Inferring planar disorder in close-packed structures via ε-machine spectral reconstruction theory: Structure and intrinsic computation zinc sulphide

D. P. Varn,† G. S. Canright‡ and J. P. Crutchfield†§

†Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Straße 38, 01187 Dresden, Germany, ‡Santa Fe Institute, 1399 Hyde Park Road, Santa Fe, New Mexico 87501, USA, †Department of Physics and Astronomy, University of Tennessee, 1408 Circle Drive, Knoxville, Tennessee 37996, USA, §Telenor Research and Development, 1331 Fornebu, Oslo, Norway, and †Computational Science & Engineering Center & Physics Department, University of California, Davis, One Shields Avenue, Davis, California 95616, USA. Correspondence e-mail: dpvarn@pks.mpg.de, geoffrey.canright@telenor.com, chaos@cse.ucdavis.edu

We apply ε-machine spectral reconstruction theory to analyze structure and disorder in four recently published zinc sulphide diffraction spectra and contrast the results with the most common alternative theory, the fault model. In each case we find that the reconstructed ε-machine provides a more comprehensive and detailed understanding of the stacking structure, often detecting stacking structures not previously found. Using the ε-machines reconstructed for each spectrum, we calculate a number of physical parameters—such as configurational energies, configurational entropies, and hexagonality—and several quantities—including statistical complexity and excess entropy—that describe the intrinsic computational properties of the stacking structures.

Keywords: x-ray diffraction; diffuse scattering; one-dimensional disorder; polytypes; planar faults; zinc sulphide; computational mechanics.

1. Introduction

In several previous papers (Varn et al., 2002; Varn et al., 2005a; Varn et al., 2005b) we presented a novel technique for the discovery and description of planar disorder in close-packed structures (CPSs): ε-machine spectral reconstruction theory (εMSR or “emissary”). We showed that the technique allows one to build the unique, minimal, and optimal model (an ε-machine) of a material’s stacking structure from diffraction spectra. In this sequel we demonstrate the technique using diffraction spectra from single crystals of disordered, polytypic zinc sulphide (ZnS). Since the discovery of polytypism in mineral ZnS crystals (Frondel & Palache, 1948; Frondel & Palache, 1950), much theoretical and experimental effort has been expended to understand this phenomenon (Steinberger, 1983; Mardin, 1986; Sebastian & Krishna, 1994).

ZnS is an attractive system to study for a number of reasons:

(i) Simplicity of the unit cell and stacking rules. While many materials are known to be polytypic (Trigunayat, 1991; Sebastian & Krishna, 1994), the constituent modular layers (MLs) (Varn & Canright, 2001) can have a complicated structure and complex stacking rules (Brindley, 1980; Thompson, 1981; Varn & Canright, 2001). For instance, in ideal micas there are more than a dozen atoms in a unit cell, and there are six ways two MLs can be stacked. Kaolins and cronstedtites present even more complexity (Varn & Canright, 2001). In contrast, ZnS is simple in the extreme: its basis is composed of but two atoms—a zinc and a sulphur (Sebastian & Krishna, 1994). They are arranged in a double close-packed hexagonal net, with one species displaced relative to the other by a quarter body diagonal (as measured by the conventional unit cubic cell) along the stacking direction (Shaw & Heine, 1990). We take this double close-packed layer to be a ML (Varn & Canright, 2001). The stacking of MLs proceeds as for all CPSs; namely, there are three absolute orientations each ML can occupy—call them A, B, and C—with the familiar stacking constraint that no two adjacent MLs have the same orientation.

(ii) Complex polytypism. ZnS is one of the most polytypic substances known with over 185 identified crystalline structures (Mardin, 1986; Trigunayat, 1991; Sebastian & Krishna, 1994). Of these, only about a dozen fairly short-period polytypes (up to 21 MLs) are common in mineral ZnS, with the remainder found in synthetic crystals. Some of the crystal structures have repeat distances that extend over 100 MLs. Also, many structures show considerable planar disorder. The wide diversity of structural complexity remains one of the central mysteries of polytypism.

(iii) Solid-state transformations. It is believed that there are only two stable phases of ZnS, the low-temperature modification being the β-ZnS or sphalerite (3C1) and the high-temperature modification wurtzite (2H) or α-ZnS (Sebastian &
Krishna, 1994). The former transforms enantiotropically into the latter at 1024 C. The plethora of structures suggests that most of them are not in equilibrium but rather structures that are trapped in a local minimum of the free energy and lack the necessary activation energy to explore all of configuration space. It is possible to observe these structures by annealing and then arresting the transformation upon quenching. One can then study the various intermediate stages of the transformation.

(iv) Availability. Polytypes of ZnS, both ordered and disordered, are easily manufactured in the laboratory by a variety of methods (Sebastian & Krishna, 1994). One of the more common is growth from the vapor phase above temperatures of about 1100 C. Crystals can also be grown from melt at high pressures, by use of chemical transport and hydrothermally. The distribution of polytypes observed depends on the method used.

Nearly a dozen theories have been proposed to explain polytypism, among them being the ANNNI model (Price & Yeomans, 1984; Yeomans, 1988), Jagodzinski’s disorder theory (Jagodzinski, 1954), and Frank’s screw dislocation theory (Frank, 1951). For a complete discussion, see for example, (Verma & Krishna, 1966; Trigunayat, 1991; Sebastian & Krishna, 1994). We will have little to say here about the mechanisms that produce various polytype structures. Instead, our focus will be on describing the disordered structures so commonly seen. We feel that an adequate description of the disordered structures—which so far has been lacking—is warranted before one can evaluate models that seek to explain the mechanisms that drive the formation of disordered structures and, especially, the solid-state phase transitions which lead to them.

Previous descriptions of planar disorder in single crystals of ZnS fall into one of two categories: the fault model (FM) (Varn et al., 2002; Varn et al., 2005a) and Jagodzinski’s disorder model (DM) (Jagodzinski, 1949a; Jagodzinski, 1949b; Jagodzinski, 1949c; Frey et al., 1986). Applications of the FM include Roth’s study of faulting induced in hexagonal crystals grown from the vapor phase upon annealing (Roth, 1960). Roth extracted correlation information from the diffraction spectra by Fourier analysis and then derived analytical expressions relating how correlation functions decayed with both increasing separation between MLs and as a function of the fault probability. He considered both randomly distributed growth and deformation faults and found that for weakly disordered specimens deformation faulting gave the best agreement with experiment.

Significant applications of the FM to planar disorder in ZnS have been carried out by Sebastian, Krishna, and coworkers. They studied the 2H-to-3C solid-state transformation in vapor-grown ZnS crystals after annealing between temperatures of 300 to 650 C (Sebastian et al., 1982). By analyzing and comparing the profiles of the integer-l reflections2 to those of the half-integer-l reflections for weakly faulted crystals, they found that the disorder was largely due to the random insertion of deformation faults. They attributed slight discrepancies between the observed and calculated profiles to the so-called nonrandom insertion of faults. Sebastian and Krishna later studied the disordered stacking in 3C crystals grown from the vapor phase, as well as those obtained from annealing 2H crystals (Sebastian & Krishna, 1984). They found that the structure of both the as-grown and annealed crystals was best explained as randomly distributed twin faults in the 3C structure. They concluded that the 2H-to-3C transformation in ZnS proceeded by the nonrandom nucleation of deformation faults occurring preferentially at two ML separations.

To better understand the nature of the nonrandom insertion of deformation faults in the 2H structure, Sebastian and Krishna introduced a three-parameter model that assigned separate probabilities to the random insertion of deformation faults, as well as deformation faulting at two and three ML separations (Sebastian & Krishna, 1987a; Sebastian & Krishna, 1987b). They derived analytical expressions for the diffraction spectra in terms of these parameters and concluded that both the 2H-to-3C and the 2H-to-6H transformations proceeded via the nonrandom nucleation of deformation faults. Their analysis showed that these transformations occurred simultaneously in different regions of the same crystal. They attributed this to variations in the stoichiometry. Sebastian gave a similar treatment that came to the same conclusions (Sebastian, 1988). With the exception of Roth, all of these analyses depended on carefully characterizing the change in Bragg peaks as one introduces a small amount of disorder. We have previously given a criticism of the FM approach elsewhere (Varn et al., 2002; Varn et al., 2005a).

