Structure and Bonding in Crystalline Materials: A Textbook for Materials Science and Engineering Students

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ABSTRACT

A textbook has been prepared for an entry level Materials Science and Engineering graduate course on structure and bonding in crystalline materials. The course is intended to serve as a foundation for other graduate courses by providing techniques to understand crystal structures and the cohesive forces that stabilize them. The intrinsically connected topics of structure and bonding are presented in the same course because without knowledge in both of these areas, it is not possible to address the fundamental relationship between the composition, structure, and properties of solid matter that motivates nearly all materials research. The purpose of this paper is to describe the rationale used during the development of the course and the textbook that has been prepared to assist Materials Science and Engineering students and instructors.

Keywords:
Textbook, Crystal Structures, Bonding in Crystals

INTRODUCTION

The interdisciplinary nature and continual evolution of the field of Materials Science and Engineering (MSE) make the choice of a core graduate curriculum a difficult issue. Nevertheless, most departments select a small subset of courses that are required for all graduate students. Ideally, the material taught in the core part of the curriculum will provide all students (even those with undergraduate training in other disciplines) with the tools necessary to address the central issue that motivates nearly all materials research: how does the composition of solid matter and the way in which it is processed influence its structure and properties? To explore this fundamental question in a systematic manner, one needs to understand how the structure of matter is described, how to experimentally probe structure, and the cohesive forces in solids that determine the structure. The scope of the course described here is limited to descriptions of ideal atomic structure (the defect structure and microstructure being course material unto themselves), the theory of diffraction, bonding in crystals, and the relationship between structure and bonding.

The intellectual match between the topics of crystal structure and bonding is difficult to dispute. This structure-bonding relationship was realized in the early part of the century and discussed extensively through the decades by Pauling [1], Hume-Rothery [2], Pearson [3], Phillips [4], and Villars [5-7]. However, the graduate curricula in most MSE departments continue to greatly emphasize structure over bonding. In many cases, students are exposed to advanced models for crystal cohesion only during courses on electrical properties or solid state physics. Clearly, there is a potential advantage to teaching the topic of crystal cohesion at the same time as the topic of crystal structures so that the connections can be emphasized.

There are numerous existing books on crystallography [8-11], structural solid state chemistry [12,13], metallurgy [14], and solid state physics [15-17] that can be used as resources when teaching a course on structure and bonding. However, none of these books is wholly appropriate and this means that one must select sections of each. In my experience, this complicates the instructor's task of educating and the student's task of learning. The motivation for preparing this textbook was to provide a self-contained, coherent resource for both students and instructors. I should mention that another book targeted for MSE curricula, "Structure and Bonding in Condensed Matter", by C.S. Nichols [18], appeared three years ago. The textbook described here differs from this mainly in the balance between the two topics. The book by Nichols, which is no longer in print, has greater detail in the quantum mechanical models for bonding, while the book described here has a more extensive description of crystal structures, diffraction, and phenomenological models for bonding.

THE SUBJECT MATTER AND ITS ORGANIZATION

The most important (and possibly contentious) organizational decision in the structure of the textbook was whether to present structure or bonding first. There are reasonable philosophical and pragmatic arguments for both possible arrangements. For example, it has been argued that the distribution of electrons in the solid (the bonding) determines the structure and, therefore, bonding must be presented before structure. While this view can be supported, it leads to two problems. The first is the implication that the relationship between bonding and structure is a one way street. In fact, the atomic configuration in a crystal and the electronic distribution (spatial and energetic) seek a joint equilibrium. Consider, for example, what happens when a phase transformation is initiated by the application of hydrostatic pressure. In this case, the interatomic distances are externally altered and the bonds respond to the structure by changing to a new configuration. The second problem with presenting the bonding section before the structure section is that it betrays the scientific process. Models to explain phenomena are developed based on observations. Models for chemical bonds in solids were developed only after extensive crystallographic studies. When examining a model, it is essential that one has a strong working knowledge of the phenomenon being explained. Since crystal structure data are the observations on which bonding models have been formulated, I have chosen to present this section in advance of the bonding models. A complete table of contents for the text is presented in Table 1.

