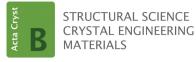
book reviews



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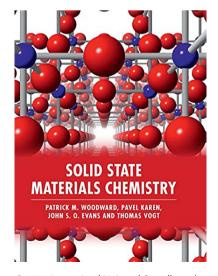
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Solid State Materials Chemistry is a very welcome book written by four of the most renowned solid-state chemists of our time, with undergraduate and graduate chemistry students in mind. This makes the book a unique resource to enter into the complex and fascinating chemistry and physics of matter in the solid state without having to deal with the most complex physical and mathematical details. The book offers intuitive explanations of some of the most complex phenomena of the solid state, relating them to simpler molecular chemistry observations, which are closer to the knowledge of an average chemistry undergraduate or recent graduate. Its fifteen chapters (see details below) cover from the basics of crystal structure and physico-chemical properties of the solid state to many of the most relevant applications that are under development nowadays based on solid materials. Each chapter discusses very didactically one specific topic; this is introduced and intuitively expanded to allow the reader to understand the main concepts, without resorting to detailed mathematical description, unless unavoidable. In order to keep the interest of the reader without perturbing the line of reasoning of the chapters, the text is adorned with short 1-2 page boxes containing details of one specific material (Materials Spotlight), a synthesis procedure (Synthetic Methods), a characterization technique (Characterizations), or a difference between nanoscale and bulk properties (Nanoscale Concepts) where interesting facts related to the chapter are introduced. In addition to the discussed topics, completed with mostly up-to-date references to relevant scientific literature, a section on further reading is provided, for the interested reader to delve deeper into the topics of each chapter. Many of these reading suggestions allow entry into the physical and mathematical details of the topic, avoided in the main text, or into more details of very specific systems. The authors explicitly highlight that students learn by practice; accordingly, each chapter ends with a list of no less than a dozen of problems and exercises that in some cases allow the reader to expand their understanding of topics discussed lightly in the text. Solutions to the problems and digital versions of the figures are also provided online for lecturers to use.

The first six of the 15 chapters are devoted to describing basic and general concepts that are used sparingly in the following nine chapters, targeting specific properties of the materials. Chapters 7 to 15 also have a specific introduction where some in-depth discussion is included to allow the reader to catch the essence of the main topic discussed. Appendices A to J expand on some very specific but important ideas such as molecular and crystallographic symmetry, specific nomenclature, bond-valence parameters, magnetic properties and behavior of matter under a magnetic field.

Chapter 1 deals with the structure of crystalline materials. It starts by describing translational and rotational symmetry in a periodic crystal in order to later define crystallographic point groups, Bravais lattices and finally space groups. The approach emphasizes the periodic nature of crystals and how this periodicity influences atomic connectivity and ultimately stoichiometry. Crystal structures are grouped based on closest packings and bonding networks; modifications caused by ordering different atomic species or expanding the networks of connected atoms are used to describe binary and ternary compounds. Databases devoted to crystal structures are mentioned. Appendices A and B expand on the *Introduction* in Chapter 1 with more details on point and space groups, respectively. Unfortunately, the 5th (print) edition (2006) of *International Tables for Crystallography*, Vol A, is referenced in Appendix B, and not the latest

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(6th print) edition (Aroyo, 2016), leading to the inclusion of information that is no longer in Vol. A, but in Vol. A1 (Wondratschek & Müller, 2011).

Chapter 2 deals with defects and more complex structures. Besides defining the different kinds of defects observed in solids and the Kröger–Vink notation used to describe them, the thermodynamics of defects formation is discussed using chemical equilibrium concepts and equations making the treatment of this complex matter more friendly. Vegard's law is introduced with solid solutions; deviations from it that lead to defect ordering are discussed. The chapter ends by introducing incommensurate and infinitely adaptive structures, presenting the full complexity of the solid state, where longrange order is observed despite the lack of (three-dimensional) periodicity.