Jagodzinski’s DM is a two-parameter model that assumes two thermodynamically stable phases in CPSs: the 2H and 3C. One therefore finds two kinds of fault (and here we mean structure and not mechanism): namely, cubic faults in the 2H and hexagonal faults in the 3C. By choosing appropriate values of the two model parameters one can also model 4H structures. Within this framework, an analytical expression for the diffracted intensity is derived that depends on the model parameters in a complicated manner. Nonetheless, one can select model parameters that give the best agreement with experiment.

Müller (Müller, 1952) used this method to analyze faulted ZnS diffraction spectra and found that while he was able to obtain reasonable agreement between theory and experiment for a few spectra, for many he was not. Singer (Singer & Gashurov, 1963) re-examined this approach and concluded that the DM applies when faulting is random, but when the faulting is nonrandom, as many ZnS specimens are suspected to be, the model fails. However, Frey et al. (Frey et al., 1986) studied the 3C-to-2H transformation in single crystals of ZnS using the DM and were able to obtain excellent agreement between theory and experiment. They fitted the experimental diffraction spectra to the DM’s analytical one. Due to the complicated nature of the expression, however, they treated eight constants that depend on the two model parameters as independent. From these eight fitted parameters they were able to find the two model parameters that best fit each spectra.

2 Notation and definitions of variables used here are introduced elsewhere (Varn et al., 2005a). Also note that our definition of l differs slightly from that used by other authors.
One cannot help but raise questions concerning the mathematical rigor used to find the model parameters in this way. The description of the stacking disorder as given by the DM is a special constrained case of the $r = 2$ computational mechanics approach. As in the latter, in the DM there is no assumption of weak faulting and one does use diffuse scattering to build the model. Since the spectra we analyze have not been previously treated using the DM and it is a special case of our own, we do not discuss the DM further here.

A third possible method of discovering structural information about disordered solids from diffraction spectra employs a reverse Monte Carlo (RMC) technique (Keen & McGreevy, 1990; Proffen & Welberry, 1998; Welberry & Proffen, 1998). In this method, one typically searches for a configuration of constituent atoms such that a signal—e.g., the diffraction spectrum—estimated from the candidate structure most closely matches the experimental signal. Notably, this technique can be applied for the case of disorder in three dimensions. One drawback, however, is that candidate structures are often found that are physically implausible. One needs to impose assumptions to eliminate these. The application of RMC to layered solids is a subject of current research (Varn & Crutchfield, 2005).

In this work, we apply computational mechanics (Crutchfield & Young, 1989; Feldman & Crutchfield, 1998; Shalizi & Crutchfield, 2001) to discover and describe disordered stacking sequences in four previously published ZnS diffraction spectra. We Fourier analyze each spectrum to find correlation information between MLs and then calculate the probability distribution of stacking sequences. From the latter, we reconstruct the $\epsilon$-machine that gives the stochastic process for the ML stacking and compare it to previous FM analyses. From the reconstructed $\epsilon$-machine, we calculate for the first time the configurational entropy per layer, average configurational energy per Zn-S pair, memory length, hexagonality, and generalized period (Varn et al., 2005b). We find that the diffraction spectra of the four samples is well described using the computational mechanics approach.

We note that our primary purpose in the following is expository; that is, we wish to demonstrate the efficacy of $\epsilon$MSR on actual materials. Since we use diffraction spectra from older studies (Sebastian & Krishna, 1994), the analyses given here are less than ideal. Specifically, we digitized data from the published spectra and found that there was significant systematic error in each original spectrum. Additionally, the experimental data was not reported with error bars. Despite these possible shortcomings, $\epsilon$MSR allows us to offer more comprehensive structural and physical analyses of the spectra than given by previous workers.

Our development is organized as follows. In §2 we outline our approach, including a brief discussion of the experimental methods and our analysis. In §3, we give the results of $\epsilon$-machine reconstruction for four experimental ZnS diffraction spectra and contrast this to the FM approach when possible. In §4 we calculate the configurational energies per Zn-S pair and the hexagonality for the various structures from our reconstructed $\epsilon$-machines. In §5 we give our conclusions and propose some directions for future theoretical and experimental work.

2. Methods

The four diffraction spectra we analyze come from Sebastian and Krishna (Sebastian & Krishna, 1994) and are labeled SKXXX by the page (XXX) on which they appear in that source. These data were collected in the 1980s and since they no longer exist in numerical form (Sebastian, 2001), we digitized them from the diffractograms given in the Sebastian and Krishna publication (Sebastian & Krishna, 1994). For each diffraction spectra, digitization process typically resulted in 200 - 500 data points. We further performed a linear interpolation between these points so that our representation of each experimental diffraction spectrum consisted of data points separated by $\Delta l \approx 0.0001$. In all of the numerical analysis we used this finer mesh. However, for the sake of clarity, when we visually compare the diffraction spectra generated from $\epsilon$MSR with experimental spectra, we display only representative experimental points.

In this section, we give a brief synopsis of the experimental procedure, discuss the assumptions made to analyze the data, and list the corrections we apply to the experimental spectra.

2.1. Experimental Details

The experimental procedure is given in more detail elsewhere (Sebastian & Krishna, 1994; Sebastian et al., 1982; Sebastian & Krishna, 1987b; Sebastian, 1988). Briefly, the crystals were grown from the vapor phase at a temperature in excess of 1100 C in the presence of H$_2$S gas. Each crystal was needle-shaped, approximately 0.1 to 0.4 mm in diameter and 1 to 2 mm in length. Two of the four crystals were further annealed for one hour at 300 and 500 C. These experiments were performed to better understand the fault structures they contain, as well as study the solid-state transformations that ZnS crystals undergo.

The intensity along the 10.1 reciprocal lattice row was recorded using a four-circle single-crystal diffractometer for each specimen in steps of approximately $\Delta l = 0.005$. [Our definition of $l$ differs slightly from that of Sebastian and Krishna, (Sebastian & Krishna, 1994) so the $l$-increment we report also differs.] The crystal and the counter were held stationary while the crystal was illuminated with MoK$_\alpha$ radiation. The sharp reflections along the $h - k = 0$ (mod) 3 rows were used to orient each crystal. The divergence of the incident beam was adjusted to cover the mosaic spread for each crystal. The experimental diffraction spectrum is reported as the total number of counts versus $l$. The crystals were examined under a vickers projection microscope and did not show signs of kinking or shearing, even after annealing. They did show parallel striations or stripes perpendicular to the stacking direction.

2.2. Assumptions

To make the analysis tractable, we employ the following assumptions common in the analysis of planar disorder in ZnS:

(i) Each ML is perfect and free of distortions and defects. We assume that each ML is identical and the MLs themselves are undefected. That is, each ML is crystalline in the

...
strict sense, with no point defects, impurities, or distortions in the two-dimensional lattice structure. This clearly precludes the possibility of screw dislocations, which are known to play a role in the polytymysm of some ZnS crystals (Sebastian & Krishna, 1994; Michalski, 1988). Since each of the crystals we analyze was examined under a vickers projection microscope and no such dislocations were seen, and the crystals retained their shape after annealing, this seems reasonable. [It is known (Sebastian & Krishna, 1994) that during solid-state transformations of specimens of ZnS with an axial screw dislocation the specimen will exhibit “kinking” with a characteristic angle of 19°28′.]