The case for presenting structure before bonding can also be argued from a pragmatic standpoint. The development of every analytical model for bonding is based on an understanding of the periodicity of the Bravais lattice and symmetry. Furthermore, the concepts of the reciprocal lattices, plane wave scattering, and systematic absences are easiest to introduce when describing diffraction, where the relationships between atomic structure and the reciprocal lattice (diffraction pattern) are concrete. It is then much easier to use these tools to describe the nearly free electron theory, the stability of electron compounds, and the reduced zone scheme for the presentation of band structures.

The decision to present the structure section before the bonding section is hedged somewhat by the first, introductory chapter. In Chapter 1, simple models for crystal structures and bonding are introduced. It is assumed that for most students in the course, this is a review. However, it does provide a foundation in bonding models before the beginning of the structure section. There are two points of emphasis in this chapter: the periodic nature of bonding, structure, and properties and the weakness of the simple models that most students were exposed to as undergraduates. This is intended to motivate the more detailed sections that follow.

Chapters 2 though 5 comprise the structural section of the course. Chapter 2 is a review of undergraduate crystallography with all of the terminology and mechanics needed for any advanced discussion. For example, the chapter includes sections on the real space lattice, crystallographic notation for locations, directions and planes, the reciprocal lattice, methods for calculating geometric parameters of the lattice, and methods for representing crystal structures. I have found that this is not only a useful review for MSE students, but it also provides an adequate foundation for students from other disciplines.

The third chapter describes the formal methods used to specify the symmetry of a crystal. The symmetry groups and operators used by crystallographers are a concise set of instructions for generating the positions of the atoms in a crystal. The goal of the chapter is not to explain the theory of groups, but to provide students with the information necessary to interpret crystallographic data written using conventional notation. This chapter contains sections on symmetry operators, the 32 crystallographic point groups, the 230 crystallographic space groups, and the interpretation of standard crystallographic data.

The goals of the fourth chapter are to acquaint the student with typical prototype crystal structures and to present a less formal, but more convenient way of describing structures. Briefly, simple structures are described as eutactic arrays with an ordered occupation of close-packed and/or interstitial sites. While this method lacks the precision of the one presented in Chapter 3, it is valuable because it leads to easy visualization and provides a means for comparison. More complex ternary and quaternary structures are described in comparison to the simple ones and noncrystalline structures (quasicrystalline, incommensurate, liquid crystalline, and amorphous structures) are described briefly in the last section.

The following example illustrates the methods emphasized in the first several chapters of the book. Chapters 3 and 4 include data for more 50 structure types in the format illustrated by Tables 2 and 3. In a worked problem, the reader is asked to describe the packing in the scheelite structure, compare this ternary structure to a more well known binary prototype structure, and to develop a geometric criterion that can be used to differentiate the ABO_4 compounds that take the scheelite structure from those that take the rutile structure. Based on the data in Table 3 and the information provided in Chapters 2 and 3, the schematic in Fig. 1 is constructed. From this sketch, we recognize that the metal atoms occupy the sites of a cubic close packed lattice and that the oxygen occupy the tetrahedral interstices. Based on this packing description, we note a similarity to the fluorite structure. However, scheelite differs from fluorite because the ordering of the two metal atoms on the close packed sites doubles the length of the unit cell along [001]. This ordering of the two metal atoms also causes the O to occupy a position that is distorted form the ideal tetrahedral coordination. To develop a geometric criterion to separate those ABO_4 compounds that take the rutile structure from those that take the scheelite structure, we recall that in rutile all of the metal atoms are 6-coordinate. In scheelite, the A cations are 8-coordinate while the B cations are 4-coordinate. This suggests an A/B size differential. To test this, the data in Tables 2 and 3 are used to make the plot in Fig. 2, which clearly illustrates that if $r_A/r_B < 1.3$, the rutile structure is preferred over scheelite.

The goal of the fifth chapter is to provide students with enough of a foundation in the theory of diffraction that they understand how structures are determined and what typical data mean. Rather than surveying crystallographic techniques or methods (most MSE departments devote an entire course to this subject), the chapter concentrates on the theory that accounts for diffraction. An emphasis is placed on understanding how the lattice and the basis of a structure can be determined from the angular positions and intensities of diffracted peaks, respectively. Intensity calculations are used to determine relative site occupations and specific position parameters. This particular section is placed after the chapters on basic crystallography and symmetry because it is not possible to have a detailed discussion of diffraction without the mechanical skills for dealing with real space and reciprocal space lattices or knowledge of the symmetry operations that lead to systematic absences.

