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Computational Chemistry of Solid State Materials

A Guide for Materials Scientists, Chemists, Physicists and others

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Foreword
Materials: the Bridge Between Chemistry and Physics

Every science has its own history. Out of which emerge distinctive ways of thinking, ways of understanding. Reductionism is a comfortable philosophy only for those who choose to avoid the reality of the way new knowledge is created.

So it is interesting when two mature sciences are forced by the facts of nature and a shared subject to confront each other's ways of thinking, both of them productive and yet, and yet… seemingly incommensurate. This is what has happened, is happening, between chemistry and physics; their preeminent and fertile shared ground is the contemporary solid state, with its exciting materials. This book, in its unique way, shapes a way not just to coexistence of chemistry and physics in materials science, but to a productive future. A future shaped by computational techniques (for theory definitely has a major role to play here) that are respectful of both chemistry and physics.

Chemistry always had its own identity, founded in part on analysis and synthesis, in another part on an immense practical exploration of reactions, of chemical change leading to new substances. That distinctly chemical identity persisted as the molecular science became quantitative, and contiguous, so to speak, with physics. Sharing with physics the common ground of atoms, physical forces, and thermodynamics, chemistry remains different, in its emphasis on structure, reactivity and that marvelous construct of the chemical bond.

The contrast is easily seen in the confrontation of chemistry and physics with the solid state. Look, for instance, at the classical triangle of bonding in materials, with its vertices of ionic substances (represented, say, by NaCl), metals (Ni, for instance), and covalent solids (diamond or silicon). In approaching theoretically any real substance, which is most unlikely to be at one or another extreme of this graph, the physics community clearly favored the ionic and metallic entry points. While chemists, addicted to the molecular compounds so easy to synthesize and analyze in the 20th century, found it much easier to analyze the new through the perspective of a directionally bonded covalent solid.

Which is right? Neither. Or both. There is much to be said for the intuition of the chemists for bonding in matter; they've had much time to think about it, a near infinity of examples. And maybe they had to think harder, just because they couldn't rely on the crutch of mathematics. But the fascinating properties of the new materials of our time – superconductivity, magnetism in all its rich manifestations, phase behavior – all of these could only be described with new physics, a physics beyond the chemist's familiar bond.

The meeting ground of the sciences is here and now, in new materials with novel properties. One is unlikely to make such materials and understand them if one is wearing pure chemical or physical blinders. Success is more likely to come from a coupled approach, a chemical understanding of bonding (in many ways deeper, as it is intuitive, than that of the physics community) merged with a deep physical description of what is really different in conductivity, magnetism and collective phenomena.

What is needed is something between a Baedeker and a Rosetta stone, something that introduces one to the two (or is it more?) cultures of chemistry and physics. As they approach an understanding of what electrons are up to in their shared ground of materials science. This book, a description of modern computational approaches to the solid state, provides the passport of a common language for creative excursions in this fertile middle ground.

Ithaca, July 2005 ROALD HOFFMANN

Preface

Since 1986, when I first started playing around in Arndt Simon's chemical laboratory as a graduate student, I have never regretted entering the fascinating field of solid-state chemistry. Indeed, I have always found that this fundamental brand of the chemical sciences and also its somewhat more applied sister subject, materials chemistry, brings us into contact with a large part of the "real world" surrounding us, and a creative solid-state (or materials) chemist is in true command, in the same way as a molecular inorganic chemist, of the whole periodic table when he or she thinks of making new compounds with often unforeseeable but exciting physical properties. It does not come as a surprise that the extraordinarily broad field of solid-state chemistry is a truly interdisciplinary one. Thus, solid-state chemistry borders with solid-state physics, crystallography, quantum theory, metal science and inorganic chemistry, to name but a few; also, it is one of the rock-solid platforms on which the increasingly popular fields of nanoscience and nanomaterials may be built.

Some of the breathtaking technological advances of the 20th, and also the early 21st century, would have been totally impossible without the fundamental research originating within solid-state chemistry. Here I am thinking of insulators with designed properties such as *dielectric ceramics* for data transmission, novel *ionic conductors* for energy storage in hand-held electrical devices, *magnetic intermetallics* and *oxides* for data storage applications, *advanced nitrides* for electro-optical and diverse mechanical purposes, and also *superconductors* for energy transport and communication applications. This list could easily be made longer, and it surely will get longer as long as solid-state chemists and materials researchers are doing their part by creating the new, particularly when they are *not* thinking of applications but are concentrating on that wonderful art of *curiosity-driven research*.

