

Practical course M

Supplement

The Wurtzite Structure

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1 Introduction

Beta-zinc sulfide ZnS has been the first mineral of Wurtzite structure that has been discovered. It was named by its discoverer Charles Friedel after his teacher the French chemist Charles-Adolphe Wurtz. However, many other crystals are isostructural e.g. AgI, ZnO, CdS, CdSe, BeO, GaN, AlN. All these crystals and many others are build up by a rhombohedral prism as unit cell that contains four ions, for instance in the case of ZnO two zinc ions and two oxygen ions.

2 Crystal structure

In general a crystal structure is determined by two components, the lattice and the unit cell. The latter is repeated periodically with respect to the former (Fig.1). Fortunately there are only 7 different crystal systems in 3 spatial dimensions which gives rise to 14 different lattices. In particular the Wurtzite structure belongs to the hexagonal lattice. A sketch of the crystal structure i.e. the positions of the ions within the crystal is shown in Fig. 2. The building blocks are corner sharing tetrahedra that consists of four oxygen ions on its corners centered by a Beryllium ion in the case of Beryllium oxide (BeO). In order to characterize the symmetry of a crystal unambiguously it is necessary to specify the so called space group which consists of all symmetry transformations

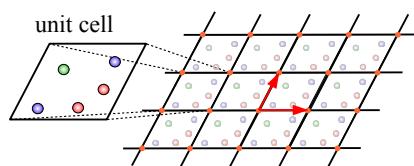


Figure 1: A crystal in 2 dimensions. The unit cell is shown on the left. The lattice is build up by repeating the unit cell in all (two) directions. The lattice vectors, i.e. the minimal translations of the lattice, are shown by the red arrows and the orange dots indicate lattice points.

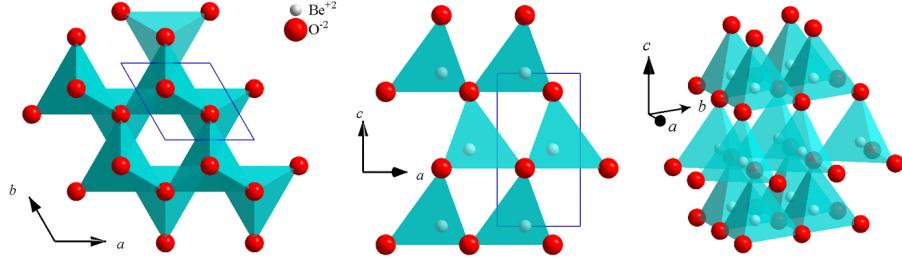


Figure 2: The crystal structure of BeO. The unit cell is indicated by blue lines, the oxygen tetrahedra around the Beryllium ions are shown in light blue. Left: view along the c -axis, middle: view along the b -axis, right: overview.

that leave the crystal structure invariant. All in all there are 230 different space groups. A space group is obtained by all translations and rotations/reflections that leave the crystal invariant. All possible translations are given by vectors that start and end on lattice points. The crystal will have at most the full point group of the lattice (called holohedry) or the symmetry is lowered to a subgroup of the holohedry. In case of the Wurtzite structure the space group is $P6_3mc$ (no. 186). The corresponding point group is C_{6v} . The symmetry elements of C_{6v} are given in Fig.3. Note, that beside pure rotations there are screw axes and glide planes which are the symmetry operators 4, 5, 6 and 10, 11, 12, respectively (from Fig. 3). The unit cell consists of four ions, as shown in Fig.3, the cell parameters are $a = b = 2.6984 \text{ \AA}$ and $c = 4.2770 \text{ \AA}$. The Be ions are at the positions $(\frac{1}{3}, \frac{2}{3}, 0)$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$, the oxygen ions at $(\frac{1}{3}, \frac{2}{3}, 0.3786)$ and $(\frac{2}{3}, \frac{1}{3}, 0.3786 + \frac{1}{2})$ with respect to the cell parameters. Note that there are only two ions of each sort within the unit cell since the positions of the oxygen and Beryllium ions are on a threefold axis, i.e. of higher symmetry than a general position. In a general position every symmetry operator will generate an additional ion position so that at most there will be 12 ions that are symmetry equivalent.

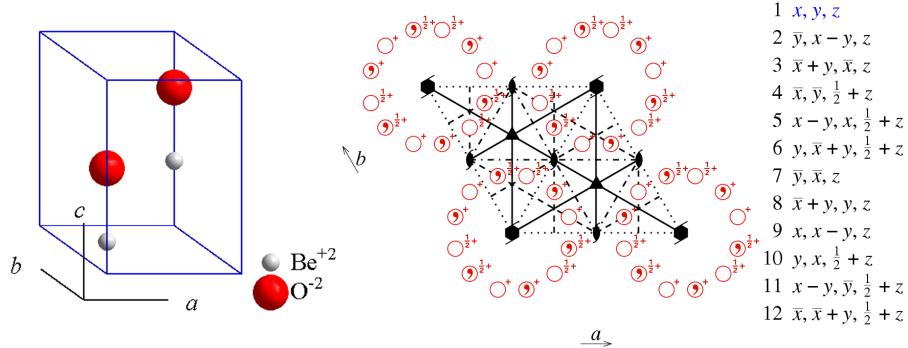


Figure 3: Left: the unit cell of BeO. Right: The location of the symmetry operators of the point group within the unit cell is shown. The action of the 12 symmetry transformations on an arbitrary position (x, y, z) is listed.