The section on bonding is found in Chapters 6 through 9. Chapter 6 is about secondary bonding, Chapter 7 is about ionic bonding, Chapter 8 is about metallic bonding, and Chapter 9 describes the linear combination of atomic orbitals (LCAO) method that can be used for the whole range of polar covalent bonding. While the subject is divided under the traditional headings, the book always emphasizes that the first three classifications (secondary, ionic, metallic) are simply limiting cases of a single phenomenon that should simply be called chemical bonding. In each case, the emphasis is placed on making quantitative calculations of structural parameters and stabilities. The order of presentation was selected for the simple reason that there is an escalation in the skills needed for each model. Chapter 6, on secondary bonding, introduces the Lennard-Jones pair potential and the methods used to account for long range forces.

In Chapter 7 on ionic bonding, the Madelung potential is added to the Lennard-Jones pair potential. The fundamental steps involved in ionic bond formation are also described in terms of the Born-Haber cycle. Effects not included in the quantitative model, including the crystal field stabilization energy and ionic polarization, are assessed. The concept of electronegativity (first introduced in Chapter 1) is revisited and different quantitative scales are described. Finally, the ability to predict structure based on these models is discussed.

The eighth chapter is about metallic bonding and begins with the development of the free electron theory. After pointing out that this provides no cohesion for the crystal, electrostatic terms are introduced so that the stability of metallic crystals can be explained. Next, the nearly free electron theory and dispersion in the reduced zone scheme are described to introduce the concepts of energy bands, zone boundaries, and energy gaps.

The objective of the ninth chapter is to describe the polar covalent bond within the framework of the LCAO model. In this final chapter on bonding, I note that the LCAO model can, in its limits, also be used to describe materials that are considered ionic or metallic in the simple models. This fact emphasizes the idea that chemical bonding is a single phenomenon that can be described by a single model. After a brief description of how the LCAO method is applied to small molecules, it is applied to two dimensional homopolar crystals, polar crystals, and three dimensional crystals. The Freidel model is used to explain the presence of covalent bonds in transition metal crystals. The factors that lead to hybridization and tetrahedral geometries are also described. While this chapter will not make the student an expert in electronic structure methods, it will provide the foundation needed to understand the electronic structure of a crystal well enough to interpret the band structure diagrams and density of states plots that are the common result of modern theoretical studies.

The methods emphasized in Chapter 9 are illustrated by the following example. The reader is asked to consider a 2 dimensional binary compound (AB) with a square lattice structure where each site in the lattice is alternately occupied by an A or B atom. Assuming that each atom has a single s valence orbital, the reader is asked to apply the nearest neighbor LCAO model and determine the dispersion along the [100] direction, plot the dispersion assuming that the hypothetical compound is LiCu, LiAl, and LiCl, and, for each case, determine the width of the s-derived bands and the gap between the occupied and unoccupied states. Although the situation is clearly fictitious and the approximations unwarranted, the results are instructive (see Fig. 3). The quantitative calculations, which can be done by hand, illustrate that increasing the polarity in a compound narrows the widths of the bands and increases the gap between occupied and unoccupied states.

The tenth and final chapter returns to the question that is central to materials research: How do the composition of solid matter and the way in which it is processed influence its structure and properties? The scope of this question is much greater than that of this course, but two parts can be addressed. First, when a given set of elements are combined, will they react to form a compound, will they dissolve in one another, or will they be immiscible? Second, what will the ideal atomic scale structure of the combination be? In this chapter, phenomenological approaches to these questions are reviewed because they have been more effective than the quantitative physical models. In the first section, Miedema's [19] and Villars' [20] methods for predicting the existence of stable compounds are reviewed. In the next section, special electron concentration and radius ratio rules are reviewed. Laves phases, interstitial compounds, and Hume-Rothery rules [2] are described. The next section describes the factors that determine structure in polar covalent crystals. Among the topics described in this section are Pauling's rules [1] and the bond valence method [21]. In the final section, structure stability maps developed by Mooser and Pearson [3], Phillips [4], and Villars [5-7] are described.