When you want to design and make new things, however, you must be able to understand (or, at least, describe) the existing ones; thus, sooner or later, theory comes into play. Not too surprisingly, the theoretical tools available in solid-state and materials chemistry are as diverse as the solid-state chemistry-related fields because this is where they originate. Thus chemists, physicists, crystallographers, and quantum theorists have all contributed to the strange blend of tools for describing, understanding and – which is now becoming increasingly important – predicting solid-state materials. At the present time, it seems that numerical approaches – which I will bravely summarize using the term *computational chemistry* – have reached a certain maturity which allows usage by the nonspecialist. Of course, computers have become more powerful, too, but this is mostly due to better hardware (solid-state materials) and, to a lesser extent, more user-friendly software.

Despite the ever-increasing importance of (quantum-theoretical) computer programs used in theoretical solid-state and materials chemistry, however, a newcomer will probably have difficulty in seeing the wood for the trees. Thus, I have felt the necessity to briefly present the type of theoretical approaches which might be used to successfully understand existing materials and also to navigate in the search for new solid-state compounds. These approaches purposely include traditional, classical ways of thinking but also quantum-mechanical approaches, because both are justified. It would be foolish to run high-scale quantum-mechanical calculations unnecessarily if an empirical back-of-the-envelope scheme is almost as predictive; also, a large amount of understanding is based upon classical ways of thinking. This may change but I am afraid it will take some time. On the other hand, why should we restrict ourselves to limited empirical methods if a reliable quantum-mechanical alternative is available? There are cases where the predictive power of quantum chemistry is so overwhelming that the experiment no longer has to be performed. Some scientists (like myself) will appreciate this, others will not. As you may have guessed, this book tries to bridge the gap.

As I write, I have imagined an intelligent reader (chemist, physicist, material scientist, crystallographer, etc.) who is already somewhat familiar with solid-state or materials chemistry, at least in terms of structure and also structure determination. However, because of space limitations, crystallographic techniques simply cannot be taught here. Also, some basic knowledge of quantum mechanics would do no harm. The rest of the book, however, is designed to be self-contained. I have tried to address a person working in the laboratory who is trying hard to make sense of his or her new discoveries. What is the best way to describe your new compound in terms of, say, energetics? What can be learned from a structural discussion using radii concepts and volume considerations? What about more general structure rationalizations? Can one approximate the strength of chemical bonding without using quantum chemistry? If quantum chemistry is needed, what are the most important ingredients? What are these band structures, really? What do you learn from densities-of-states? Can chemical bonding in the solid state be quantified?

What are the pluses and minuses of the diverse quantum-chemical routes? Although it is a crystal, are the atoms really standing still? Can solid-state materials be predicted? Do we have quantum-theoretical access to chemical thermodynamics? Can one design new compounds? (The answer is yes). In general, how do you interpret the quantum-chemical result and how do you transfer the message into a language that can be used in the laboratory? In the end, the book should enable the reader to theoretically handle his or her own materials in the sense of correctly describing and understanding the compounds under study. If it would make you (yes, *you*) predict and synthesize new compounds, I would be truly happy. To ease the difficult life of the busy synthetic materials scientist, I have tried to make the book an entertaining, extremely light read, and I keep my fingers crossed that the "pure" theorists will kindly agree. For those who want to drill deeper, there are many superb monographs available, stuffed with lots of mathematics, and the appropriate references are also included in this little book.

This book would not be here if I had not gladly accepted the honorable invitation of Tohoku University (Sendai) for a guest professorship in the summer of 2004. I am especially grateful to my colleagues and students at the Center of Interdisciplinary Research, in particular to Professor Hisanori Yamane and his family, who did a spectacular job in making my visit a most memorable one. I am extending my thanks to Professor Shinichi Kikkawa at Hokkaido University (Sapporo) for his hospitality and for the great time I was able to enjoy. Sapporo is a wonderful place for beer, too.

