

### Appendix D. Deposited as an electronic file only

Table 2. The main concepts introduced when preliminary considering crystal structures of elements

Elements	Examples of problems discussed	Concepts introduced	References (see Appendix C)
Noble gases	<p>How can one pack equal balls most efficiently in space?</p> <p>Which types of interactions would favour a close-packed structure?</p> <p>Are there several ways of stacking densely-packed 2D-layers to form a 3D- close-packing?</p> <p>Which type of close packing dominates among the structures of noble gases? Why?</p>	<p>Close packing of equal spheres;</p> <p>Coordination number;</p> <p>Packing coefficient;</p> <p>Interactions: specific / non-specific, directional / non-directional;</p> <p>Polytypes</p>	<p>Pimentel &amp; Spratley, 1969, any "classical" crystallography and crystal chemistry text-book</p>
Group VII (halogens)	<p>Compare the structures of chlorine, bromine, iodine.</p> <p>Compare the conditions, under which these elements condense into liquids and then crystallize. Relate them to the electronic structure of elements (position in the Periodic Table).</p> <p>Consider a pressure-induced transition in iodine from a molecular crystal to a 2D-metal with a 2D-polymeric structure: compare the changes in the intra- and intermolecular bond lengths and angles</p>	<p>Molecular crystals.</p> <p>Intra- and intermolecular bonds.</p> <p>Polymeric structures.</p> <p>Effect of P,T conditions on the crystal structures</p>	<p>Takemura <i>et al.</i>, 2003, 2004 a,b</p>
Group VI (oxygen, sulphur, selenium, tellurium)	<p>Compare the structures of elements moving downwards the Periodic Table (from molecular crystals to polymeric networks).</p> <p>Compare the conditions, under which these elements condense into liquids and then crystallize. Relate them to the electronic structure of elements (position in the Periodic Table).</p> <p>Compare the high-pressure structures of lighter elements with the ambient-pressure structures of the heavier ones.</p> <p>Predict magnetic and conducting properties of the structures of oxygen polymorphs analyzing the distances between the atoms and the way how they are arranged in space (apply the MO approach).</p> <p>Compare the S-S distances, the S-S-S angles, the number of atoms in the closed cycles in different sulphur allotropes. Are there any invariants in all the various structures?</p> <p>Comparing the energy of a S-S bond (265 KJ mol<sup>-1</sup>), the range of S-S distances (1.8 Å-2.6 Å) and S-S-S angles (90° - 120°) present in different structures, suggest an explanation, why sulphur is able to give so many allotropes (several tens).</p>	<p>Molecular crystals and polymeric structures (continued).</p> <p>Interrelation between electronic properties of elements and crystal structures (continued). Directional interactions.</p> <p>Theory of molecular orbitals and interpretation of crystal structures.</p> <p>Structural invariants (structure-forming units).</p> <p>Crystal structures with several independent molecules in a cell. A difference between a solid solution and a regular structure with several independent components (S<sub>6</sub> + S<sub>10</sub> example).</p>	<p>Degtyareva <i>et al.</i>, 2005, 2007 a, b; Fujihisa <i>et al.</i>, 2006; Heiny <i>et al.</i>, 2005; Lundegaard <i>et al.</i>, 2006; Pimentel &amp; Spratley, 1969; Steudel, 2004; Tse &amp; Boldyreva, 2010; Weck <i>et al.</i>, 2009</p>