Throughout the book, an emphasis is always placed on quantitative data, numerical examples, and problem solving. For example, the extensive data allow students to examine how chemical periodicity, electronic structure, and size factors influence structure selection. In the chapter on diffraction, all of the data needed for the calculation of diffraction peak intensity are included and sample calculations are carried out. The bonding models in Chapters 6-9 are all presented in such a way that quantitative solutions can be determined using simple calculations. In this regard, the methods and parameters established by Harrison [17] are followed. While these models are not at the state-of-the-art, they are qualitatively accurate and have the advantage of being simple enough that numerical results for specific compounds and elements are readily obtained and compared by the student. Whenever appropriate, the text includes worked numerical examples and each chapter concludes with an extensive set of problems.

THE COURSE'S TIMING AND TRACK RECORD

In the MSE department at Carnegie Mellon University, this course is taught to all first semester graduate students. A smaller number of senior MSE undergraduates and graduate students from Chemical Engineering, Electrical and Computer Engineering, Mechanical Engineering, and Physics also enroll. The class is held on a normal semester schedule and meets for 28, 110 minute lectures. The chapter structure of the text book is by no means evenly divided. The approximate schedule that I have used is illustrated in Table 4. This is covers 26 of 28 lecture periods and leaves two exam and/or review classes.

I have taught this course annually since 1992 and each class has consisted of 17 to 27 students; the total number of students that have taken this course is 130. At the end of each semester, students are asked the question, "What was the overall quality of this course?" The response is an integer rating, from 1 to 5, with 5 being the best. The results for the first 5 years (the 1997 results are not yet available) are summarized in Table 5. As a baseline for the rating system, consider the fact that this question is asked of every student in every class in the college and the mean for all courses taught during the same five years was 3.98.

In the first year, there was no text for the course. Students were asked to read from one of about 10 different existing books before each lecture. During this period, the course was rated as slightly above average. The second year was much the same, but I made a transcribed version of my lecture notes available to students a few days before each lecture. During this year, the course was rated well below the college average. Before the third year, I organized, corrected, and greatly expanded the transcription of the notes and made a draft version of the book available to the class before the semester. This draft version was the primary source for the class. At this point, the students' opinions of the class improved significantly. During subsequent years, the content and the organization of the book were continuously refined and the ratings of the course have also improved.

CONCLUSION

A textbook has been prepared from which it is possible to teach the topics of crystal structures and crystal cohesion in an integrated way. Student approval of a course based on this text has been high. Currently, there are no firm plans for publication. However, I anticipate that in the near future, this book will be available for use by others; students and instructors interested in this text prior to publication are encouraged to contact the author.

ACKNOWLEDGMENT

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Figure Captions

Figure 1. A sketch of the atomic positions in the scheelite structure. The projection is shown along the [100] direction.

Figure 2. The radius ratios for the rutile and scheelite structured ABO_4 compounds listed in Tables 2 and 3, respectively. For a consistent comparison, the octahedral radii are used.

Figure 3. Dispersion relations for three hypothetical Li compounds. (a) The two different atoms alternately occupy the vertices of a square lattice. (b) The dispersion of electron energy levels along [100] for three combinations of atoms. The dispersion relation, or energy (E) as a function of wave vector, (**k**), is shown below. E_A is the term state for the valence s electron of the A atom and E_B is the term state for the valence s electron of B atoms. $V_{ss\sigma}$ is the covalent energy for the overlap of the s states, and r_1 and r_3 are the vectors defined in (a).

