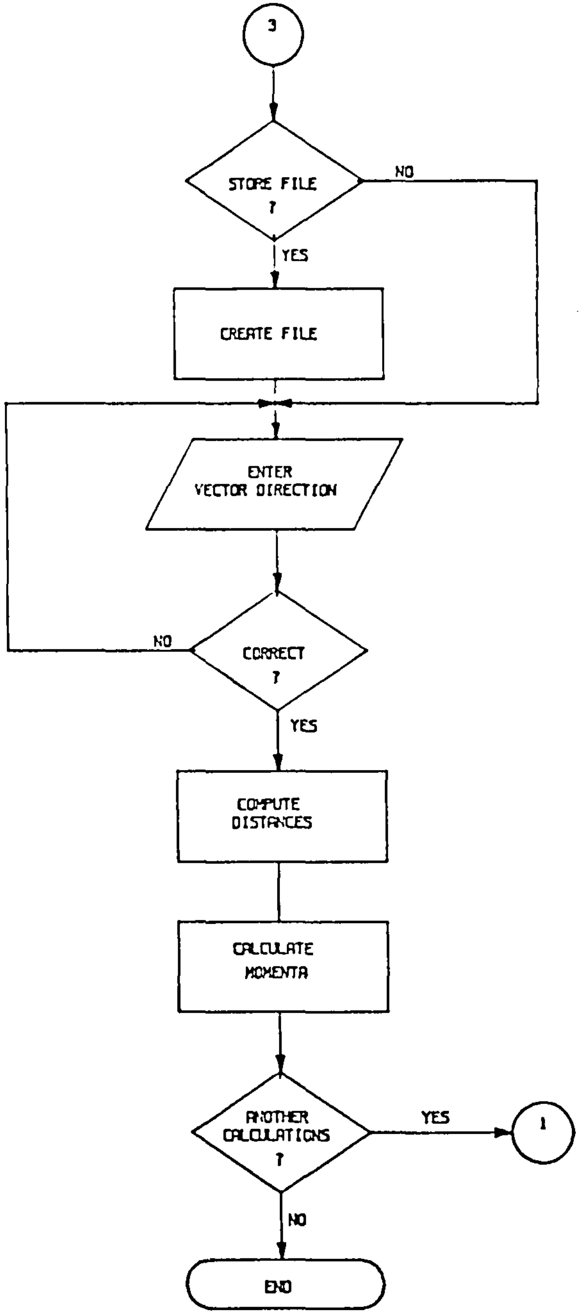


Figure 7: flowchart for program Momenta Momentorum, page 1

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15. Supplementary Notes

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16. Abstract

A 3-step theory of crystal growth is proposed which involves first an association of molecules or ions in solution to form an impinging growth unit, then second the orientation of this unit prior to its impact on the surface of a crystal, and finally the attachment of this unit to the crystal face. From this theory the habit of a crystal is dependent upon the moments of momentum of the impinging growth unit. The results of sample calculations are presented for sodium chloride, succinic acid, sucrose, and chromium boride. The faces predicted by this proposed theory are compared with those predicted by other, energy-based calculations and with those experimentally observed.

The proposed theory suggests alternative strategies for crystallization and habit modification which may be of technological importance.

Listings of the two computer programs that were used are provided in Appendix B.

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