Chapter 3 deepens the discussion into defect chemistry introducing nonstoichiometry in oxides and one of its consequences, ionic diffusion. Several examples of structures that will be discussed in later chapters are introduced, preparing the field for the applications. Extensive equilibrium equations are introduced in this chapter to explain the evolution of oxygen nonstoichiometry and defect fractions of the ions present in the solid. The resolution of complex equilibrium states with different kinds of defects for different kinds of materials is valuable to link the solid state with traditional chemical physics equilibrium studies.

Chapter 4 describes phase diagrams and transitions. Extensive case description is presented for two and three component phase diagrams, with plenty of examples for each possible situation. It is also an excellent chapter to learn about the different approaches to rationalizing phase transitions and explaining transition order parameter and Landau Theory of phase transitions, including phonon softening. This is the most didactic chapter of the book and one of the best on phase transitions I have read so far.

Chapter 5 discusses chemical bonding. Ionic compounds are described first using the fundamental ideas of close packing of spheres developed in Chapter 1. Crystal formation energy (Madelung constant, etc) is introduced here. The logic of analyzing extended atomic arrangements is broken when the basis for understanding covalent bonding takes the text to the introduction and analysis of atomic orbitals and later molecular orbitals for isolated molecules. However, this is a practical way to transition to electronic band structures in solids in the next chapter. Practical concepts such as the definition of HOMO and LUMO to explain electronic and spectroscopic properties, or Jahn-Teller distortions in coordination complexes to explain magnetic properties, set the stage for the applications chapters. This is a long chapter containing a lot of concepts and examples starting with atomic hydrogen and finishing with bond valence sums. It can be exhausting to read in one session, but abundant graphical aid alleviates the visualization of orbital overlap in one, two and three dimensions. Again, a large number of different compounds are described to exemplify the many alternatives of covalent bonding, preparing the reader for the last introductory chapter on electronic band structure.

Chapter 6 uses molecular orbital diagrams and the Bloch function to introduce electronic band structure. A simple monoperiodic theoretical hydrogen chain is used to introduce the main concepts such as band structure diagrams and density of states plots, discussed in a very clear and intuitive way without the use of equations. The extensions to more realistic diperiodic systems such as graphene or CuO²⁻ planes are preceded by the definition of the Brillouin zone, introduced in order to represent band structure diagrams in higher dimensions. Once in three-dimensions, electronic structure diagrams are discussed for insulators, semiconductors and metallic conductors, defining the Fermi energy, band gap, etc. Again multiple examples of real materials are considered starting from metallic Po and ending with the electronic structure diagram of an ideal ABO_3 perovskite, with a very informative discussion on the different roles of A (cuboctahedral site) and B (octahedral site) cations in the structure.

Chapter 7 discusses optical materials defining color and relating them to electronic properties. Luminescence, photoluminescence and electroluminescence are explained and exemplified with inorganic and organic examples. The final part of Chapter 7 highlights materials for lighting, explaining how different materials fit into everyday devices. Chapter 8 deepens into optical properties discussing dielectrics, nonlinear optical properties, pyro/ferro/piezoelectricity and second-harmonic generation materials. Nonlinear optical materials are presented, together with symmetry limitations of optical properties. Three boxes are used in this chapter to exemplify different materials, connecting structural and electronic properties with applications. In the two chapters, the discussion jumps from molecular to extended systems, bringing a lot of different examples from inorganic and organic (molecular and extended) materials.

Chapter 9 discusses magnetic materials in another long chapter that covers all the commonest cases of extended and molecular magnetism. The band structure of ferro/ferri magnetic materials is very well explained emphasizing that magnetism in solids can be understood as a collective phenomenon. However, the classical picture of localization of spins to represent the different magnetic structure types is well utilized. A complete discussion of magnetic susceptibility for each case is given, relating theory with experiment. Explanation of exchange interactions between cations in oxides is straightforward after the extended discussion on orbital overlap in Chapter 6. Box 9.1 enters into magnetic neutron diffraction; however, the absence of discussion of X-ray diffraction or Bragg law before this section makes it unclear.