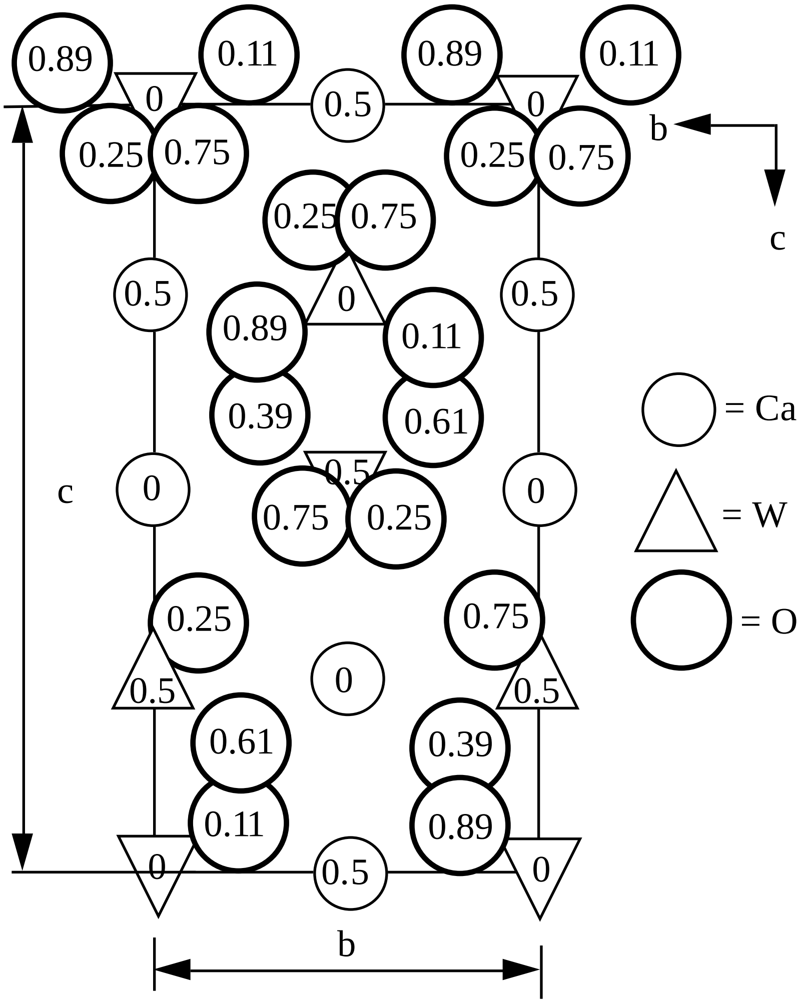


Figure 1. G.S. Rohrer

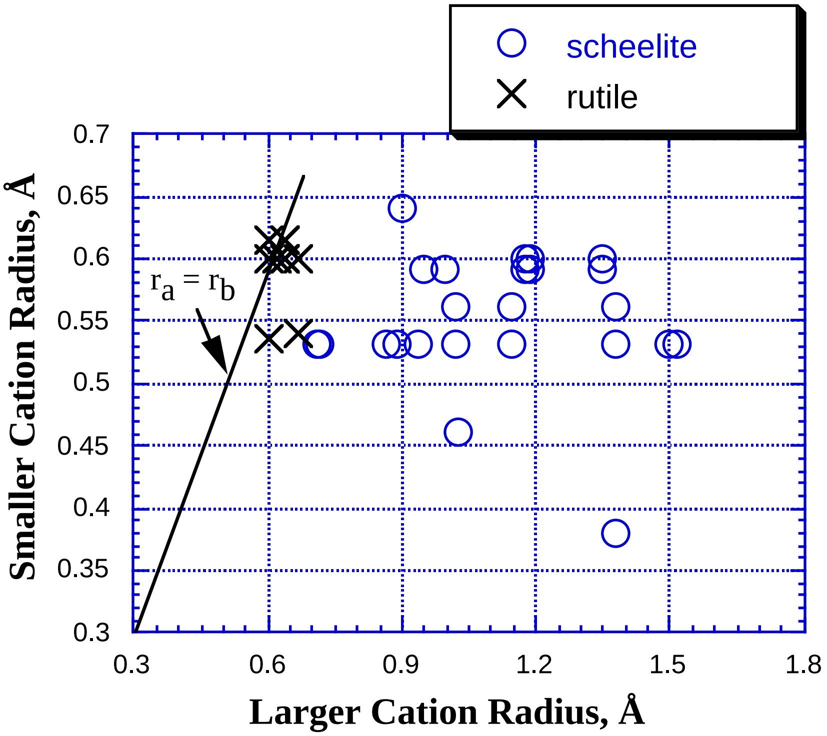
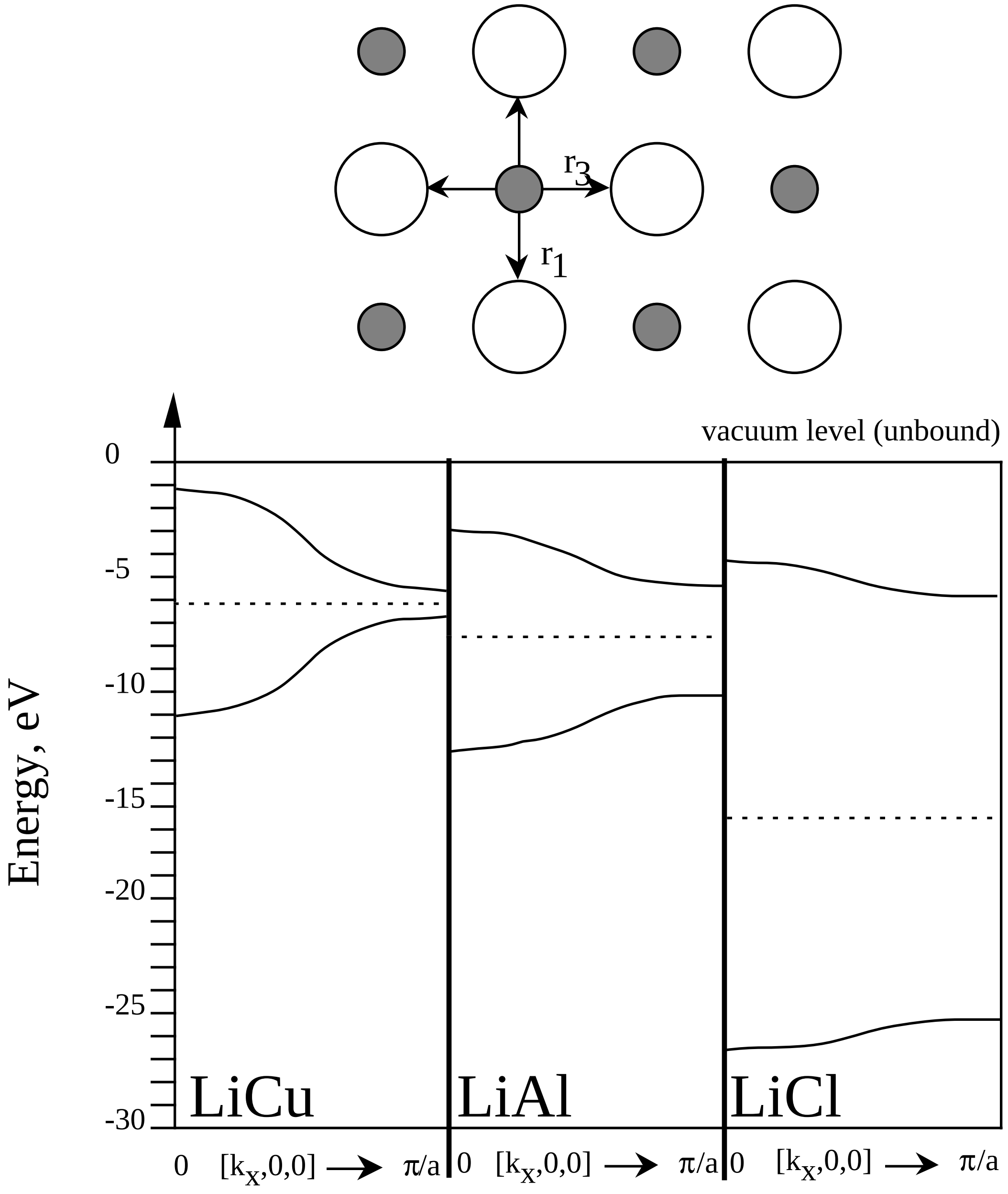


Figure 2. G.S. Rohrer



$$E(\mathbf{k}) = 1/2(E_A+E_B) \pm \sqrt{1/4(E_A-E_B)^2 + \{2V_{ss\sigma}[\cos\mathbf{k}\bullet\mathbf{r}_1+\cos\mathbf{k}\bullet\mathbf{r}_3]\}}$$

Figure 3. G.S. Rohrer

Table 1. Table of Contents for Structure an Bonding in Crystalline Materials

Table 1, continued. Table of Contents for Structure an Bonding in Crystalline Materials

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Table 1, continued. Table of Contents for Structure an Bonding in Crystalline Materials

Table 2. The structure of rutile (C4), titanium dioxide

Formula Unit	TiO_2, *titanium dioxide*		
Space group:	$P4_2/mnm$ (no. 136)		
Cell dimensions:	a = 4.594Å, c = 2.958Å		
Cell contents:	2 formula units		
Atomic positions:	Ti in (2a)	mmm	$0\ 0\ 0;\ \tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}$
	O in (4f)	m2m	$x\ x\ 0;\ \bar{x}\ \bar{x}\ 0$ $(\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2}), (\frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{2})$ x ~ 0.3