Also, I would like to express my thanks to my own research group at RWTH Aachen University; without them, most of the things I find important to communicate to the reader would simply be nonexistent. Over the last eight years, it has been a great pleasure to lead a group of experimentalists (challenging theory) and theorists (challenging experiment), and I would like to acknowledge the important contributions of all former and present coworkers. Thank you very much for your scientific and personal input. A good number of improvements to the first version of the manuscript were suggested, after careful reading, by Jörg von Appen, Bernhard Eck, Boniface Fokwa, Andreas Houben, Michael Krings, Marck-Willem Lumey, Paul Müller, and Holger Wolff; whom I also thank. During my stay in Japan, Mona Marquardt did a wonderful job in keeping the group together and taking care of the communication; thank you so much. The manuscript has also profited from the critical remarks of some of my colleagues, namely Peter Blöchl (Clausthal), Lothar Fritsche (Karlsruhe), Karl Jug (Hannover), Gordon J. Miller (Ames), Rainer Pöttgen (Münster), Michael Ruck (Dresden), and Gerhard Raabe (Aachen); thank you for your time. It is fascinating to observe how differently chemists, physicists, experimentalists, and theorists may consider the same subject, and I hope to have come up with a sensible compromise. Birgit Renardy did a nice job in proof-reading the many references; thanks are due to her. At Wiley-VCH, Elke Maase, Linda Bristow, Uschi Schling-Brodersen, and Manfred Köhl provided helpful guidance. I also thank Roger De Souza (Aachen) for consulting his English dictionary on my behalf. If there are scientific or typographical errors left (and I am afraid they are there), I am solely responsible for them.

Finally, my colleagues from the Institute of Inorganic Chemistry at RWTH let me flee from the remarkable teaching burden of our institution for one semester, and I am very grateful to them for having made this possible. Needless to say, a thousand thanks go directly to my family for their inspiration and support. Gabriele was of tremendous help in the final formatting steps.[1]

This book appears at a time where the high reputation of Germany's university system and even its top academic institutions are endangered by the thoughtless words and actions of some of our highly political elite. To comment on the recent embarassing large-scale experiments (with whatever future outcome) or to name their political inventors would give these people more honor than they deserve. Instead, I devote this book, with affection, to the University of Münster and its Chemistry and Physics Divisions because this is the great place where I had the pleasure to study in the first half of the 1980s.

Aachen, June 2005 RICHARD DRONSKOWSKI

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1) All text was written on a Linux workstation using my beloved editor vim, and the entire book was processed by means of the glorious typesetting system LaTeX2e and further handled using xdvi, dvips, ghostscript/ghostview, ps2pdf, and pdftk. The figures were generated using gnuplot, wxdragon, xfig, and xmgrace. A toast to fast, reliable, compact and open-source software!

1
Classical Approaches

> *Study the past if you would define the future.*
> CONFUCIUS
>
> *Anyone who wants to harvest in his lifetime*
> *cannot wait for the* ab initio *theory of weather.*
> HANS-GEORG VON SCHNERING

Sooner or later, every solid-state chemist will realize that there is nasty time-related problem in solid-state chemistry. Because of the low mobility of the atoms in the solid state, solid-state reactions usually take much longer to complete than reactions for molecules in liquids and gases, so that a good amount of patience is the main requirement for the busy solid-state chemist! Even when high-temperature reactions involving ceramic routes and *lots* of energy are pursued, a solid-state chemist will sooner or later find himself *waiting* for nature to complete its job [1]. I suppose that these periods of contemplation are responsible for the fact that, clearly, there is a long tradition of deep thinking about three-dimensional *structures* and *energetics* in solid-state chemistry.

At present, a newcomer to solid-state chemistry might therefore believe that this science must have been a key proponent in challenging quantum mechanics (and quantum chemistry, too) for the solution of solid-state chemical problems. Strangely, this is not at all the case. Let us remind ourselves that the puzzle of chemical bonding was ingeniously clarified in 1927, not for a crystalline solid but for the hydrogen *molecule*. The rapidly emerging scientific discipline, quantum chemistry, also focused on the *molecular* parts of chemistry both because of technical and "political" reasons: first, the most important quantum-chemical workhorse (Hartree–Fock theory) has been particularly resistant to adaptation to the solid state (see Section 2.11.3) and, second, we surely must be aware of the fact that the solid-state chemical community is limited in size such that the number of "customers" for quantum chemists is relatively small. As a sad consequence, the solid-state chemists have been left alone for some decades when it comes to questions of theoretical understanding, although Bloch's theorem (see Section 2.4) dates back to the year 1929! Go and try to find the "solid state" in introductory textbooks of quantum chemistry; good luck!