	<p>What holds sulphur cycles together in a solid?</p> <p>Why is S<sub>6</sub> the smallest cycle, which has ever been observed in solid sulphur? Why, as the S<sub>n</sub> cycle size <i>n</i> increases, at some stage polymeric structures substitute the structures built of isolated cycles?</p> <p>Which structural type should be expected to be favored at selected (P, T)- conditions?</p>		
<p>Group V (nitrogen, phosphorous, arsenic, antimony and bismuth)</p>	<p>Compare the structures of elements as moving downwards the Periodic Table (from molecular crystals to polymeric networks).</p> <p>Compare the conditions, under which these elements condense into liquids and then crystallize. Relate them to the electronic structure of elements (position in the Periodic Table).</p> <p>Compare the non-ambient structures of lighter elements with the ambient-conditions structures of the heavier ones.</p> <p>Compare the bond lengths and angles in various structures and try to find some “invariants”, which are transferred from one allotrope to another, maybe slightly distorted.</p>	<p>Molecular crystal - polymeric structure transitions (continued). Correlation with changes in colour and conductivity.</p> <p>Host-guest structures. Co-existence of non-equivalent atoms of the same element in the same crystal structure.</p>	<p>Degtyareva <i>et al.</i>, 2004, 2007c; Fujihisa <i>et al.</i>, 2007; Häussermann <i>et al.</i>, 2002; Ishikawa <i>et al.</i>, 2006; Marqués <i>et al.</i>, 2008; McMahon and Nelmes, 2004, a; McMahon <i>et al.</i>, 2007; Ormeci and Rosner, 2004; Schwarz <i>et al.</i>, 2003</p>
<p>Group IV (carbon, silicon, germanium, tin, lead)</p>	<p>Compare the structures of elements as moving downwards the Periodic Table and from the right to the left. Correlate with the electronic structure of elements.</p> <p>Suggest possible carbon structures using with sp, sp<sup>2</sup>, sp<sup>3</sup> hybridization. Consider the structure of graphene, and try to predict its properties.</p> <p>Suggest new structures using graphene sheets as a building block (carbon nanotubes and the two forms of graphite).</p> <p>Compare the non-ambient structures of lighter elements with the ambient-conditions structures of the heavier ones.</p> <p>Interpret the effect of P and T on crystal structures.</p> <p>Which properties of diamond are related to the covalent type of bonds and which - to its low packing coefficient?</p> <p>Compare the densities of graphite and of diamond, and suggest, which of the two forms should be expected to be stable at high pressures.</p> <p>Suggest a hypothetical a hypothetical evolutionary transformation from a graphite structure to the diamond one and reverse.</p>	<p>Structure-properties relations (continued). Conductivity, colour, mechanical properties.</p> <p>Polymorphs and polytypes (revisited).</p> <p>Directional bonds.</p> <p>Intercalation.</p>	<p>Fayos, 1999; Duclos <i>et al.</i>, 1987; Geim and MacDonald, 2007; Hanfland <i>et al.</i>, 1999; Hu and Spain, 1984; Li <i>et al.</i>, 2009; McMahon and Nelmes, 1993; Olijnyk <i>et al.</i>, 1984; Tse, 2005;</p>

	<p>Compare the structures of fullerenes with that of graphene.</p> <p>Compare the packing of fullerene "balls" in a crystal structure with that of the noble gases. Explain the origin of the differences.</p>		
Group III (boron)	<p>Find similarity between the boron polymorphs and interpret it in terms of the unique electronic structure of this element</p>	<p>Structure-properties relations (continued). Conductivity, colour, mechanical properties.</p>	<p>Albert and Hillebrecht, 2009; Oganov and Solozhenko, 2009; Shang <i>et al.</i>, 2010</p>
Metals	<p>Which metals form close-packed structures at ambient conditions, and which not? The same question for non-ambient P, T conditions. Suggest an interpretation.</p> <p>Why the (ABC)-type of close packing is more common than the (AB)-type? Why the (AB)-type packing in metals is more common than in the structures of noble gases? Why do some metals form structures with the stacking repeat unit higher than three?</p> <p>Why cannot a crystal structure be formed from close-packed tetrahedra, although forming a tetrahedron would be the densest way of organizing four spheres in a three-dimensional space?</p>	<p>Close-packed structures (revisited).</p> <p>The role of the inner-core and outer-shell, of s-, p-, d-electrons in determining the crystal structure at different P, T conditions.</p> <p>Metal-to-isolator transitions with increasing pressure.</p> <p>Host-guest structures, co-existence of non-equivalent atoms of the same element in the same crystal structure.</p> <p>Polymorphism and polytypism (revisited).</p> <p>Structures of amorphous metals in relation to conditions when they can be obtained.</p>	<p>Degtyareva, 2010; Gregoryanz <i>et al.</i>, 2005 &amp; 2008; Hanfland <i>et al.</i>, 2000; Katsnelson <i>et al.</i>, 2000; Lundegaard <i>et al.</i>, 2009 a, b; Ma <i>et al.</i>, 2009; Maksimov <i>et al.</i>, 2005; McMahon and Nelmes, 2004 a, b, 2006; McMahon <i>et al.</i>, 2006; Matsuoka and Shimizu, 2009; Neaton and Ashcroft, 1999; Pickard and Needs, 2009; Schwartz, 2004; Tonkov and Ponyatovsky, 2005; Yao <i>et al.</i>, 2009, a, b; Young, 1991; Zhou <i>et al.</i>, 2009</p>