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Bilayer sliding mechanism for the wurtzite-to-rocksalt transition

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We have theoretically investigated the mechanism of the reconstructive wurtzite-to-rocksalt phase transition. Using COMSUBS, we found five different bond-preserving transitions pathways. These transition paths share a common underlying mechanism: bilayer sliding of (010) hexagonal planes along the [100] hexagonal directions.

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Increasing interest is being given to understand the mechanism of reconstructive phase transitions both from the theoretical and the experimental side. Understanding the transition mechanism means knowing the changes which take place at the atomic level and implies the possibility of controlling transition properties and a guide to interesting new experiments.

Over the years, there has been an effort to understand the reconstructive phase transition from the wurtzite (WZ) to the rocksalt (RS) crystalline structures. This transition occurs under temperature and pressure changes in III-V and II-VI semiconductors such as GaN, InN, CdS, CdSe, and CdTe. These compounds have interesting technological applications as high-temperature refractory ceramics and coatings, display devices, blue-light emitting diodes, and semiconductor lasers, as well as wide band gap semiconductors with large hardness.

The space-group symmetries of the WZ and RS structures do not have a group-subgroup relation. Hence, the transition from WZ to RS cannot take place with small deformations but requires large strains and atomic displacements. The coordination number of nearest neighbors changes from 4 to 6 during this transition.

Obtaining the detailed transition mechanism is a challenging problem. Experimentally, Knudson *et al.*[1] reported a method for obtaining a mechanism for the WZ to RS transition in shocked CdS using information from real-time picosecond time-resolved electronic spectroscopy coupled with *ab initio* calculations. Wickham *et al.*[2] reported results on the transition mechanism in CdSe using information from changes in nanocrystal shape determined by x-ray diffraction. Jacobs *et al.*[3] measured activation volumes, while Tolbert and Alivisatos[4] considered surface energies in CdSe to obtain information about the transition mechanism.

On the theoretical side, there are an infinite number of ways that one structure can be deformed into another. It is well known that diffusionless phase transitions (including those that are reconstructive) with atomic displacements and shear can often be described by looking for a nucleation free transition path (TP) defined by a common subgroup of both structures.[5–8] Molecular dynamics[9–11] and first principles[12,13] methods, as well as geometrical sphere packing methods,[14,15] have been used to study the transition.

We have developed a systematic procedure for obtaining possible microscopic mechanisms for reconstructive phase transitions. Some details of the algorithm are described by Stokes and Hatch[16,17] and has been used in our studies of the B1-to-B2 transition in sodium chloride and lead sulfide[16–18] as well as the zinc-blende-to-rocksalt transition in silicon carbide.[19] The procedure lets the user control the search by restricting allowed strain, nearest-neighbor distances along the TP, unit-cell size along the TP, atomic shuffle, and number of broken bonds and has been implemented in the computer program COMSUBS.[17]

In our procedure, we assume that periodicity is retained along the TP, that the atoms throughout the crystal are displaced coherently (defects are neglected), and that the crystal, as it moves from the initial to the final structure, is well defined by a space-group symmetry which is a common subgroup of both the WZ and RS structures. This model, of course, ignores the effects of nucleation and propagation of local deformations[3,11,20] but nevertheless provides useful information about the atomic mechanism of the actual transition. For example, we often obtain TPs which are very similar to local deformations observed in molecular dynamics, a much more realistic but more difficult approach in modeling a reconstructive phase transition.

We used COMSUBS[16,17] to find possible TPs for the WZ-RS transition. (As the notes in Ref. 17 indicate, the algorithm described in Ref. 16 has undergone some major revisions.) A number of studies[9,13,14] have suggested that the most energetically favorable TPs are bond preserving, so we constrained COMSUBS to search for TPs which preserve the number of bonds. In the WZ structure, each atom is bonded to four nearest neighbors. In the RS structure, each atom is bonded to six nearest neighbors. By "preservation of bonds" we mean that the four nearest neighbors in WZ are still nearest neighbors in RS after the transition. Two new bonds are created, but no old bonds are broken. We do not list here the other search constraints because the important constraint is

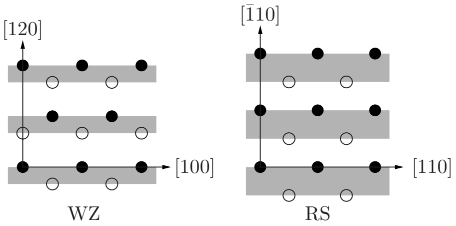

FIG. 1. Projection of the WZ and RS structures onto the (001) plane.

TABLE I. Bond-preserving transition paths (TPs) for the phase transition from the wurtzite (WZ) to the rocksalt (RS) structure. Each TP is defined by a common subgroup G' of both WZ and RS. At each end of the transition, we give the lattice vectors of G' in terms of the lattice vectors of G, and we give the atomic positions (Wyckoff positions) of the cations and anions in the setting of G'.