Chapter 10 is devoted to conducting materials, with special emphasis on semiconductors, organic, inorganic and hybrid. Once more, a very intuitive explanation is given to intrinsic and extrinsic semiconductors with direct and indirect bandgap. Association of conductivity with number and mobility of carriers is also very well explained. Correlation between conductivity and magnetism is well developed in Chapter 11, where magnetotransport is discussed. Spin-polarized currents are introduced and colossal magnetoresistance is presented. In this chapter the strong correlation between structure and electronic structure is explained with several interesting examples where 'lattice' distortions (an imprecise term for structural distortions), defect formation and Fermi level variations are used to show different transport behavior in crystalline solids.

Chapter 12 follows naturally from Chapter 11 introducing superconductivity. The classical low-temperature superconductors following Bardeen–Cooper–Shrieffer theory are discussed first, and the explosion of research on cuprates following the discovery of high- T_c superconductivity in $La_{2-x}Ba_xCuO_{4+\delta}$ is a highlight in the book. Magnesium diboride, fullerides and pnictides are also discussed. Again, the strong correlation between crystal structure, electronic structure and defects is shown clearly in this chapter, that develops naturally and beautifully on the previous ones.

Chapter 13 describes energy materials. Ionic conductivity is the thread that links Li/Na ion (and other) conducting materials for batteries with mixed ionic–electronic conductors for fuel cells, including graphite intercalation chemistry. Liquid electrolytes are extensively discussed, although perhaps less interesting to solid state chemists; however, Box 13.1 is a short and interesting description of supercapacitors. The latest developments of Li-ion batteries and solid oxide fuel and electrolyzer cells are absent in this chapter with rather outdated references (the newest from 2015 and only a few post-2010), missing many of the newest exciting materials and technological applications (green hydrogen production among others) under development.

Chapter 14 introduces zeolites, a very specific and technologically important family of compounds, and the discussion on nano/micro/meso-porous materials includes aerogels and metal–organic frameworks (MOFs). Covalent organic frameworks (COFs), a new area of solid state organic chemistry development, are not mentioned.

Chapter 15 closes the book discussing amorphous and disordered materials. Characterization by atomic pair distribution function analysis is presented, despite the paucity of X-ray scattering in previous chapters. Different kinds of materials are described, from glasses to high-entropy alloys, going through to quasicrystals. An interesting discussion on preparation, physical properties and application of glasses for optic fibers, or cellphone screens, contrasts with somehow detailed physicochemical properties of disordered materials at very low temperatures.

Some omissions may be surprising from the point of view of a crystallographer, such as a mention of Bragg law so instrumental in the determination of one of the most important crystal structures discussed (NaCl) in Chapter 1. The first appearance is in Chapter 2, p. 78, and only three times in the text (not counting boxes, problems or appendices), twice referring to diffuse (non-Bragg) scattering. The Rietveld method (Rietveld, 1969), that has been so relevant to establish the structures of the majority of the materials discussed in the applications chapters but especially of high-Tc superconductors in Chapter 12, is also absent from the text. Some common language abuses, such as describing the substructure of anions in an oxide as 'oxygen sublattice' (Nespolo, 2019) or talking about 'lattice energy' and 'lattice vibrations' are also present, although 'lattice' is correctly defined in Section 1.1.1.

In summary, *Solid State Materials Chemistry* is an excellent introduction to understanding the structure, properties and applications of materials in the solid state for undergraduate and graduate students in chemistry. It captures the essence of the area highlighting the most important applications and current research without swamping the text with equations. Additionally, it provides references to additional specific literature that could be used to delve deeper into the physics behind the properties and applications. I will for sure use this book in my Materials Chemistry course and I am sure it would be of use to lecturers worldwide, specially if it were available in different languages.

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