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Total energy calculations on zinc sulphide polytypes

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Abstract. We report the results of first-principles pseudopotential calculations of the total energies of the $\langle 1 \rangle$, $\langle \infty \rangle$, $\langle 2211 \rangle$, $\langle 2 \rangle$ and $\langle 3 \rangle$ polytypes of ZnS. These results are compared with previous work on SiC polytypes. The lowest energy ZnS polytype is calculated to be $\langle \infty \rangle$, in agreement with the experimental observation that $\langle \infty \rangle$ is the stable low temperature modification. We find that, in contrast to SiC, all ZnS polytypes are very close in energy. We discuss the implications of our results for theories of polytypism in ZnS.

1. Introduction

ZnS is the chemical symbol for the rather common natural mineral Zincblende, and we might therefore expect it to be the ideal example of a material crystallising in the corresponding zincblende structure. In fact ZnS forms in a large variety of different crystallographic modifications, known as polytypes. The structures of these polytypes are all very closely related and differ only in the way identical ZnS double layers (referred to as 'layers' hereafter) are stacked on top of one another along the c -direction of a hexagonal unit cell, yielding the bonding arrangement in the $(1, -1, 0)$ plane shown in figure 1. Structures with periodicities of up to a few hundred Angstroms have been reported in experimental work (Mardix 1986).

In this paper we present some calculations and a theoretical discussion which should lead to a better understanding of ZnS polytypes. Recently there has been a considerable amount of theoretical work on polytypism in SiC (Cheng *et al* 1987, 1988, 1989a, b), which has the same basic structure as ZnS. The picture that has emerged from this work is that the lowest energy SiC polytypes belong to a subset with certain common structural features. There are a large number of members of this subset and they are almost degenerate in energy. Experimentally it is members of this lowest energy subset that are normally observed. This indicates that equilibrium thermodynamics plays a crucial role in determining which polytypes are observed and which are not. On the other hand it seems likely that other factors, such as the precise growth conditions and the presence of defects such as screw dislocations, are important in determining which member of the low energy subset is actually formed in an experiment. This work on SiC has raised the question of whether a similar picture holds for ZnS. Interestingly the set of ZnS polytypes which are most commonly observed is quite different from that for SiC, even though the structures are formed from the same type of structural unit. While the commonly observed SiC polytypes have very definite structural features in common, ZnS forms in a much wider variety of structures (Mardix 1986).

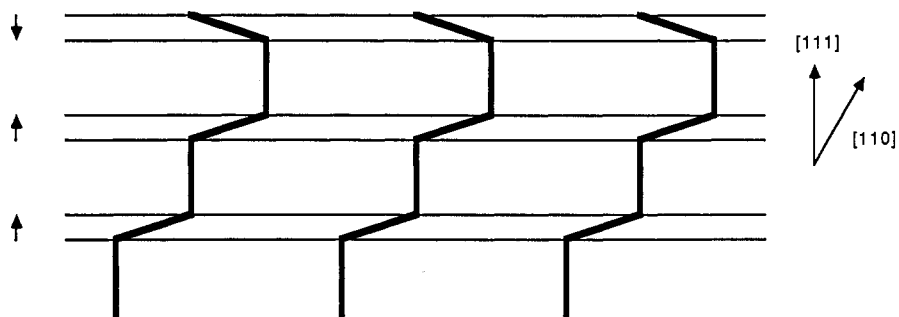


Figure 1. An example of the stacking of ZnS layers. The plane of the paper corresponds to a $(1, -1, 0)$ plane of the zincblende structure and the directions $(1, 1, 0)$ and $(1, 1, 1)$ are indicated. The two ways of stacking correspond to a bond pointing either to the right or to the left in the $(1, -1, 0)$ plane. These are referred to as an up spin (\uparrow) or a down spin (\downarrow) layer respectively.