(ii) **The spacing between MLs is independent of the local stacking arrangement.** There is known to be some slight dependence of the inter-ML spacing depending on the polytype. (Sebastian, 1988; Sebastian & Krishna, 1994) For the 2H structure in ZnS, the inter-ML spacing is measured to be 3.117 Å. For the 3C structure, the cubic cell dimension is \( a = 5.412 \text{ Å} \) which gives a corresponding inter-ML spacing of 3.125 Å. Therefore, to an excellent approximation, this spacing is independent of the local stacking environment in ZnS.

(iii) **The scattering power of each ML is the same.** We assume that each ML diffracts x-rays with the same intensity. There is no reason to believe that this is not so, unless absorption effects are important or the geometry of the crystal is such that each ML does not have the same cross-sectional area.

(iv) **The stacking faults extend over the entire fault plane.** Examination under microscope indicates that this is generally true. However, Akizuki (Akizuki, 1981) found evidence that the faults do not extend completely over the faulted MLs by examining a partially transformed ZnS crystal under an electron microscope.

(v) **We assume that the “stacking process” is stationary.** We simply mean that the faults are uniformly distributed throughout the crystal. Put another way, we assume that probability of finding a particular stacking sequence is independent of its location in the crystal. This does not, however, preclude regions of crystal structure interspersed between regions of disorder. It simply means that the statistics of the stacking does not change as one moves from one end of the crystal to the other.

Notably absent from this list are any assumptions about the crystal structure present (if any) and how the sample might deviate from that structure. In contrast to the FM, we invoke no **a priori** structural assumptions concerning the stacking sequence.

### 2.3. Corrections to the Experimental Spectra

We corrected each spectrum for the following effects:

(i) **The atomic scattering factor.** This correction accounts for the spatial distribution of electrons, as well as for the wavelength of the incident radiation and angle of reflection. Calculations of these effects are given in standard tables (Hahn *et al.*, 1992) and we employ them in our work.

(ii) **The structure factor.** The structure factor (Sebastian & Krishna, 1994) accounts for the two-atom basis in ZnS.

(iii) **Anomalous scattering factors.** Also called dispersion factors, the anomalous scattering factors correct for the binding energy of the electrons and the phase shifts (Hahn *et al.*, 1992). For our case, we find these to be small, but have included them nonetheless.

(iv) **Polarization factor.** We use the standard correction factor for unpolarized radiation (Warren, 1969).

Factors we did not correct for include the following:

(i) **Thermal factors.** At room temperature, this effect is small for ZnS (Varn, 2001).

(ii) **Absorption factor.** For the geometry of the ZnS crystals we analyze, the linear mass coefficient (Woolfson, 1997; Millburn, 1973) is much larger than the thickness, therefore we ignore it.

(iii) **Instrument resolution.** This is not reported with the experimental data, so we do not deconvolve the spectrum.

### 3. Analysis

We now give the structural analysis of four experimental diffraction spectra taken from (Sebastian & Krishna, 1994). We apply cMSR to each to build a model that describes the stacking process (Varn *et al.*, 2005a). From our model, we calculate various measures of intrinsic computation for each spectra. We compare our results with that obtained by previous researchers using the FM. Since the experimental spectra are not reported with error bars, we are unable to set an error threshold \( \Gamma \) as required in cMSR. Instead, we found that each increase in the memory length \( r \) continues to give a better description of each spectra (Varn, 2001). We perform \( \epsilon \)-machine reconstruction up to \( r = 3 \) for each spectra. Note that at \( r = 3 \), the resulting \( \epsilon \)-machine is specified by \( 2^3 = 8 \) parameters. To find the correlation functions (CFs) from the \( \epsilon \)-machines, we take a sample length 400 000, as generated by the \( \epsilon \)-machine. The diffraction spectra are calculated using 10 000 MLs. The experimental spectra are normalized to unity over the \( l \)-interval used for reconstruction, as are the spectra calculated from each \( \epsilon \)-machine. For the spectra calculated from the FM, we set the overall scale to best describe the Bragg peaks as shown in (Sebastian & Krishna, 1994). We also calculate the profile \( R \)-factor (Varn *et al.*, 2005a) to evaluate the agreement between experiment and theory for each spectrum.

We note that we have given a discussion of two of the spectra, SK134 and SK135, previously (Varn *et al.*, 2002). Here we present the background for claims made there as well as provide a more in-depth analysis.

#### 3.1. SK134

The corrected diffraction spectrum along the 10.l row for an as-grown 2H ZnS crystal is shown in Fig. 1. One immediately notices that the spectrum is not periodic in \( l \), as it should be, but instead suffers from variations in the intensity. The peaks at \( l = 0.0 \) and \( l = 1.0 \) are of similar intensity, but the peaks at \( l = -0.5, 0.5 \) and 1.5 seem to suffer from a steady decline in intensity. We can therefore be confident that this spectrum
contains substantial systematic error as reported by the exper-
imentalists.

This difference in diffracted intensity between peaks results
from the finite thickness of the Ewald sphere due to the
divergence of the incident beam. (Sebastian & Krishna, 1987b;
Sebastian & Krishna, 1994). A suitable choice of geometry can
minimize, but not eliminate these effects, such that one finds
only a gradual variation in $I$ with $\Delta l$. Since analysis by the FM
depends only on the change of the shape and the position of the
Bragg-like peaks, such a slow variation of the diffracted intensity
with $I$ will not affect the conclusions drawn from an
FM analysis. It is possible to correct these effects, (Pandey et al., 1987;
Sebastian & Krishna, 1994) but this has not been
done in the literature.

Our analysis depends on selecting an appropriate $l$-interval
where variations in diffracted intensity due to these experi-
mental effects are minimized. It is important, then, to select an
interval that is relatively error-free. There are two criteria, called
figures-of-merit and denoted $\gamma$ and $\beta$, one can use for this (Varn et al., 2005a). It can be shown that in an error-free spectrum
the parameters must be equal to constant values $-1/2$ and $1$,
respectively, for any unit $l$-interval, regardless of the amount of
planar disorder present. The extent that $\gamma$ and $\beta$ differ from their
theoretical values over a given $l$-interval measures how well the
diffraction spectrum over the interval can be represented by a
physical stacking of MLs. It makes sense, then, to choose an
$l$-interval for $\epsilon$-machine reconstruction such that the theoretical
values of the figures-of-merit are most closely realized. This
does not, of course, guarantee that the interval is error-free.
Glancing at Fig. 2 shows that $\gamma = -0.51$ and $\beta = 0.95$ over the
interval $l \in [0.04, 1.04]$.

We perform $\epsilon$-MSR (Varn et al., 2005a) and find that the
smallest-$r \epsilon$-machine that gives reasonable agreement between
the measured and $\epsilon$-machine spectra has a memory length of
$r = 3$. The reconstructed $\epsilon$-machine is shown in Fig. 2 of (Varn et al., 2002). The large asymptotic state probabilities for the
C and H causal states (CSs), as well as the large inter-state
transition probabilities between them, indicate this is predom-
inantly a 2H crystal. More specifically, the probability of see-
ing sequences $1010$ and $0101$, corresponding to the 2H crys-
tal structure, have a combined total weight of about 64%. The
remaining probability is distributed among the other fourteen
length-4 sequences. It is tempting to interpret the remaining
structure in terms of faults and, indeed, it seems we can.

Let us treat the transitions $s = 0$ from causal state E and
$s = 1$ from state F as though they are missing for the purposes
of a fault analysis. This implies that the sequences 0001 and
1000 are disallowed. Of course, this cannot be exactly true, as
the CS F would then be isolated from the rest of the $\epsilon$-machine.
In this case, we would say that the $\epsilon$-machine is not strongly
connected and, as such, cannot represent a physical stacking of
MLs. However, the combined probability weight of these two
sequences is < 1%, so neglecting them gives only a small error
in our intuitive understanding of the faulting structure.