Theoretically isolated, the solid-state chemistry community therefore had to find other ways to rationalize their synthetic, structural findings, for better or for worse. Let me just mention the extremely useful (but intrinsically non-quantum-mechanical) Zintl–Klemm concept [2] or, to give another prominent example, the grossly oversimplified notion of trying to understand solid-state compounds *only* by considering their electrostatic (Madelung) energies (see Section 1.2). As odd as it may seem, the latter concept is still being used today – and sometimes it *is* a useful concept – although Hans Hellmann already showed in the early 1930s that quantum systems comprising only potential but no kinetic energy are thermodynamically unstable [3]. Also, as Roald Hoffmann carefully observed in 1988, the dominating philosophy within solid-state chemistry had isolated the community even more by not "seeing" chemical bonds between the atoms [4]. That may be the reason why, even today, a freshman student will probably get the wrong idea, by looking into regular chemistry textbooks, that molecules are held together by covalent bonds, whereas solids are taken care of by ionic forces. What a complete nonsense that really is! Nonetheless, let us start with the ionic notion.

1.1
Ionic Radii and Related Concepts

Amongst solid-state materials, those phases which appear to be salt-like (transparent, brittle, insulating) are probably among the easiest to understand in terms of structure[1] and, in many cases, also electronic structure; here we have abstained, for purposes of simplicity, from likewise transparent molecular crystals or covalently bonded arrays (e.g., diamond). In fact, rock salt (sodium chloride, NaCl) may be regarded as the most fundamental insulator, and its crystal structure (see Figure 1.1(b)) is the one most often found for solid-state materials of general composition AB. What can be said about the [NaCl] type in terms of structure – not necessarily in terms of electronic structure – can easily be generalized to other simple compounds such as alkali halides (e.g., LiF, KBr, RbI), silver halides (e.g., AgF, AgCl, AgBr), alkaline-earth chalcogenides (e.g., MgO, BaS, CaSe), simple nitrides (e.g., CeN, CrN, YbN), and many others.

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1) For a number of good reasons, solid-state chemists are structure aficionados. For self-training purposes, it is therefore *highly* recommended to get an overview of the structures and structural principles within inorganic chemistry [5].

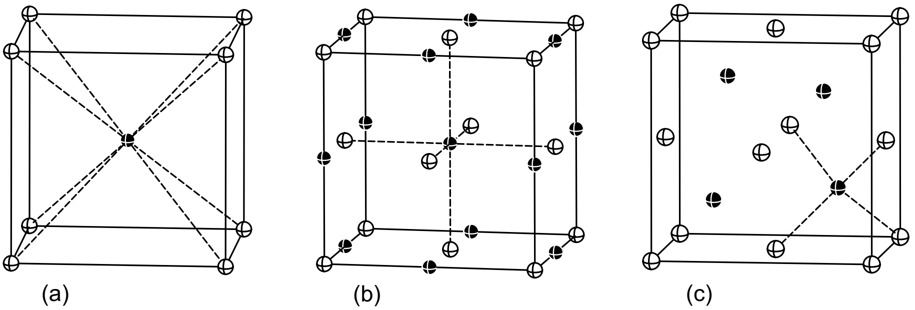

Fig. 1.1 The three fundamental AB structure types with coordination numbers of eight (caesium chloride, (a)), six (sodium chloride, (b)), and four (zinc-blende, (c)). Because the coordinations are identical for atoms A and B, the atomic assignment to A and B may be freely chosen by the reader.

Chemists have long since realized that compositions such as NaCl, MgO, and CeN point towards an ionic description of the chemical bondings, namely because the above formulae suggest formulations such as "Na^+Cl^-", "Mg^{2+}-O^{2-}", and "$Ce^{3+}N^{3-}$" as *plausible*. This is because experimental data show fairly low ionization energies for the metals, many ionic solids form melts composed of ions at higher temperatures, and the atomic charges (or oxidation states) of the nonmetals (-1, -2, and -3 for Cl, O, and N) match our ideas of a noble-gas configuration for the anionic partners; in other words, the compositions seem to be compatible with the *octet rule* of general chemistry. While a quantitative energetic calculus (see Section 1.2) shows this qualitative reasoning to be acceptable *only* for solids and other condensed phases, but *not* for molecules, the idea of a full charge transfer from the metal to the nonmetal is at least good enough to establish the corresponding space partitioning of the crystal structure in terms of *ionic radii*.