We will show that, in fact, a roughly similar picture does hold for ZnS as for SiC, with both equilibrium and non-equilibrium properties playing important roles. The precise nature of the equilibrium and non-equilibrium properties of ZnS and SiC are different from one another and consequently the commonly observed polytypes are different. In a separate paper (Engel 1989) we will discuss the detailed mechanisms which we believe are responsible for the formation of the particular ZnS structures, but in this paper we will confine ourselves to answering the following questions:

- (a) Is there a thermodynamic reason favouring the phenomenon of polytypism in ZnS?
- (b) What is the main difference between SiC and ZnS which allows ZnS to form a much larger variety of structures?

The answers to these questions must be sought at the atomic level: a fully quantum-mechanical calculation of the total energies of the different polytypes is required.

2. Structures of ZnS and SiC polytypes

We use the Zhdanov notation (Zhdanov 1945) to label the different structures. This notation is based on a representation of the layer sequence of a given polytype by a row of spins, where up and down spins represent the two ways a double layer can be stacked on top of the preceding one (see figure 1). The Zhdanov numbers simply give the widths of bands of parallel spins. Hence the cubic (zincblende) structure ($\dots \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \dots$) is written as $\langle \infty \rangle$, the hexagonal (wurtzite) structure ($\dots \uparrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \dots$) as $\langle 1 \rangle$ and the structure ($\dots \uparrow \uparrow \uparrow \uparrow \downarrow \downarrow \downarrow \uparrow \uparrow \uparrow \dots$) as $\langle 3 \rangle$.

The observed structures of ZnS are quite different from those of SiC. Whereas the SiC polytypes consist mostly of bands of width 2 and 3 with no 1s occurring except in the rare hexagonal modification, the list of almost 200 ZnS polytypes given, for example, by Mardix (1986) shows a much larger variety of bandwidths. It is striking that very long and very short bands coexist in many of these structures, which is not found for SiC. Also, a small number of polytypes contain 1s in combination with larger bands.

It is difficult to determine any definite temperature stability ranges from experimental data even for the simplest polytypes in the two materials. However, some important differences between growth conditions in SiC and ZnS are worth mentioning. For both materials, polytypic crystals are often obtained by growing them from the vapour phase; for SiC at temperatures above 2000 °C and for ZnS between 1300 °C and 1400 °C. The high temperature phase of ZnS is the hexagonal modification $\langle 1 \rangle$, which undergoes a phase transition to the cubic modification $\langle \infty \rangle$ at about 1020 °C (Allen 1912). Detailed investigations by Mardix *et al* (1970) have shown that, in whiskers grown from the vapour phase, this transformation is often incomplete and results in polytypic layer arrangements.

In SiC, the high temperature modification is believed to be $\langle 3 \rangle$, but below 2000 °C the experimental findings are often contradictory, and transformations between all sorts of structures take place depending on the temperature, applied pressure and the presence of impurities (see, for example, Pandey and Krishna (1982)). It is not really clear what the low temperature modification of this material is. Theoretical work (Cheng *et al* 1987, Cheng *et al* 1989a) predicts that either $\langle 2 \rangle$ or $\langle 3 \rangle$ is the stable modification at low temperatures, these two being almost precisely degenerate. If this is correct, the frequently observed cubic modification is a result of the growth process rather than a thermodynamically stable phase.

3. Calculations of the total energies of ZnS polytypes

To evaluate the total energies, we used a plane wave pseudopotential technique formulated within density functional theory and using the Ceperley–Alder form of the local density approximation for the exchange–correlation energy (Ceperley and Alder 1980, Perdew and Zunger 1981). Excellent reviews of the total energy pseudopotential method, and applications of it, can be found in the articles by Srivastava and Weaire (1987) and Ihm (1988). In this technique the wavefunctions and potentials are expanded in a plane wave basis set and the resulting matrix equations solved self-consistently. In our work we use an efficient iterative diagonalisation scheme to solve the matrix equations (Nex 1987, Hodgson and Nex 1988). Integrations over the Brillouin zone were performed by sampling on a regular grid of points in reciprocal space using the method of Monkhorst and Pack (1976). The calculational techniques used in the present study are essentially identical to those employed in earlier work on SiC polytypes (Cheng *et al* 1987, 1988, 1989b).