Then, on the left half of the $\epsilon$-machine, there is structure
associated with a 2H deformation fault [ABCD] with probabil-
ity weight $0.16 = P(1011) + P(0111) + P(1110) + P(1101)$.
We can interpret the causal-state cycle (CSC) [DBEGHC] as a
layer-displacement fault and see that it is assigned a probabil-
ity weight of 0.06. The right portion contains the CSC [EGH]
with probability weight 0.06, which is associated with growth
faults. The CSCs $[A]$ and $[F]$, identified as 3C structure, have a
combined weight of 0.08.

Given these observations, a possible interpretation suggested
by the $\epsilon$-machine is that SK134 has crystal structures and faults
in the proportions given in Table 1. The decomposition there is
sensible since there is an underlying crystal structure present
and the smaller, faulting paths are not too probable. As we
will see, these need not always be the case. Sebastian and
Krishna (Sebastian & Krishna, 1994) have analyzed this diffrac-
tion spectrum using the FM and found that approximately one in
every twenty MLSs is deformation faulted, so they described the
stacking structure as a faulted 2H crystal with 5% random deforma-
tion faulting. This is equivalent to assigning CSCs responsi-
ble for deformation faulting a total probability weight of 0.17.

We compare the structure analyses of the two models in Table
1. We see that both analyses agree that the dominant structure is
2H, though the $\epsilon$-machine attributes less of the crystal structure
to this “parent” phase. Similarly, both find that structures asso-
ciated with deformation faulting are important and assign them
almost equal weights.

They differ, however, in that the $\epsilon$-machine finds additional
faulting structures (growth and layer-displacement faulting), as
well as 3C crystal structure. Since this crystal, if annealed at suf-
ficient temperatures for a long enough time, will transform into
a twinned 3C structure, the latter is easily understood as nascent
structure in that process. Finding the presence of weak 3C struc-
ture is not unreasonable since there is some slight enhance-
ment of the diffracted intensity at $l \approx 1/3$ and $l \approx 2/3$. The
other faulting structures seen are less easily understood. Growth
faults, so-named because they primarily are formed during the
growth of the 2H crystal, are not expected to play an important
role in solid-state transformations of ZnS (Roth, 1960). Their
presence here may result from the initial growth of the crys-
tal. The small amount of layer-displacement structure could be
seen as two adjacent, yet oppositely oriented deformation faults.
That is, a deformation fault in a 2H structure is simply a spin
flip in the Hågg notation (Varn et al., 2005a), so that a sequence
...010101... transforms to ...011101... as a result of one
deforation and then to ...011001... upon another resulting
in a layer-displacement fault ...011001.... This might imply
some coordination between faults. Or, the mechanism of layer-
displacement faulting may play some minor role in the solid-
state transformation.

However, one cannot disambiguate these from the available
spectra and the reconstructed $\epsilon$-machine. The $\epsilon$-machine only
provides information about the structure. We must look out-
side the $\epsilon$-machine to formulate an understanding of how the
polytype came to be stacked in this way. This is the critical
difference between faulting mechanism and faulting structure.
In the former, a physical process is responsible for causing the
MLs to shift or deviate from a perfect crystal. In the latter,
in the limit of weak faulting, the physical process leads to a given (statistical) structure. In this limit it may be possible to postulate with some certainty that the mechanism resulted in the observed structure. For more heavily faulted crystals, however, such an identification of structure with mechanism is dubious. Other techniques, such as numerical simulations (Kabra & Pandey, 1988; Engel, 1990; Shrestha et al., 1996; Shrestha & Pandey, 1996a; Shrestha & Pandey, 1996b; Shrestha & Pandey, 1997; Gosk, 2000; Gosk, 2001) or analysis of a series of crystals in various stages of the transformation, are necessary to unambiguously determine the mechanism (Varn & Crutcherfield, 2004).

Returning to the analysis of SK134, Fig. 3 compares the CFs obtained from the experimental diffraction spectrum, those obtained from the $\epsilon$-machine and those from the FM. There is reasonable agreement between the experimental and $\epsilon$-machine-predicted CFs. For small $n$, however, the FM overestimates the amplitude in the oscillations in $Q_s(n)$.

The experimental diffraction spectrum is compared to that calculated from the FM and from the $\epsilon$-machine in Fig. 1 of (Varn et al., 2002). Both models give good agreement near the Bragg peaks at $l = 0.5$ and $l = 1.0$, with perhaps the FM performing a little better at $l = 1.0$. The diffuse scattering near the shoulders of the $l = 0.5$ peak are better represented by the $\epsilon$-machine. We calculate the profile $R$-factor between experiment and the FM to be $R_{FM} = 33\%$ and between experiment and $\epsilon$MSR to be $R_{\epsilon MSR} = 20\%$.

So, our analysis of SK134 is an improvement over the FM analysis in several important ways. (i) Even in the limit of weak faulting, $\epsilon$MSR finds closer agreement with experiment than the FM, as measured by the profile $R$-factors. (ii) Again in the limit of weak faulting, the $\epsilon$-machine can be decomposed (though not necessarily uniquely) to give an estimate of crystal and fault structure present. (iii) As such, we were able to identify and quantify several additional structures in the crystal, namely the presence of a small amount of 3C crystal, growth and deformation faults.

### 3.2. SK135

The next sample we examine is a twinned 3C crystal obtained by annealing a 2H crystal at 500 C for 1 h. The diffraction spectrum for this crystal is given in Fig. 3 of (Varn et al., 2002). We find that the figures-of-merit are closest to their theoretical values over the interval $l \in (-0.80, 0.20]$ with values $\beta = -0.50$ and $\gamma = 0.93$. The smallest-$r$ $\epsilon$-machine that gives reasonable agreement with experiment was found at $r = 3$ and has a profile $R$-factor of $R_{\epsilon MSR} = 13\%$. The resulting $\epsilon$-machine is shown in Fig. 4 of (Varn et al., 2002). Based on the presence of asymmetrically broadened peaks and the absence of peak shifts, a FM analysis (Sebastian & Krishna, 1994) finds this sample to be a twinned 3C crystal with 12\% twinned faulting. The profile $R$-factor between experiment and the FM is found to be $R_{FM} = 33\%$.

The large CS probabilities associated with CSs A and F, as well as their large self-loop transition probabilities, suggest that this is a twinned 3C crystal. We also note that the transitions corresponding to antiferromagnetic paths (0101 and 1010) have a relatively small combined weight of only about 4\%. In fact, the transition from CS H to CS C is missing. This indicates that the 2H structure has largely been eliminated. In addition to the 0101 path, the 1001 and 0010 paths are also missing. This implies that twinned faulting is important, but also the remnant of the 1010 path has some role. Instead of a simple twinned fault [ABEF] giving the sequence . . . 1111[0000] . . . , where the vertical line indicates the fault plane, the path [ABCEF] giving the sequence . . . 1111[0100] . . . has approximately twice as much probability weight associated with it. In the $\epsilon$-machine’s right portion twinned faulting [FGDA] is largely responsible for the (0)° 3C cycle converting to the (1)° 3C cycle and we also observe that double deformation faulting [FGDBE] plays a role.

It is interesting to mention that, while a ML of ZnS has spin-inversion symmetry (Varn & Canright, 2001) and, thus, the one-dimensional Hamiltonian describing the energetics of the stacking is also spin invariant, in general $\epsilon$-machines need not be spin-inversion invariant. [Note that the $\epsilon$-machine in Fig. 4 of (Varn et al., 2002) is not spin-inversion invariant.] There is, of course, no reason why one should demand spin-inversion invariance. After all, then one could never have a crystal of purely one 3C structure or the other. However, since this crystal was initially in the 2H structure—which is spin-inversion invariant—it is curious that this is not preserved as the crystal is annealed. That is, there is no reason to expect that faulting should occur preferentially with one chirality. Notably, the FM always assumes spin-inversion symmetry.