TP	G'	G	Lattice	Cation	Anion
1	36 $Cmc2_1$	WZ	(1, 1, 0), (−1,1,0), (0, 0, 1)	(*a*) 0, 2/3, 0	(*a*) 0, 2/3, *u*
		RS	(0, 1, 0), (−1,0,0), (0, 0, 1)	(*a*) 0, 3/4, 0	(*a*) 0, 3/4, 1/2
2	33 $Pna2_1$	WZ	(1, 2, 0), (−1,0,0), (0, 0, 1)	(*a*) 1/3, 0, 0	(*a*) 1/3, 0, *u*
		RS	(1,−1,0), (1/2,1/2,0), (0, 0, 1)	(*a*) 3/8, −1/4, 0	(*a*) 3/8, −1/4, 1/2
3	4 $P2_1$	WZ	(−1,0,0), (0, 0, 1), (0, 3, 0)	(*a*) 2/3, 0, 8/9	(*a*) 2/3, *u*, 8/9
				(*a*) 1/3, 1/2, 7/9	(*a*) 1/3, *u*+1/2, 7/9
				(*a*) 2/3, 0, 5/9	(*a*) 2/3, *u*, 5/9
		RS	(1/2,1/2,0), (0, 0, 1), (2,−1,0)	(*a*) 1/3, 0, 11/12	(*a*) 1/3, 1/2, 11/12
				(*a*) 0, 1/2, 3/4	(*a*) 0, 1, 3/4
				(*a*) 2/3, 0, 7/12	(*a*) 2/3, 1/2, 7/12
4	33 $Pna2_1$	WZ	(2, 4, 0), (−1,0,0), (0, 0, 1)	(*a*) 19/24, 3/4, 0	(*a*) 19/24, 3/4, *u*
				(*a*) 1/24, 1/4, 0	(*a*) 1/24, 1/4, *u*
		RS	(2,−2,0), (1/2,1/2,0), (0, 0, 1)	(*a*) 13/16, 1/4, 0	(*a*) 13/16, 1/4, 1/2
				(*a*) 1/16, 1/4, 0	(*a*) 1/16, 1/4, 1/2
5	4 $P2_1$	WZ	(−1,0,0), (0, 0, 1), (0, 4, 0)	(*a*) 2/3, 0, 11/12	(*a*) 2/3, *u*, 11/12
				(*a*) 1/3, 1/2, 5/6	(*a*) 1/3, *u*+1/2 5/6
				(*a*) 2/3, 0, 5/12	(*a*) 2/3, *u*, 5/12
				(*a*) 1/3, 1/2, 1/3	(*a*) 1/3, *u*+1/2, 1/3
		RS	(1/2,1/2,0), (0, 0, 1) (5/2,−3/2,0)	(*a*) 5/16, 0, 15/16	(*a*) 5/16, 1/2, 15/16
				(*a*) −1/16, 1/2, 13/16	(*a*) −1/16, 1, 13/16
				(*a*) 13/16, 0, 7/16	(*a*) 13/16, 1/2, 7/16
				(*a*) 7/16, 1/2, 5/16	(*a*) 7/16, 1, 5/16

the bond condition. Other constraints only need to be liberal enough to allow the transition process.

Searching for TPs where the common subgroup contains no more than eight atoms per unit cell (four cations and four anions), we obtained five bond-preserving TPs. In Table I, we specify each TP by describing the end points (the WZ and RS structures) in terms of the space-group setting of the common subgroup. This is simply a convenient way of denoting how the atoms in the WZ structure are mapped onto atoms in the RS structure. The actual path from WZ to RS is determined by the topography of the energy landscape and may even exhibit lower symmetry than the common subgroup shown in the table.

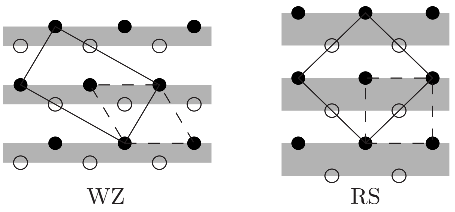

FIG. 2. Unit cell of the structure along TP 1. Note that for clarity, we have chosen the origin of the unit cell in the figure at the position of an atom. (The actual origin of the space group $Cmc2_1$ in Table I is not at the position of an atom.)

We compared our TPs with those from previous studies. Almost all previous papers[1,9–14] include a TP with the same atomic mapping as our TP 1. This includes TPs with intermediate structures which are hexagonal[9,13] or tetragonal.[1,12] Three papers (Shimojo *et al.*,[9] Zahn *et al.*,[11] and Sowa[15]) also describe a TP with the same atomic mapping as our TP 2, and Shimojo *et al.*[9] even describe a third TP with the same atomic mapping as our TP 3.

An analysis of how the atoms may move along each of our TPs reveals a common mechanism involving sliding of atomic layers. Recently, both Zahn *et al.*[11] and Sowa[15] have also described this mechanism. In Fig. 1, we show a projection of the WZ and RS structures onto the (001) plane. In

TABLE II. For each of the five TPs, the sequence of sliding bilayers is given.