We have used norm-conserving pseudopotentials to represent the potentials of the zinc and sulphur ions. The sulphur pseudopotential was obtained from the tables calculated by Bachelet *et al* (1982). Because ZnS forms tetrahedrally coordinated structures it is clear that the cohesion is predominantly due to sp^3 hybrid bonding. This implies that the zinc 3d electrons may be treated as core electrons and removed from the problem in forming the pseudopotential. In fact, the zinc 3d orbitals are quite extended and there is a considerable overlap between the valence 4s orbitals and the 3d orbitals. In such cases one must be careful to treat the exchange–correlation energy properly. The problem is that the exchange–correlation energy is a non-linear functional of the charge density and hence cannot properly be divided into valence and core contributions, as would normally be done in a pseudopotential calculation. If, by forming the solid, the valence electron density in the small core region is changed significantly from its atomic form, then the exchange–correlation energy must be calculated from the sum of the

Table 1. Results of total energy calculations on the five ZnS polytypes, $\langle 1 \rangle$, $\langle \infty \rangle$, $\langle 2211 \rangle$, $\langle 2 \rangle$ and $\langle 3 \rangle$, for different values of the plane wave cut-off energy EPW. The last two columns give the values of the inter-layer interaction parameters J_1 and J_2 . All energies are given in eV per pair of ZnS atoms.

EPW	$\langle 1 \rangle$	$\langle \infty \rangle$	$\langle 2211 \rangle$	
15 Ryd	-334.724 78	-334.728 01	-334.725 96	
20 Ryd	-335.551 56	-335.555 13	-335.552 85	
25 Ryd	-335.793 98	-335.797 71	-335.795 32	
EPW	$\langle 2 \rangle$	$\langle 3 \rangle$	J_1	J_2
15 Ryd	-334.726 55	-334.727 05	0.001 62	-0.000 08
20 Ryd	-335.553 50	-335.554 06	0.001 79	-0.000 08
25 Ryd	-335.796 00	-335.796 59	0.001 87	-0.000 08

valence and core charge densities. Such non-linear core exchange–correlation corrections were studied by Louie *et al* (1982) who produced a practical scheme for implementing such corrections which we have used in our work. A pseudopotential generated using the Kerker (1980) method and including these non-linear core exchange–correlation corrections greatly improved the results of calculations of various structural properties. For instance, the calculated lattice constant was only 3.5% less than the experimental value of 5.404 Å, compared with an error of 13% if the corrections were not included. We have used this pseudopotential, *including* non-linear core exchange–correlation corrections, in all of the calculations on ZnS polytypes presented in this paper. A complete report of our calculations of the structural properties of cubic ZnS and the use of non-linear core exchange–correlation corrections will be published elsewhere (Engel and Needs 1989).

The energy differences between the polytypes are very small and one must be very careful to ensure convergence of the calculations with respect to the size of the basis set and the sampling of the Brillouin zone. To test the convergence of the energy differences between polytypes with respect to the size of the basis set, we calculated the total energies of the five polytypes considered with three different basis set cut-off energies. These cut-off energies were 15 Ryd, 20 Ryd and, for our most accurate calculations, 25 Ryd. The results of these calculations are given in table 1, the convergence of the differences in total energies between polytypes is very good, and the error from this source is estimated to be less than 10^{-4} eV per ZnS pair. Care must be taken to sample the wavefunctions at precisely equivalent points in reciprocal space for the different structures. The procedure for this has been described in detail by Cheng *et al* (1988). All the structures were specified in terms of hexagonal unit cells whose heights were 2, 3, 4, 6 and 6 ZnS double layers for the $\langle 1 \rangle$, $\langle \infty \rangle$, $\langle 2 \rangle$, $\langle 3 \rangle$ and $\langle 2211 \rangle$ structures respectively. The Brillouin zone integrations were performed by sampling reciprocal space on a grid of points arranged in a regularly spaced stack of planes with the stacking direction along the *c*-axis. Each plane contained 16 sampling points and to ensure equivalent k-point sampling for each structure we took 6, 4, 3, 2 and 2 of these planes for the five structures respectively. Tests were also made by increasing the number of k-points sampled in the Brillouin zone integration, and the energy difference between the hexagonal and cubic structures was found to vary with k-point sampling by less than 10^{-4} eV per ZnS pair. The error due to