Examining the CF $Q_s(n)$ estimated from experiment with those found from the $\epsilon$-machine in Fig. 4, we find reasonable agreement up to $n \approx 20$. The $Q_s(n)$ found from the FM generally overstate the magnitude of the oscillations in the CFs.

We can further examine the diffraction spectra. In Fig. 3 of (Varn et al., 2002), the diffraction spectrum found from the FM and the $\epsilon$-machine are compared with experiment. The $\epsilon$-machine gives a good fit, except perhaps at a shoulder in the experimental spectrum at $l = -0.6$ and the small rise at $l = -0.16$. The latter might be understood as a minor competition between the 3C and 6H CSCs that is not being well modeled at $r = 3$. Comparison of the diffraction spectrum from the FM with that from experiment reveals good agreement with the peak at $l = -0.33$ and poor agreement with the one at $l = -0.67$. This is not surprising as the FM did not use the peak at $l = -0.67$ to find the faulting structure. Likewise, the diffuse scattering between peaks is not at all well represented by the FM. Additionally, the small rise in diffuse scattering at $l = -0.16$ is likewise absent in the FM diffraction spectrum.

A comparison between the FM and $\epsilon$MSR analyses SK135 illustrates several important points. (i) This diffraction spectrum shows considerable disorder, and as such the FM is considerably less successful in reproducing the experimental diffraction pattern. ($R_{\epsilon MSR} = 13\%$ vs. $R_{FM} = 33\%$). Since $\epsilon$MSR does not assume any kind or amount of crystal or fault structure, and uses all of the information in the diffraction spectrum, it functions considerably better than the FM for highly
disordered crystals. (ii) Therefore, eMSR captures the diffuse scattering between the Bragg-like peaks more effectively. (iii) eMSR shows that faulting structure between the two 3C crystal structures is not simply due to twin faulting. Rather, the sequence ...1111/01000... is more likely than the simpler fault ...1111/0000... (iv) eMSR does not require spin inversion symmetry as the FM does.

3.3. SK137

The third experimental spectrum we analyze comes from an as-grown disordered, twinned 3C crystal. The diffraction spectrum for this crystal along the 10.1 row is shown in Fig. 5. The figures-of-merit are closest to their theoretical values over the interval $l \in [-0.8, 0.2]$ with values of $\gamma = -0.49$ and $\beta = 0.98$. We performed $\epsilon$-machine reconstruction up to $r = 3$ and found that this produces reasonable agreement with experiment giving a profile $\mathcal{R}$-factor of $\mathcal{R}_{\text{FM}} = 17\%$. The $r = 3$ $\epsilon$-machine in shown in Fig. 6. A FM analysis finds SK137 to be a twinned 3C crystal with 6.8% twinned faulting (Sebastian & Krishna, 1994). The FM-calculated diffraction spectrum has a profile $\mathcal{R}$-factor of $\mathcal{R}_{\text{FM}} = 58\%$ when compared with experiment.

A comparison of the CFs from experiment, the FM, and the $\epsilon$-machine in shown in Fig. 7. For smaller $n$, the $\epsilon$-machine gives good agreement with experiment, although the error increases at larger $n$. As shown elsewhere (Varn, 2001), the experimental CFs maintain small, but persistent oscillations about their asymptotic value of 1/3 up to $n \approx 40$, while the CFs derived from the $\epsilon$-machine effectively reach this asymptotic value at $n \approx 25$. This leads us to speculate that there is some structure in the stacking process that the $\epsilon$-machine is missing. We expect that reconstruction at $r = 4$ will prove interesting here. This has not yet been completed.

The FM fares markedly worse. It substantially overestimates the strength of the oscillations in the CFs for all $n$.

A comparison of the diffraction spectra for experiment, the FM, and the $\epsilon$-machine is shown in Fig. 5. The $\epsilon$-machine gives reasonable agreement everywhere except around the Bragg peaks at $l = -0.33$ and $l = -0.67$. Here the $\epsilon$-machine gives a value for the peak intensity 15% and 35% lower, respectively, than experiment. The FM does much better at the Bragg peaks, as one might expect. The diffuse scattering between the peaks, and especially the broad-band rise in intensity near $l = -0.5$, are simply missing in the FM diffraction spectrum, however. The $\epsilon$-machine fit in this region is substantially better, picking up a number of important spectral features, such as broadband components and broadened peaks.

What does the $\epsilon$-machine imply about the stacking process? All CSs and allowed transitions are present except for the transition between $S_1$ and $S_3$. This absent transition implies that the 0011 stacking sequence is not present in SK137. This, then, means that the 000111 sequence, and hence the CSC $[S_7S_6S_5S_4S_3S_2S_1S_0]$ associated with the 6H structure (Varn et al., 2005a), is also absent. Therefore, in this twinned 3C crystal there is no 6H structure. This is surprising, since many ZnS spectra show enhancement about the 6H positions during solid-state phase transitions from 2H to 3C. In Fig. 5 there is (arguably) a slight increase in diffracted intensity at $l = -0.16$ and $l = 0.16$. So the absence of the 6H structure does seem echoed in the experimental spectrum. There is, however, a large broadband increase in intensity about $l = -0.5$ and a much smaller increase about $l = 0.0$. Reflections at these $l$ are usually associated with 2H structure, with the half-integer peaks carrying three times the intensity of the integer peaks. The $\epsilon$-machine does show that the CSC $[S_7S_6S_5]$ associated with the 2H structure is present. The frequency of occurrence of the 0101 and 1010 stacking sequences together make up about 12% of the total probability weight on the $\epsilon$-machine. Even though $P_{\text{CSR}}([S_7S_6S_5]) < 1$, it is not unreasonable to suggest that 2H structure is present.

We find several important lessons from the analysis of SK137. (i) Again, eMSR shows significant improvement over the FM in reproducing the experimental spectrum, especially the diffuse part. (ii) As with the eMSR analysis of SK134, we find evidence for two crystal structures, both the twinned 3C and the 2H. (iii) eMSR can also exclude the possibility of certain crystal structures, such the 6H, based on the absence of the CSC associated with this crystal structure. (iv) eMSR can have difficulty in reproducing the Bragg-like peaks, such as those at $l = -0.67$ and $l = -0.33$. This, coupled with difficulty at reproducing the small but persistent oscillation in the CFs at larger $n$, hints that there stacking structures that can only be captured at longer memory lengths.

3.4. SK229

Lastly, we examine an as-grown 2H crystal. The diffraction spectrum for this crystal is shown in Fig. 8. We find the figures-of-merit closest to their theoretical values over the interval $l \in [-0.33, 0.67]$ with values of $\gamma = -0.49$ and $\beta = 1.00$. We find that the smallest-$r$ $\epsilon$-machine that gives reasonable agreement between the measured and $\epsilon$-machine spectra has a memory length of $r = 3$. The reconstructed $\epsilon$-machine is shown in Fig. 9. The large asymptotic state probabilities for the $S_2$ and $S_3$ CSs, as well as the large inter-state transition probabilities between them, indicate this is predominantly a 2H crystal. More specifically, the probability of seeing sequences 1010 and 0101, corresponding to the 2H cycle, have a combined total weight of about 82.5%. The remaining probability is distributed among the other fourteen length-4 sequences. It is tempting to interpret the remaining structure as faults and, indeed, we can.

Let us treat the transitions $s = 0$ from $S_6$ and $s = 1$ from $S_1$ as though they are missing. These are the least probable transitions in the $\epsilon$-machine: $P(0, S_0) = P(S_6)P(0|S_6) \approx 0.004$ and $P(1, S_1) = P(S_1)P(1|S_1) \approx 0.002$. Then, in the left half of the $\epsilon$-machine there is structure associated with a 2H deformation fault $[S_7S_6S_5S_3]$, with probability weight 0.040 = $P(1011) + P(0111) + P(1110) + P(1011)$. In the right half there likewise is a 2H deformation fault structure $[S_6S_5S_4S_3]$ with weight 0.049 = $\frac{1}{4}P(0101) + P(1000) + P(0001) + \frac{1}{4}P(0010)$. The right portion contains the CSC $[S_7S_6S_5S_4S_3]$, which is associated with growth faults. The CSCs $[S_6]$ and $[S_7]$, identified as 3C struct-
international union of crystallography

ture, have a combined weight of 0.041. Given these observations, the interpretation suggested by the ϵ-machine is that SK229 has crystal structures and faults in the proportions given in Table 2. The decomposition there is reasonable since there is an underlying crystal structure present and the smaller, faulting paths are not too large.