TP	Sequence
1	+
2	+ −
3	+ + −
4	+ + −−
5	+ + + −

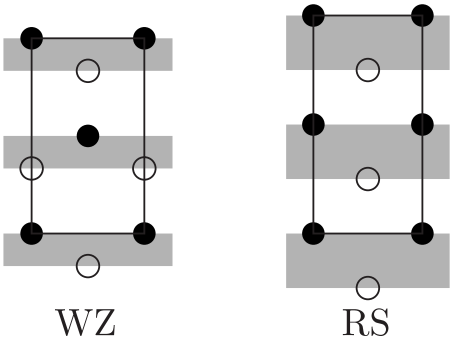

FIG. 3. Unit cell of the structure along TP 2. Note that for clarity, we have chosen the origin of the unit cell in the figure at the position of an atom. (The actual origin of the space group $Pna2_1$ is not at the position of an atom.)

WZ, the solid circles represent the cations and anions stacked on top of each other, the cations being in the $z=0$ planes and anions in the $z=u\approx 3/8$ planes. Similarly, open circles represent cations and anions stacked on top of each other, the cations being in the $z=1/2$ planes and anions in the $z=u-1/2\approx -1/8$ planes. In RS, the solid circles represent cations in the $z=0$ planes and anions in the $z=1/2$ planes, and the open circles represent cations in the $z=1/2$ planes and anions in the $z=0$ planes.

Along each TP, three types of atomic movements occur. (1) Anions in the WZ $z=u$ and $z=u-1/2$ planes move in the [001] direction (out of the page) into the $z=1/2$ and $z=0$ planes, respectively. This places the anions in the same planes as the cations. (2) Atoms in alternating WZ (010) planes (perpendicular to the hexagonal [120] direction) move in the ±[120] direction so that the resulting RS $(\bar{1}10)$ planes are equally spaced apart. (3) Pairs of WZ (010) planes (called bilayers, indicated by the shaded regions in the figure) slide in the ±[100] direction. Adjacent bilayers are displaced $\pm a/2$ (a=hexagonal lattice parameter in WZ) relative to each other. This sliding accounts for most of the atomic movement during the TP.

The different TPs in Table I are distinguished only by the relative direction adjacent bilayers slide. TP 1 is shown in Fig. 2. The space-group symmetry of the structure along the TP is 36 $Cmc2_1$. The solid line in the figure shows the conventional unit cell of $Cmc2_1$, and the dashed line shows the primitive unit cell. As can be seen, the middle bilayer in the figure slides $+a/2$, and the top bilayer slides $+a$, which is $+a/2$ *relative* to the middle layer. In this TP, as we move along the [120] WZ direction, every bilayer slides $+a/2$ relative to the previous bilayer. We denote this pattern of sliding by $++++\cdots$ or, equivalently, by simply the repeat unit $+$.

TP 2 is shown in Fig. 3. The middle bilayer slides $+a/2$ and the top bilayer does not slide at all, which is equivalent to sliding $-a/2$ *relative* to the middle bilayer. We denote this pattern of sliding by $+-+-\cdots$ or equivalently by simply the repeat unit $+-$.

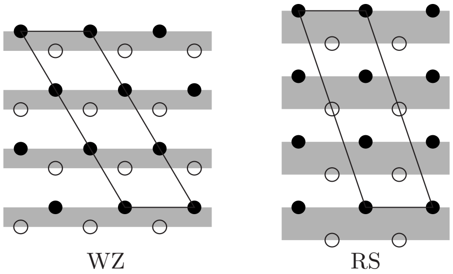

FIG. 4. Unit cell of the structure along TP 3. Note that for clarity, we have chosen the origin of the unit cell in the figure at the position of an atom. (The actual origin of the space group $P2_1$ is not at the position of an atom.)

TP 3 is shown in Fig. 4. The second bilayer from the bottom slides $+a/2$. The third bilayer slides $+a$, which is equivalent to sliding $+a/2$ relative to the second bilayer. The fourth bilayer slides $+a/2$, which is equivalent to sliding $-a/2$ relative to the third bilayer. We denote this pattern of sliding by $++-++-\cdots$ or equivalently by simply the repeat unit $++-$.

In Table II, we give the repeat unit of the patterns of sliding for each of the TPs. We can see that these are all of the possible nonequivalent patterns of sliding up to a repeat unit of 4. We can easily generate, by inspection, sliding patterns with even larger repeat units (for example, $++++-$, $+++--$, $++-+-$, etc.). These results are exactly what Sowa[15] had in mind when he predicted the existence of TPs where the unit cells have longer translational periods in one direction.

Shimojo *et al.*[9] found from DFT calculations that the energy barrier in CdSe is approximately equal for all three of his TPs (corresponding to our TPs 1, 2, and 3). This behavior results from the similar local atomic environment along each TP. Differences in the TPs are only manifested between atoms in next-nearest bilayers. Sowa[15] concluded that the energy barriers for all such TPs are expected to be very similar.

On the other hand, Zahn *et al.*[11] conclude from their molecular dynamics simulations in CdSe that TPs which avoid excessive strains should be favored. These are the TPs with equal numbers of bilayer sliding in the two directions, such at TP 2 and TP 4.

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