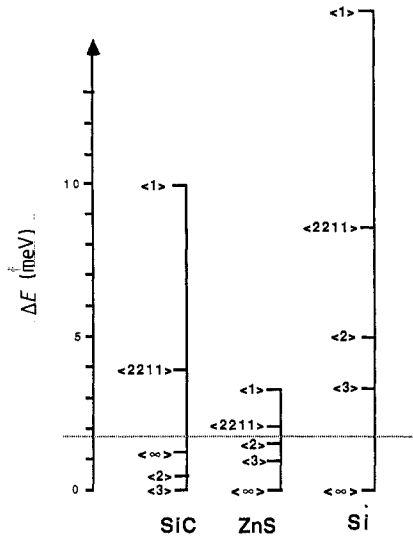


Figure 2. Energies of the $\langle 1 \rangle$, $\langle \infty \rangle$, $\langle 2211 \rangle$, $\langle 2 \rangle$ and $\langle 3 \rangle$ polytypes of ZnS, Si and SiC obtained from the calculated inter-layer interaction parameters. Polytypes below the dotted line are commonly observed in experiments while those above the dotted line are not. All energies are in meV per pair of atoms.

lack of self-consistency is completely negligible; all calculations were cycled until full self-consistency was reached.

All of our calculations were performed with the atoms in their ‘ideal’ positions and with the experimental lattice constant $a = 5.404/\sqrt{2} \text{ \AA}$ and the ideal c/a ratio. In reality, of course, the a and c lattice constants and the positions of the atomic planes in the c -direction undergo small relaxations. The effect of these relaxations was calculated by Cheng *et al* (1989b) for SiC and found to be of the order of $5 \times 10^{-4} \text{ eV}$ per SiC pair and hence small on the scale of figure 2. In addition it is known from experiment that ZnS shows only very small variations in both c/a ratio and lattice parameter with hexagonality (Skinner 1961, Skinner and Bethke 1961). We therefore neglect the effect of structural relaxation in the present analysis.

4. Results and analysis of the energies

In this section we present the results of our total energy calculations for the five ZnS polytypes and analyse them in detail. The calculated energies for each structure are given in table 1. The energies, which correspond to the free energies at $T = 0$, may be modelled in terms of the interactions between ZnS layers, following Cheng *et al* (1988). By analogy with magnetic spin systems, we write the total energy for a stacking sequence of N layers as

$$E = E_0 - J_1 \sum_i s_i s_{i+1} - J_2 \sum_i s_i s_{i+2} - J_3 \sum_i s_i s_{i+3} - K \sum_i s_i s_{i+1} s_{i+2} s_{i+3} \quad (1)$$

where $s_i = +1$ or -1 according to whether the layer has up or down spin. The J_n are effective interactions between spins which can be related to the interactions between atomic layers. Equation (1) is the most general expression possible for inter-layer interactions up to third nearest neighbours (Shaw and Heine 1989).