SK229 has not been analyzed quantitatively using the FM. By comparing the FWHM of the integer-l to half-integer-l peaks, Sebastian and Krishna (Sebastian & Krishna, 1994) concluded that deformation faulting is the primary vehicle responsible for the deviation from crystallinity seen here. We are in agreement, except that we also detect small amounts of 3C crystal structure and some growth faults.

Figure 10 compares the CFs from experiment and the ϵ-machine. The agreement is good, although the reconstructed ϵ-machine underestimates somewhat the magnitude of the oscillations in ϵ and some growth faults. The agreement is good, although the reconstructed ϵ-machine underestimates somewhat the magnitude of the oscillations in ϵ and some growth faults.

In Table 2, we list the measures of intrinsic computation and characteristic lengths calculated for each sample, as well as for three crystal structures for comparison.

4.1. Characteristic Lengths in Polytypes

We first note that it was necessary to perform ϵMSR up to r = 3 for each spectrum. This is not surprising since the mechanism of deformation faulting is expected to be important in ZnS, and the minimum ϵ-machine on which deformation faulting structure can be modeled is r = 3. This implies, of course, a longer memory length that either pure 3C or 2H structure alone requires.

The generalized periods for the 2H and 3C structures at P = 2 ML and P = 1 ML, respectively, are also much shorter than for the disordered structures which average P = 5.7 ML. This shows that there is spatial organization over a modest range—6 MLs—for disordered ZnS crystals. This pales in comparison to crystalline polytypes with repeat distances over 100 MLs, but is still much larger than the calculated range of inter-ML interactions of ~1 ML. We note that many of these long-period crystalline polytypes are believed to be associated with giant screw dislocations that are expressly absent here. For both r and P, the disordered structures have values much closer to that expected for the 6H structure.

In contrast to a perfect crystal, the correlation lengths are finite rather than infinite. Interestingly, the sample that has the most stacking disorder [as measured by h], SK137, also has a comparatively long correlation length. While this was previously classified as an as-grown 3C crystal (Sebastian & Krishna, 1994) we find that it also contains a significant amount of stacking sequence associated with the 2H structure. Since we cannot assume that any of these structures are in equilibrium or the ground state, we can draw no conclusions about the range of inter-ML interactions.

4.2. Intrinsic Computation

Each of the diffraction spectra we analyze also shows considerable stacking disorder. Even a spectrum that is quite crystalline, like SK134, has a configurational entropy of $h_{\mu} = 0.50$ bits/ML. Of course, for a crystal the entropy rate is zero and for the case of completely disordered stacking one would have $h_{\mu} = 1$ bits/ML. If we compare SK134 and SK135, each beginning as a 2H crystal but annealed at different temperatures, we see that the latter is slightly more disordered, as we expect. The statistical complexity, a measure of the average history in MLs needed to predict the next ML, is also relatively constant at 2.3 bits and 2.5 bits, respectively.

In fact, the measures of intrinsic computation are nearly equal, except those for SK229. But SK134 and SK135 have very different structures. SK134 is largely 2H in character while SK135 is largely twinned 3C. Assuming that they were identical before annealing, this would suggest that the disordering process has little effect on these measures. This is, of course, tentative, since such a conclusion can only be drawn after examining many disordered samples. Experimental spectra in the midst of the 2H-to-3C transformation would be of significant interest here. It is possible, though, that SK137 might be such an
instance. While this is an as-grown twinned 3C crystal, as noted above this, this crystal also has some significant 2H character. Since an earlier analysis (Sebastian & Krishna, 1994) found that both of these were well described by a random distribution of twin faults, they concluded that disordered 3C crystals found in the growth furnace result from a phase transformation from the 2H structure upon cooling the furnace. We find that the two samples [SK135 and SK137], while similar, do have qualitative differences. We can understand this either as a crystal not completely transformed or that the mechanism which created SK137 is not simple. We feel that more experimental data is needed in order to arrive at a more complete understanding. Since $h_{\mu} = 0.65$ bits/ML for SK137 and is thus more disordered than either SK134 or SK135, the interpretation of this crystal being in the midst of a phase transition is a plausible explanation. The most striking feature of the measures of intrinsic computation is their relative consistency [except for SK229] even while the structure of the crystal changes significantly.

4.3. Configurational Energies

One physical quantity amenable to calculation from the $\epsilon$-machine is the difference in configurational energies of the particular disordered polytypes. Considering possible interactions up to the third nearest neighbor, a first-principles pseudopotential calculation of the total energy of five ZnS polytypes (Engel & Needs, 1990) determined that the configurational energy depends only the nearest and the next-nearest neighbors in the stacking arrangement. The most general expression possible for inter-ML interactions up the third nearest neighbors is given by (Shaw & Heine, 1990)

$$E = E_0 - J_1 \sum_i s_i s_{i+1} - J_2 \sum_i s_i s_{i+2}$$

$$- J_3 \sum_i s_i s_{i+3} - K \sum_i s_i s_{i+1}s_{i+2}s_{i+3}.$$  \hspace{1cm} (1)

Terms with an odd number of spins do not appear due to symmetry considerations. We take $s_i = \pm 1$ here. It was found that $J_1 = 0.00187$ eV per ZnS pair and $J_2 = -0.00008$ eV per ZnS pair and that $J_3$ and $K$ are negligible (Engel & Needs, 1990).

Given this let us rewrite Eq. (1) in terms of the energy per ZnS pair and take $E_0 = 0$. Then the configurational energy is

$$\tilde{E} = -J_1 \langle s_i s_{i+1} \rangle - J_2 \langle s_i s_{i+2} \rangle,$$  \hspace{1cm} (2)

where brackets indicate the expectation value over the stacking sequence. The expectation values are found directly from sequence probabilities, as follows:

$$\langle s_i s_{i+1} \rangle = P(11) + P(00) - 2P(01)$$

$$= 1 - 4P(01)$$

$$\langle s_i s_{i+2} \rangle = P(111) + P(101) + P(000) + P(010)$$

$$-2P(110) - 2P(100).$$  \hspace{1cm} (3)

The configurational energy in terms of meV per Zn-S pair is shown in Table 4 for several crystalline structures and each of the four disordered samples. The configurational energies are bounded above and below by the 2H and 3C structures with relative configurational energies of 1.95 meV/ZnS-pair and -1.79 meV/ZnS-pair, respectively. For SK134, the annealing process has introduced faults and has lowered the average configurational energy from the original 2H structure to 1.13 meV/ZnS-pair, while increasing the configurational entropy. If we assume that SK137 is a partially transformed 2H-to-3C crystal [though mostly 3C], then we see that the crystal experiences further disordering and the configurational energy falls to -0.57 meV/ZnS-pair. SK135 shows the most advanced transformation with the 2H structure almost completely eliminated and configurational energy not too far from the ideal minimum at -1.02 meV/ZnS-pair. The configurational entropy begins to fall, however, as the transformation nears a disordered 3C crystal. Being only a slightly disordered 2H crystal, SK229 shows the highest configurational energy of 1.56 meV/ZnS-pair. As we might expect from the relative magnitudes of $J_1$ and $J_2$, the contribution from the $J_1$ term completely dominates the energy.