A serious, general problem with the determination of any kind of radii is given by the fact that, for obvious reasons, atomic or ionic species do not have a well-defined border; also, the different radii must be a function of the chemical bonding present. For molecular species, however, common sense lets us determine atomic radii quite easily. Since the term *atomic* radius has a somewhat diffuse meaning, one usually speaks of *covalent* radii instead. A few examples may help here. Because the nucleus–nucleus distance in the hydrogen molecule, H–H, is 0.74 Å, the covalent radius of hydrogen *must* be 0.37 Å. Likewise, the covalent radius of oxygen should be half the O–O single-bond distance in H_2O_2 (1.46 Å), that is, 0.73 Å. Note that we can also derive another, shorter bonding radius for oxygen ($\approx$ 0.60 Å), namely from the O=O distance (1.21 Å) in the oxygen molecule, O_2, in which there is a double bond. Trivially, the covalent radius of carbon might be either derived from the C–C distance in diamond or from the one occurring in the ethane molecule, H_3C–CH_3, in both cases yielding 0.77 Å. When combining these covalent radii for the prediction of interatomic distances, one should keep in mind that ionic contributions will have a small impact on the final interatomic distances.

For extended elemental solids, sets of van der Waals radii and also metal radii are simple to determine, at least if the atoms are closely packed. For example, the metal copper crystallizes in its own (Cu) structure type – the face-centered cubic (fcc)[2] crystal structure exhibiting 74% space filling if we assume spherical, nonoverlapping atoms – with a lattice parameter of a = 3.61 Å (see Figure 1.2(b)), and a simple geometrical calculus gives the copper metallic radius as $\frac{a}{4}\sqrt{2}$, that is, 1.28 Å; here we have again assumed that the atomic spheres will *touch* but will not overlap. The same argument holds for the noble gas xenon which also crystallizes in the fcc structure (a = 6.20 Å at a temperature of 40 K) such that the van der Waals radius of Xe is found to be 2.19 Å. Note that this calculation can only be performed because there is only *one* radius that needs to be determined such that the partitioning of space is straightforward. The calculation already becomes a little more complicated for the likewise dense (74% space filling) hexagonal close-packed (hcp) structure (see Figure 1.2(a)) because there are two lattice parameters (a and c) and, therefore, variability in the a/c ratio; thus, a maximum hcp packing density only results for the ideal ratio. The body-centered cubic (bcc) structure (see Figure 1.2(c)) is no longer closely packed (68% space filling) such that a certain arbitrariness is unavoidable for the determination of the metal radius (unless one still assumes touching hard spheres); a useful parameter can be derived, though (see [6]). For intermetallic compounds, things may become quite complicated because the structural hierarchies effectively determine the sizes of the metal radii [7].

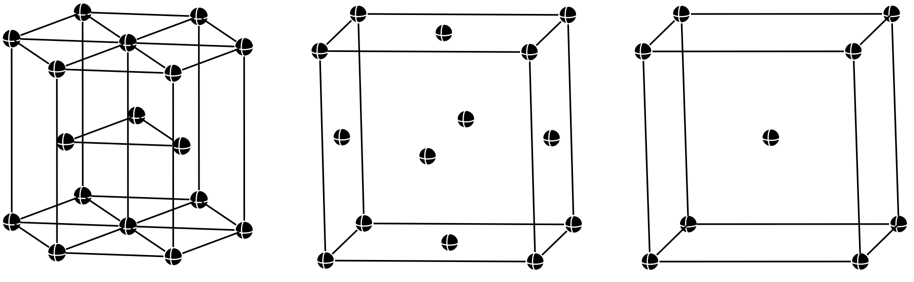
(a) (b) (c)

Fig. 1.2 Three fundamental packings of structural chemistry, hexagonal close-packed (hcp, (a)), face-centered cubic (fcc, (b)), and body-centered cubic (bcc, (c)).

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[2] Our language is rather casual here. The crystal structure of copper is of the cubic close-packed (ccp) type and, because there is only one type of atom, this is equivalent to the face-centered cubic (fcc) structure for this special case. Although not every F-centered crystal structure belonging to the cubic system (e.g., Si or NaCl) can be considered closely packed, the simplified notion ccp = fcc is so ubiquitous in the literature that we also use it in this book.