The energies of the five different polytypes can be expressed in terms of the energy expression of equation (1) giving

$$\begin{aligned}
 E_{(1)} &= E_0 + J_1 - J_2 + J_3 - K \\
 E_{(\infty)} &= E_0 - J_1 - J_2 - J_3 - K \\
 E_{(2211)} &= E_0 + \frac{1}{3}J_1 + \frac{1}{3}J_2 - \frac{1}{3}J_3 - \frac{1}{3}K \\
 E_{(2)} &= E_0 + J_2 - K \\
 E_{(3)} &= E_0 - \frac{1}{3}J_1 + \frac{1}{3}J_2 + J_3 + \frac{1}{3}K.
 \end{aligned} \tag{2}$$

For each energy cut-off, the J s and K were determined by inverting this equation. In each case the values of J_3 and K were found to be completely negligible. Therefore the final values of J_1 and J_2 were obtained from a least squares fit of the calculated energies to the parametrisation of equation (2), setting J_3 and K to zero. The results for J_1 and J_2 are listed in table 1. The differences between fitted and calculated energies never exceeds 2×10^{-5} eV per ZnS pair. Any longer ranged interactions are therefore believed to be at least one order of magnitude smaller than J_2 . Our most accurate energies for ZnS give:

$$\begin{aligned}
 J_1 &= 0.00187 \text{ eV per ZnS pair} & J_3 &\text{ negligible.} \\
 J_2 &= -0.00008 \text{ eV per ZnS pair.} & K &\text{ negligible.}
 \end{aligned} \tag{3}$$

The precise value of J_2 is beyond the accuracy of our calculations, but we can be confident that it is extremely small. For comparison we give the corresponding values for SiC found by Cheng *et al* (1988):

$$\begin{aligned}
 J_1 &= 0.00533 \text{ eV per SiC pair.} & J_3 &= -0.00039 \text{ eV per SiC pair.} \\
 J_2 &= -0.00342 \text{ eV per SiC pair.} & K &= -0.00021 \text{ eV per SiC pair.}
 \end{aligned} \tag{4}$$

The values of J_1 , J_2 , J_3 and K determine which polytypes are thermodynamically stable. J_1 is calculated to be positive for both SiC and ZnS. This interaction favours spin arrangements where neighbouring spins are parallel to one another. If a structure other than the cubic one is to be stabilised as an equilibrium phase within this inter-layer interaction model, then J_2 must be of opposite sign and of similar magnitude to J_1 (alternatively, if $J_1 = J_2 = J_3 = K = 0$, then obviously all polytypes are degenerate). For SiC Cheng *et al* (1988) found that the parameters (which are given in equation (4) of this paper) almost exactly satisfy the conditions $J_1 > 0$, $J_2 < 0$, $J_3 < 0$ and $J_1 + 2J_2 - 3J_3 = 0$. For this choice of parameters, all polytypes containing 2- and 3-bands are degenerate in energy and lower in energy than any polytype containing bands of width other than 2 or 3. This explains why 2s and 3s are so common in this material. Also, in this picture very small variations in the values of the inter-layer interaction parameters with temperature or pressure could lead to transitions between the phases. The inclusion of longer ranged interactions may result in an even more complicated phase diagram, with an even larger number of stable phases for different values of the interaction parameters. However, it is doubtful whether such longer ranged interactions, which are certainly extremely small, are really more important in determining which structures are observed than other effects arising from the particular growth conditions. Rather, the structures may well be metastable in the strict thermodynamic sense, but the energy calculations have clearly shown that they are close to being equilibrium phases.

In ZnS, the story is essentially the same; the commonly observed polytypes turn out to be very close in energy. Here, J_1 is a factor of about 3 smaller than in SiC, while the calculated value of J_2 is a factor of about 40 smaller than in SiC, although as we mentioned above, in ZnS, J_2 is so small that we cannot give a precise value for it. The smallness of the inter-layer interaction parameters explains why the range of bands covered by ZnS polytypes is larger than for SiC. In particular, the energy difference between narrow and wide bands, which is mainly determined by J_1 , is small enough to allow their coexistence in a single polytype. The main contribution to the energies is from J_1 , which makes the cubic modification the thermodynamically stable one at low temperatures. This is in good agreement with experiment (Pandey and Krishna 1982).