4.4. Hexagonality

The degree of birefringence of ZnS crystals is known to depend only a single structural parameter—the hexagonality $\alpha_h$ (Brafman & Steinberger, 1966). This parameter is defined as that fraction of MLs which are hexagonally related to their neighbors. That is, $\alpha_h$ is defined as the frequency of occurrence of sequences $ABA$ and $BAB$ and their cyclic permutations. In terms of the Hågg notation, these are simply $P(01)$ and $P(10)$, respectively. Since $P(01) = P(10)$ (Varn et al., 2005a), we have

$$\alpha_h = 2P(01).$$  \hspace{1cm} (4)

Sequence probabilities are directly calculable from the $\epsilon$-machine, so that the hexagonality of a disordered crystal can be easily found.

In Table 4 we show the hexagonality calculated for all of the spectra, as well as for several crystal structures for comparison. We make several observations. The first is that the hexagonality is strongly correlated with the configurational energy [a high hexagonality implies a high configurational energy]. This is to be expected, as the configurational energy term is dominated by the $J_1$ term, which itself is strongly dependent on the $P(01)$ sequence. The $P(01)$ also determines the hexagonality. We also see that the 6H crystal structure has a higher hexagonality and configurational energy than the one disordered spectra, SK135. This suggests that during a solid state transformation initiating in the 2H structure, a disordered 3C, rather than a 6H crystal, is the more likely end result. This is in agreement with experiment for ZnS. Other materials, such as SiC, may follow different routes to disorder, in part, to different $J_1$ and $K$ terms.

5. Discussion

We have successfully applied computational mechanics to the discovery and description of stacking order in single crystals of polytypic ZnS. In doing so, we reconstructed from experimental diffraction spectra the minimal, optimal, and unique description of the stacking process as embodied in the $\epsilon$-machine. In contrast to previous analyses (Sebastian & Krishna, 1994), we used all of the information in the diffraction spectra, both in the Bragg peaks and in the diffuse scattering between them.
We imposed no restrictions on the kind of structures to be found, save that they be representable by $\epsilon$-machines. Further, the computational mechanics approach was not limited to the case of weak faulting, but can be used to treat even highly disordered samples. Additionally, the $\epsilon$-machine can naturally accommodate more than one parent crystalline structure as seen in SK134.

For two of the spectra, a sensible decomposition of the $\epsilon$-machine into crystal and faulting structure was possible, allowing a direct comparison between the computational mechanics approach and the FM. The $\epsilon$-machine detected structures not previously found by the FM. For example, in SK134 we found that not only was structure associated with deformation faulting important, but there was also structure related to growth faults and layer-displacement faulting. We even found nascent sequences leading to the 3C structure. For the other two cases, while no FM-like decomposition of the $\epsilon$-machine was proposed, we still found significant structure as embodied in the $\epsilon$-machine. From the $\epsilon$-machine, physical insight into the structure of the stacking was possible. For example, in the $r = 3$ reconstructed $\epsilon$-machine for SK137 we could eliminate 6H structure based on the absence of a transition between CSs. We also found that 2H structure was present. Even when no sensible decomposition into a simple pure-crystal and weak-faulting structure is possible, the $\epsilon$-machine still directly provides sequence frequencies, which can be used to build physical insight into the stacking structure.

From a knowledge of the $\epsilon$-machine, it is possible to calculate a number of physical characteristics. In Table 3 we tabulated the configurational entropy per ML for each sample. Given the coupling parameters between MLs we calculated the average configurational energy for the samples, as shown in Table 4. We were also able to find the hexagonality for the disordered crystals. Knowing the $\epsilon$-machine allowed us to find various characteristic lengths associated with each disordered crystal, such as the memory length and the generalized period. We believe that additional physics can be calculated from the $\epsilon$-machine.

We also calculated measures of intrinsic computation from the $\epsilon$-machine. We found that the minimum memory length for all samples was $r = 3$, which is in excess of the calculated inter-ML interaction range of $\sim 1$ ML for ZnS. We further found that the statistical complexity, a measure of the amount of information stored by the stacking process, was also much larger than that of either the pure 2H or 3C structures. Also, the range over which structures are found in the disordered samples is about 6 ML.

Characterizing solid-state transitions in polytypic materials is of considerable interest. Let us review what an $\epsilon$-machine does and does not imply. Most simply put, the $\epsilon$-machine is the answer to the question, “What is the minimal, optimal, and unique description of the one-dimensional stacking structure of the sample?” Any physical parameters that depend on this description are in principle calculable from $\epsilon$-machine. The $\epsilon$-machine does not answer the question, “How did the crystal come to be stacked in this way?” To determine this, one must augment structural knowledge [as embodied in the $\epsilon$-machine] with additional information or assumptions. Such information can come in the form of a time series of structures obtained either from a series of numerical simulations or experiments or, in the theoretical domain, perhaps from assumptions about weak faulting.

Since we have discovered structures in polytypic ZnS that were undetected before, we feel that the mechanism of faulting—previously attributed to deformation faulting—deserves re-examination. We have provided a firm theoretical foundation for the discovery and description of disordered stacking sequences in polytypes and believe that additional experimental studies are warranted. Additionally, computer simulations of solid-state transformations in polytypes with proposed faulting mechanisms, accompanied by the concomitant reconstruction of the $\epsilon$-machine directly from the sequence of MLs from the simulation, should provide a powerful method to understand the gross features of the transformations (Varn & Crutchfield, 2004).

Before such studies can be definitive, a quantitative understanding of the effects of experimental error on the reconstructed $\epsilon$-machine is needed. With the exception of our introduction of the figures-of-merit, $\gamma$ and $\beta$, we have not addressed this important issue here. We note that the original experimental data was not reported with error bars and this means that comparison with the desired $\epsilon$-machine error analysis would have not been possible. Additionally, the necessity to digitize the data undoubtedly introduced errors. It is therefore difficult to assess the amount of error in each spectrum. Our intuition tells us that error in the diffraction spectrum will likely lead to suppression of the more delicate structures on an $\epsilon$-machine. Therefore, one should expect to find less structure and more randomness.

We mention that the application of computational mechanics to the description of one-dimensional sequences is the most general approach possible to this problem. Thus, its application here to polytypism represents the end point in the evolution of models to describe the disordered sequences seen in these substances. Any alternate description can be expressed as an equivalent $\epsilon$-machine and none can be more general, since in the language of statistics an $\epsilon$-machine is the minimal sufficient statistic for the underlying process. It may be possible to find specialized algorithms that are more sensitive or more efficient in determining an $\epsilon$-machine than the one we introduced in $\epsilon$-machine spectral reconstruction. However, the answer, in its most general form, will be expressible as an $\epsilon$-machine.

We also note that our work here represents a solution to a significant theoretical problem—How does one extract structural information from a power spectrum? Our application has been to polytypism, but the principles underlying our solution may be applied quite generally to domains in which spectral information is available.

Future directions for this work include an application of $\epsilon$-MSR to other polytypes, as well as to substantially more complex materials. The extension of these ideas to the more common cases of disorder in two and three dimensions is also desir-

---

3 Recall that this decomposition is not unique due to assumptions used in the FM (Varn et al., 2005a).
able. The development of computational mechanics in higher dimensions would significantly aid in the classification and understanding of disorder in many physical systems. Some recent progress has been made in the understanding of pattern and computation in higher dimensions (Lindgren et al., 1998; Feldman, 1998; Feldman & Crutchfield, 2003; Shalizi et al., 2004; Young et al., 2005).

Acknowledgements

We thank D. P. Feldman, R. Haslinger, C. Moore, C. R. Shalizi and E. Smith for helpful conversations. This work was supported at the Santa Fe Institute under the Networks Dynamics Program funded by the Intel Corporation and under the Computation, Dynamics, and Inference Program via SFI’s core grants from the National Science and MacArthur Foundations. Direct support was provided by NSF grants DMR-9820816 and PHY-9910217 and DARPA Agreement F30602-00-2-0583. DPV’s original visit to SFI was supported by the NSF.