Examples

compound	a(Å)	c(Å)	x	compound	a(Å)	c(Å)	x
TiO_2	4.5937	2.9581	0.305	$CrSbO_4$	4.57	3.042	
CrO_2	4.41	2.91		$CrTaO_4$	4.626	3.009	
GeO_2	4.395	2.859	0.307	$FeNbO_4$	4.68	3.05	
IrO_2	4.49	3.14		$FeSbO_4$	6.623	3.011	
β-MnO_2	4.396	2.871	0.302	$FeTaO_4$	4.672	3.042	
MoO_2	4.86	2.79		$GaSbO_4$	4.59	3.03	
NbO_2	4.77	2.96		$RhSbO_4$	4.601	3.100	
OsO_2	4.51	3.19		$RhVO_4$	6.607	2.923	
PbO_2	4.946	3.379		CoF_2	4.6951	3.1796	0.306
RuO_2	4.51	3.11		FeF_2	4.6966	3.3091	0.300
SnO_2	4.7373	3.1864	0.307	MgF_2	4.623	3.052	0.303
TaO_2	4.709	3.065		MnF_2	4.8734	3.3099	0.305
WO_2	4.86	2.77		NiF_2	4.6506	3.0836	0.302
$AlSbO_4$	4.510	2.961	0.305	PdF_2	4.931	3.367	
$CrNbO_4$	4.635	3.005		ZnF_2	4.7034	3.1335	0.303

Table 3. The structure of scheelite, $CaWO_4$

Formula unit $CaWO_4$
Space group: $I4_1/a$ (no. 88)
Cell dimensions: a = 5.24 Å, c =11.38 Å
Cell contents: 4 formula units
Atomic positions:

Ca	(4b)	0,0,1/2; 1/2,0,1/4; + I
W	(4a)	0,0,0; 0,1/2,1/4; + I
O	(16f)	$x,y,z; \bar{x},\bar{y},z; x,y+1/2,1/4-z; \bar{x},1/2-y,1/4-z;$ $\bar{y},x,\bar{z}; y,\bar{x},\bar{z}; \bar{y},x+1/2,z+1/4; y,1/2-x,z+1/4; +I$ x=0.25, y=0.15, z=0.075

Examples

compound	a(Å)	c(Å)	compound	a(Å)	c(Å)
$AgReO_4$	5.378	11.805	$NaReO_4$	5.362	11.718
$AgTcO_4$	5.319	11.875	$NaTcO_4$	5.339	11.869
$BaMoO_4$	5.56	12.76	$PbMoO_4$	5.47	12.18
$BaWO_4$	5.64	12.70	$PbWO_4$	5.44	12.01
$BiAsO_4$	5.08	11.70	$RbReO_4$	5.803	13.167
$CaMoO_4$	5.23	11.44	$SrMoO_4$	5.36	11.94
$CdMoO_4$	5.14	11.17	$SrWO_4$	5.40	11.90
$CeGeO_4$	5.045	11.167	$ThGeO_4$	5.14	11.54
$HfGeO_4$	4.849	10.50	$TlReO_4$	5.761	13.33
$KReO_4$	5.675	12.70	$UGeO_4$	5.084	11.226
$KRuO_4$	5.609	12.991	$YNbO_4$	5.16	10.91
$KTcO_4$	5.654	13.03	$ZrGeO_4$	4.871	10.570

Table 4 Approximate Schedule for Structure and Bonding in Crystalline Materials

Chapter Number and Title	**Number of Lectures**
1. Introduction	1.5
2. Basic Structural Concepts	1.5
3. Symmetry in Crystals	3
4. Crystal Structures	3
5. Diffraction	4
6. Secondary Bonding	1
7. Ionic Bonding	2.5
8. Metallic bonding	2.5
9. LCAO Model for the Polar Covalent Bond	4
10. Models for Predicting Phase Stability and Structure	3

Table 5. Student Evaluations of the Course

Year	Mean Course Rating	Number of Students
1992	4.07	17
1993	3.65	27
1994	4.45	22
1995	4.52	23
1996	4.65	20
1997	NA	21