Figure 2 illustrates the energy range covered by various ZnS, SiC and Si polytypes. The energies, calculated from the interaction parameters, are plotted on an equal energy scale. The interaction parameters for Si were deduced from the stacking fault energies calculated by Chou *et al* (1985), with the assumption that only J_1 and J_2 are significant, giving $J_1 = 0.0078$ eV and $J_2 = -0.0014$ eV per pair of Si atoms. These calculations were performed using techniques which are essentially identical to those of the present work. The plot shows that the energy range for the polytypes that are commonly observed in nature (those below the dotted line in figure 2) is rather similar for ZnS and SiC, but that this includes a larger variety of polytypes in ZnS than in SiC. In Si normally only the cubic structure is observed, which is now easily understood from the comparatively large stacking fault energies in this material. Polytypes above the dotted line in figure 2 may be observed under some circumstances. For instance, in SiC the $\langle 1 \rangle$ polytype may be formed under some growth conditions (Pandey and Krishna 1982), in ZnS the $\langle 1 \rangle$ polytype is quite common (Pandey and Krishna 1982) and, for Si, samples containing small regions of the $\langle 1 \rangle$ phase may be obtained from $\langle \infty \rangle$ by a process involving the application of stress (Wentorf and Kaspar 1963).

The fact that we calculate lower energies for those structures which are most commonly found in nature indicates that the differences in total energies at $T = 0$ do indeed influence the stability of the various structures. However, at finite temperatures other effects may become important and alter the energy diagrams in figure 2. For example the contribution to the free energy from phonons will be different for the different polytypes, giving rise to temperature dependent interaction parameters J_n and K . A detailed analysis of this effect has been carried out for SiC by Cheng *et al* (1989a). At the high temperatures of growth, of about 2500 K, the following contributions were found (Cheng *et al* 1989a):

$$\begin{aligned}
 J_1(T = 2500 \text{ K}) - J_1(T = 0) &= 2.398 \times 10^{-4} \text{ eV per SiC pair.} \\
 J_2(T = 2500 \text{ K}) - J_2(T = 0) &= 0.215 \times 10^{-4} \text{ eV per SiC pair.} \\
 J_3(T = 2500 \text{ K}) - J_3(T = 0) &= 0.042 \times 10^{-4} \text{ eV per SiC pair.} \\
 K(T = 2500 \text{ K}) - K(T = 0) &= -0.045 \times 10^{-4} \text{ eV per SiC pair.}
 \end{aligned}
 \tag{5}$$

The temperature dependences of the interaction parameters are rather small and, even at the high temperatures of growth, the SiC polytypes containing only 2- and 3-bands are still almost degenerate and more stable than any of the other polytypes.

As mentioned above, it is known from experiment that there is a phase transition from the cubic (∞) phase to the hexagonal $\langle 1 \rangle$ phase at about 1100 °C in ZnS. Hence we conclude that the phonon contribution should invert the diagram for ZnS in figure 2. However, a detailed analysis of the phonon contribution to the total free energies has

not yet been carried out. It is somewhat surprising to assume that the phonons should give a contribution large enough to change the sign of J_1 , especially as this would require them to favour the hexagonal structure in ZnS whereas they favour the cubic structure in SiC. Whether the effect of the phonons is indeed different for the two materials has to be left open to future investigation. Of course it is also possible that the errors in our calculations are substantial on the small scale of the energy differences between ZnS polytypes and that in reality J_1 is smaller than we have calculated.