Coming back to ionic compounds, such as NaCl in Figure 1.1(b), we need to define the sum of cationic and anionic radii to coincide with the interatomic distance; the figure shows that the lattice parameter a (the edge of the cube) is exactly twice the sum of the cationic and anionic radii. It remains to be seen, however, how the interatomic distance between cation and anion can be *partitioned* into the two radii.

A "modern" approach would probably go as follows: Grow a nice NaCl crystal, perform an X-ray diffraction measurement to determine the electron density along the line Na–Cl, search for the minimum density somewhere between the two atoms, and then interpret this value as the crossover from the cation (Na^+) to the anion (Cl^-). Yet, the systems of ionic radii we know of have been generated following other recipes [8], and three approaches seem to be especially worth mentioning.

The first approach from the early 20th century dates back to Victor Moritz Goldschmidt, one of the founders of crystal chemistry [9]. Goldschmidt's system [10] is based on the two standard radii of O^{2-} (1.32 Å) and F^- (1.33 Å) which were derived a little earlier by Wasastjerna [11]; this author simply measured the molar refractions of the alkali halides and set them proportional to the ionic volumes. Goldschmidt then came up with a complete set of ionic radii corresponding to a coordination number (CN) of six. When the coordination polyhedron increases in size, the enlargement of the ionic radius under consideration is usually given by an approximate scaling

$$^{(\mathrm{CN})}r = {}^{(6)}r \left(\frac{(\mathrm{CN})}{6} \right)^{\alpha}, \tag{1.1}$$

in which (CN) designates the new coordination number. The exponent α varies from atom to atom but an operational value lies around $\alpha \approx 1/8$; *any* ionic radius is a function of the coordinating environment but the small α exponent indicates that the variation cannot be excessively large.

At about the same time, another system was proposed by Pauling which is strongly influenced by quantum-chemical ideas [6]. According to Pauling, the ionic radius will enlarge upon filling up the ion's electronic shells and it is therefore proportional to the atomic constant C_n, determined by the main quantum number of the outermost electrons. On the other hand, the ionic radius will shrink as a function of the effective nuclear charge which is the difference between the bare nuclear charge Z and the electronic screening s by the inner core electrons. In short, we simply write

$$r = \frac{C_n}{Z - s}. \tag{1.2}$$

For isoelectronic ions such as Na^+ and F^- which both have the electronic configuration of Ne, $[1s^2 2s^2 2p^6]$, the values for C_n must be identical, whatever they are. Also, a quantum-chemical estimate will show that the screening s is the same (4.52) for both ions,[3] and the effective nuclear charges thus arrive at $Z - s = 11 - 4.52 = 6.48$ for Na^+ and at $9 - 4.52 = 4.48$ for F^-. Consequently, the *ratio* of their ionic radii must be 6.48/4.48 = 1.446 such that, for the given Na^+–F^- distance in NaF (2.31 Å, sodium chloride-type), we have $r(Na^+) = 0.95$ Å and $r(F^-) = 1.36$ Å. An important consequence of this procedure is that Pauling's radius for the six-coordinate O^{2-} ion arrives at a larger 1.40 Å if compared to Goldschmidt's 1.32 Å. The complete Pauling set of ionic radii, dubbed *crystal radii* by himself, has been very influential because of the elegance of the arguments and the fame of the author.

Third, a different strategy was pursued by Shannon in the 1970s [14], and he generated a set of self-consistent ionic radii based on crystallographic information, augmented by bond-valence ideas (see Section 1.5). The strength of Shannon's approach surely lies in the large size of the empirical data on which it is based, such that the influence of both the oxidation states of cations/anions and also of the coordination numbers can be sensibly taken into account. This is probably the reason why Shannon's data have replaced – but not superseded – the sets of radii given by Goldschmidt and Pauling. For convenience, we present Shannon's radii in Table 1.1. This tabulation, as well as all others, shows the general trends, that is, that cations are usually smaller than anions, and cationic radii decrease rapidly with overall charge.

---

[3] Quantum-mechanically inspired recipes for the calculation of the screening values s have been proposed by Pauling [12] and Slater [13].

Tab. 1.1 Effective ionic radii according to Shannon [14]. The superscripts indicate the coordination numbers, the electronic state (hs = high-spin, ls = low-spin), and the geometry (sq = square, py = pyramidal).