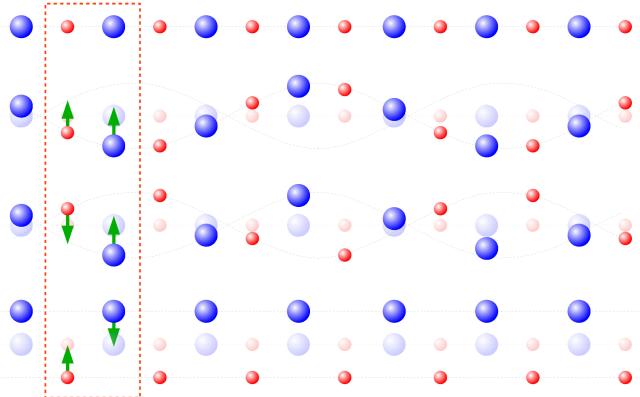


Figure 4: Acoustic and optical modes in a two atomic chain. The orange box indicate the unit cell. Top row: atoms at rest position. Second row: acoustic mode - all atoms in the unit cell move in the same direction. Third row: for the optical mode the ions within the unit cell move in different directions. Note, that acoustic and optical mode are at a finite wavelength. Bottom row: optical mode at infinite wavelength. The energy of the optical mode is finite even for infinite wavelength ($k = 0$), whereas the acoustic mode at infinite wavelength ($k = 0$) corresponds merely to a translation of the crystal. Hence it does not change the internal energy.

3 Phonons

In a crystal the ions have fixed positions that are repeated within a periodical lattice. For these positions the potential energy of the crystal is minimized therefore deviations of these equilibrium positions will raise the total energy. In a quantum mechanical point of view one thinks of excited states separated from the ground state by one (or several) energy quantum (phonons) analogous to the discrete energy levels of the harmonic oscillator.

For these excited states the displacement of the ions will not have an arbitrary pattern since the elongation of one single ion would in general cause other ions to be displaced, too via interactions between them. However there exist patterns of displacements that are independent of each other in the sense that if one pattern is excited it does not involve the other patterns. The vibrational excitations that correspond to these patterns are called Eigenmodes of the crystal. These Eigenmodes have characteristic frequencies ω_i (energies $\hbar\omega_i$). The frequency of the Eigenmodes depend on the particular pattern of elongations as

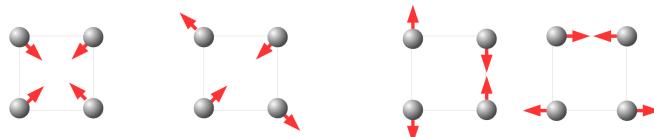


Figure 5: Eigenmodes of different symmetry of a square. Consider a rotation by $\frac{\pi}{2}$ that takes the square onto itself. The left pattern is mapped onto itself whereas its right neighbor is mapped onto minus itself. The two patterns on the right are mapped onto the respective other, i.e. they are degenerate.

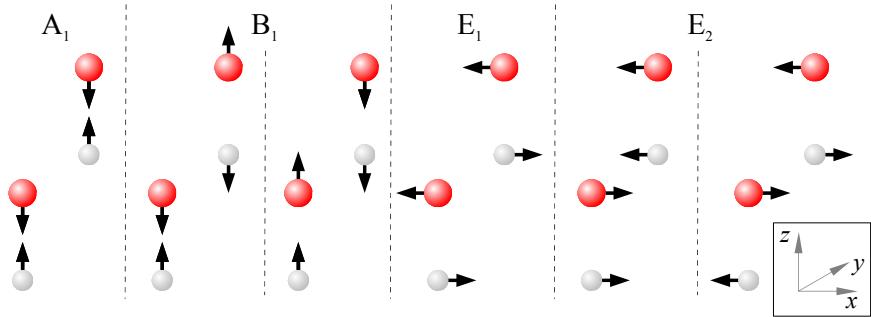


Figure 6: The movement of ions within the unit cell for the different phonon symmetries of the Wurtzite structure. To each of the E modes corresponds a second mode with an elongation along the y -direction. These modes are degenerate to the ones in x -direction and are not shown for clarity.

well as the wavelength λ or the wavevector $\mathbf{k} = \frac{2\pi}{\lambda}$, respectively, i.e. the spatial periodicity. The number of independent patterns can be easily obtained by considering the case of infinite wavelength ($k = 0$), since one has only to account for the displacement patterns within the unit cell. Assuming N ions within the unit cell each of them provides three degrees of freedom one for a displacement in x - y - and z -direction. Hence the total number turns out to be $3N$. The 3 acoustic modes become for $k = 0$ merely translations of the hole crystal that do not change the internal energy so that they have to be subtracted from this number. Therefore $3N - 3$ is the number of optical phonons. All these patterns of elongations q_i have to go under the symmetry transformations of the crystal either onto itself (q_i) or onto minus itself ($-q_i$) in order to restore the energy of the mode, which is quadratic in the elongation ($U \propto q_i^2$). There might occur as well the case that two (or in general also three) modes have the same pattern and differ only in direction, i.e. they are degenerated. The behavior of the pattern of Eigenmodes under application of symmetry operators can be classified by irreducible representations of the symmetry group¹.

The displacements of the ions within the unit cell are shown in Fig. 6 for the different phonon modes at $k = 0$ of the Wurtzite structure. The number of modes is determined to be $3 \times 4 - 3 = 9$ (four ions in the unit cell). Note that the modes of E_1 and E_2 symmetry are degenerate with modes of the same pattern elongated in the y -direction. So that they account for two modes, respectively. Whether a phonon mode occurs in the infrared spectrum or not depends whether the mode changes the dipole moment within the unit cell or it does not. In order to occur in a Raman spectrum the mode has to change the polarizability of the crystal.

¹A set of matrices that obey the same product relations than the elements of the symmetry group is called representation of the group. If all matrices of the representation cannot be brought into block-diagonal form simultaneously, the representation is said to be irreducible. The irreducible representations according to which the patterns of vibrations transform are only used here to label the different vibrations.