It is known from experiment (Mardix *et al* 1987) that the solid state transformation from the hexagonal to the cubic phase plays an important role in the formation of polytypes in ZnS. This feature makes ZnS quite different from SiC, where polytypic structures are likely to be formed during growth itself. At the temperatures of growth (1400 °C), ZnS crystals are almost certainly formed in the hexagonal phase. During annealing, partial transformations take place, probably via a periodic slip mechanism where single stacking faults expand along the helical basal planes provided by a screw dislocation (Alexander *et al* 1970). Such a mechanism is able to explain the periodicity of the observed structures. In this sense, polytypes in ZnS can probably not be fully understood in terms of purely equilibrium thermodynamic considerations, and a deeper understanding of the dynamics of the phase transition is required. However, any transformation mechanism will drive the structure towards a thermodynamically more stable one, and in this sense the knowledge of the free energies is important whatever the detailed mechanism of the transformation turns out to be.

5. Conclusions

Perhaps the most striking feature of our results is that we find that all possible ZnS polytypes are very close in energy. This does not follow simply from the fact that ZnS forms polytypes; indeed SiC, which exhibits polytypism and has the same basic structure as ZnS, is a counter example. In SiC, polytypes containing only 2- and 3-bands are almost degenerate in energy and all other polytypes are higher in energy. We believe that this is the reason why 2s and 3s are so common in the structures of SiC polytypes. The fact that *all* ZnS polytypes are close in energy is probably the reason why it forms such a wide variety of polytypes. However, our calculations have also shown that the remaining small differences in energy between the ZnS polytypes are mainly determined by their degree of hexagonality, making the cubic phase the most stable one at low temperatures. This is important because it gives a thermodynamic driving force for the phase transition between the $\langle 1 \rangle$ and $\langle \infty \rangle$ polytypes at low temperatures, as the stacking fault energy of a cubic stacking fault in a hexagonal crystal will be negative. It is likely that the $\langle 1 \rangle$ phase is stable at the temperatures of growth and that, on cooling, a solid state transition towards the $\langle \infty \rangle$ phase results in polytype formation.

Another interesting result of our investigation is the short range of the inter-layer interaction parameters. In contrast to SiC, these are found to be significant only up to next nearest neighbour layers, and the dominant contribution to the total energies is from nearest neighbour interactions J_1 . The parameter J_2 is a factor of about 40 smaller than the corresponding parameter in SiC, and the ratio $J_1/|J_2|$ changes from 1.6 in SiC to 23 in ZnS. It is possible that the short range of the interactions also plays an important role in the transition from the hexagonal to the cubic phase which occurs during cooling. With only nearest neighbour interactions being significant, a single cubic stacking fault in a hexagonal crystal will not tend to nucleate a transformation to the cubic phase. This

is because, if the atomic process of the transformation is assumed to be the subsequent introduction of single stacking faults into the crystal, it is, in the absence of longer ranged interactions, energetically no more favourable to introduce a second stacking fault in the immediate vicinity of the first than anywhere else. Rather than creating a large cubic domain, the transformation results in a number of small cubic domains of varying size separated by hexagonal regions. Screw dislocations provide a plausible explanation for the periodicity of the incompletely transformed structures (Alexander *et al* 1970). In a separate paper (Engel 1989), these ideas will be extended to a simple dynamical model for the wurtzite to zincblende transition in ZnS in the presence of a suitable screw dislocation, which is based on the stacking fault energies calculated from the present work. This model gives a good account of the polytypic sequences in ZnS that are actually observed.

6. Summary

In summary we have calculated the total energies of five ZnS polytypes using first-principles pseudopotential techniques. The lowest energy polytype is calculated to be $\langle\infty\rangle$, in agreement with the experimental observation that $\langle\infty\rangle$ is the stable modification at low temperatures. In contrast to SiC and Si, all possible polytypes of ZnS are very close in energy. We believe that this is the thermodynamic reason for polytype formation in ZnS and also the reason why a wider variety of different ZnS polytype structures is observed as compared with SiC. For both ZnS and SiC, the polytypes most commonly observed are indeed those with the lowest structural energies, and the energy range covered by them in the two materials is roughly equal and very small. It is likely that at high temperatures the $\langle 1\rangle$ phase is stable and that the polytypes are formed by a solid state transition towards the $\langle\infty\rangle$ phase which occurs during cooling.

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