References


Table 1

<table>
<thead>
<tr>
<th>Structure</th>
<th>ε-Machine</th>
<th>Fault Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H</td>
<td>64%</td>
<td>83%</td>
</tr>
<tr>
<td>3C</td>
<td>8%</td>
<td>0%</td>
</tr>
<tr>
<td>Deformation fault</td>
<td>16%</td>
<td>17%</td>
</tr>
<tr>
<td>Growth fault</td>
<td>6%</td>
<td>0%</td>
</tr>
<tr>
<td>Layer-displacement fault</td>
<td>6%</td>
<td>0%</td>
</tr>
</tbody>
</table>
The Fault Model structural interpretation of the reconstructed ε-machine of Fig. 9. This is valid only under the assumption of weak faulting.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H</td>
<td>82%</td>
</tr>
<tr>
<td>3C</td>
<td>4%</td>
</tr>
<tr>
<td>Deformation fault</td>
<td>9%</td>
</tr>
<tr>
<td>Growth fault</td>
<td>4%</td>
</tr>
<tr>
<td>Other disorder</td>
<td>1%</td>
</tr>
</tbody>
</table>

A comparison of the three characteristic lengths and three measures of intrinsic computation that one can calculate from knowledge of the ε-machine. We calculate them for the experimental diffraction spectra, as well as for three crystal structures for reference. Recall that \( \Delta = C_{\mu} - E - rh_{\mu} \) (Varn et al., 2005a).

<table>
<thead>
<tr>
<th>System</th>
<th>( \lambda )</th>
<th>( P )</th>
<th>( r_1 )</th>
<th>( h_{\mu} )</th>
<th>( C_{\mu} )</th>
<th>( E )</th>
<th>( \Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H</td>
<td>( \infty )</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3C</td>
<td>( \infty )</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>6H</td>
<td>( \infty )</td>
<td>6</td>
<td>3</td>
<td>0</td>
<td>2.6</td>
<td>2.6</td>
<td>0.0</td>
</tr>
<tr>
<td>SK134</td>
<td>9.5 ± 0.5</td>
<td>4.8</td>
<td>3</td>
<td>0.50</td>
<td>2.3</td>
<td>0.75</td>
<td>-0.1</td>
</tr>
<tr>
<td>SK135</td>
<td>4.4 ± 0.7</td>
<td>3.6</td>
<td>3</td>
<td>0.59</td>
<td>2.5</td>
<td>0.71</td>
<td>0.0</td>
</tr>
<tr>
<td>SK137</td>
<td>12 ± 3</td>
<td>6.7</td>
<td>3</td>
<td>0.65</td>
<td>2.7</td>
<td>0.79</td>
<td>0.0</td>
</tr>
<tr>
<td>SK229</td>
<td>19 ± 2</td>
<td>3.5</td>
<td>3</td>
<td>0.30</td>
<td>1.8</td>
<td>0.89</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Relative configurational energies \( E \) and hexagonality \( \alpha_0 \) of experimental polytypes and several pure-crystalline polytypes. The last column gives the history of each sample, where PC stands for perfect crystal, AG as-grown, and D disordered. We use the energy coupling constants, \( J_1 \) and \( J_2 \), calculated by Engels and Needs along with the reconstructed ε-machine for the disordered processes to find the configurational energy of the disordered structures via Eqs. (2) and (3).

\[
\langle s_i s_{i+1} \rangle = \langle s_i s_{i+2} \rangle = \frac{E}{\alpha_0} = \text{History}
\]

Table 4

\[
\begin{array}{cccccc}
\text{System} & \langle s_i s_{i+1} \rangle & \langle s_i s_{i+2} \rangle & E & \alpha_0 & \text{History} \\
2H & -1.00 & 1.00 & 1.95 & 1.00 & PC \\
3C & 1.00 & 1.00 & -1.79 & 0.00 & PC \\
6H & 0.33 & -0.33 & -0.65 & 0.33 & PC \\
SK134 & -0.58 & 0.63 & 1.13 & 0.80 & D 2H, 300 C for 1h \\
SK135 & 0.56 & 0.45 & -1.02 & 0.24 & D 2H, 500 C for 1h \\
SK137 & 0.32 & 0.45 & -0.57 & 0.34 & AG 3C \\
SK229 & -0.80 & 0.86 & 1.56 & 0.90 & AG 2H \\
\end{array}
\]

Figure 1

Diffraction spectrum along the 10.1 row from SK134 corrected for atomic scattering factors, the structure factor, dispersion factors, and the polarization factor. (Hahn et al., 1992; Woolfson, 1997; Warren, 1969) We see that the spectrum is not periodic in \( l \), as it should be. This indicates that there exist significant errors in the data.

Figure 2

Experimental and theoretical figures-of-merit—\( \beta \) and \( \gamma \)—as a function of \( l_0 \) for diffraction spectrum SK134. We define \( l_0 \) as the point at which integration over a unit \( l \)-interval is initiated. We find that \( l_0 \approx 0.04 \) gives the best agreement with the theoretical values.

Figure 3

\( Q_s(n) \) versus \( n \) for experimental spectrum SK134 (open squares connected by solid line), the fault model (open circles), and the \( r = 3 \) ε-machine (solid squares). The \( Q_s(n) \) are defined only for integer values of \( n \), but lines are drawn connecting adjacent points as an aid to the eye. We see good agreement up to \( n \approx 15 \), after which the \( r = 3 \) approximate correlation functions die too quickly to their asymptotic value of 1/3.

Figure 4

Comparison of the \( Q_s(n) \) versus \( n \) for experimental spectrum SK135 (open squares), the ε-machine (solid squares), and the FM (open circles). The ε-machine gives good agreement with experiment, while the FM overestimates the oscillation magnitude.
**Figure 5**
Comparison of the experimental diffraction spectrum SK137 along the 101 row (triangles) for a disordered 3C single crystal with the diffraction spectra calculated from the FM with 6.8% twinned faulting (dashed line) and the ϵ-machine (solid line). The profile R-factor between experiment and the ϵ-machine calculated diffraction pattern is $R_{EM} = 17\%$. The FM gives considerably worse agreement, with a calculated profile R-factor of $R_{FM} = 58\%$ between it and experiment.

**Figure 6**
The reconstructed $r = 3$ ϵ-machine for SK137. The strong self-loop transition probabilities between causal states $S_0$ and $S_4$, as well as their large asymptotic state probabilities, suggest that the ...0000... and ...1111... structures are important. Notice that, unlike the ϵ-machine for SK135, the CSC $[S_2S_3]$ is present, suggesting that associated 2H structure is present. The absence of the transition between CSS $S_1$ and $S_3$ implies that the 0011 sequence, and therefore the CSC associated with the 6H structure, is not present.

**Figure 7**
Comparison of the CF $Q_4(n)$ versus $n$ for experimental spectrum SK137 (open squares), the $r = 3$ approximate ϵ-machine (solid squares), and the FM (open circles).

**Figure 8**
A comparison of the experimental diffraction spectrum SK229 (dashed line) and that calculated from the reconstructed ϵ-machine (solid line). There is generally good agreement between two, except that the Bragg-like peaks from the ϵ-machine are slightly displaced from the experimental spectra and the maximum from the ϵ-machine overestimates experiment. The ϵ-machine also has some difficulty reproducing the shape of the experimental spectra. The profile R-factor between the two spectra is $R_{EM} = 29\%$.

**Figure 9**
The $r = 3$ ϵ-machine reconstructed for SK229. The large asymptotic state probabilities for the $S_2$ and $S_3$ states, as well as the large state-transition probabilities between them, show that this is predominately a 2H crystal with some faulting.

**Figure 10**
Comparison of the CF $Q_4(n)$ versus $n$ for experimental spectrum SK229 (solid squares) and the ϵ-machine (open squares).