Ion	$^{\text{(coordination number)}}r_{\text{eff}}$ (Å)						
Ac^{3+}	$^{(6)}1.12$						
Ag^{+}	$^{(2)}0.67$	$^{(4)}1.00$	$^{(4,sq)}1.02$	$^{(5)}1.09$	$^{(6)}1.15$	$^{(7)}1.22$	$^{(8)}1.28$
Ag^{2+}	$^{(4,sq)}0.79$	$^{(6)}0.94$					
Ag^{3+}	$^{(4,sq)}0.67$	$^{(6)}0.75$					
Al^{3+}	$^{(4)}0.39$	$^{(5)}0.48$	$^{(6)}0.535$				
Am^{2+}	$^{(7)}1.21$	$^{(8)}1.26$	$^{(9)}1.31$				
Am^{3+}	$^{(6)}0.975$	$^{(8)}1.09$					
Am^{4+}	$^{(6)}0.85$	$^{(8)}0.95$					
As^{3+}	$^{(6)}0.58$						
As^{5+}	$^{(4)}0.335$	$^{(6)}0.46$					
At^{7+}	$^{(6)}0.62$						
Au^{+}	$^{(6)}1.37$						
Au^{3+}	$^{(4,sq)}0.68$	$^{(6)}0.85$					
Au^{5+}	$^{(6)}0.57$						
B^{3+}	$^{(3)}0.01$	$^{(4)}0.11$	$^{(6)}0.27$				
Ba^{2+}	$^{(6)}1.35$	$^{(7)}1.38$	$^{(8)}1.42$	$^{(9)}1.47$	$^{(10)}1.52$	$^{(11)}1.57$	$^{(12)}1.61$
Be^{2+}	$^{(3)}0.16$	$^{(4)}0.27$	$^{(6)}0.45$				
Bi^{3+}	$^{(5)}0.96$	$^{(6)}1.03$	$^{(8)}1.17$				
Bi^{5+}	$^{(6)}0.76$						
Bk^{3+}	$^{(6)}0.96$						
Bk^{4+}	$^{(6)}0.83$	$^{(8)}0.93$					
Br^{-}	$^{(6)}1.96$						
Br^{3+}	$^{(4,sq)}0.59$						
Br^{5+}	$^{(3,py)}0.31$						
Br^{7+}	$^{(4)}0.25$	$^{(6)}0.39$					
C^{4+}	$^{(3)}-0.08$	$^{(4)}0.15$	$^{(6)}0.16$				
Ca^{2+}	$^{(6)}1.00$	$^{(7)}1.06$	$^{(8)}1.12$	$^{(9)}1.18$	$^{(10)}1.23$	$^{(12)}1.34$	
Cd^{2+}	$^{(4)}0.78$	$^{(5)}0.87$	$^{(6)}0.95$	$^{(7)}1.03$	$^{(8)}1.10$	$^{(12)}1.31$	
Ce^{3+}	$^{(6)}1.01$	$^{(7)}1.07$	$^{(8)}1.143$	$^{(9)}1.196$	$^{(10)}1.25$	$^{(12)}1.34$	
Ce^{4+}	$^{(6)}0.87$	$^{(8)}0.97$	$^{(10)}1.07$	$^{(12)}1.14$			
Cf^{3+}	$^{(6)}0.95$						
Cf^{4+}	$^{(6)}0.821$	$^{(8)}0.92$					
Cl^{-}	$^{(6)}1.81$						
Cl^{5+}	$^{(3,py)}0.12$						
Cl^{7+}	$^{(4)}0.08$	$^{(6)}0.27$					
Cm^{3+}	$^{(6)}0.97$						
Cm^{4+}	$^{(6)}0.85$	$^{(8)}0.95$					
Co^{2+}	$^{(4,hs)}0.58$	$^{(5)}0.67$	$^{(6,ls)}0.65$	$^{(6,hs)}0.745$	$^{(8)}0.90$		
Co^{3+}	$^{(6,ls)}0.545$	$^{(6,hs)}0.61$					
Co^{4+}	$^{(4)}0.40$	$^{(6,hs)}0.53$					
Cr^{2+}	$^{(6,ls)}0.73$	$^{(6,hs)}0.80$					
Cr^{3+}	$^{(6)}0.615$						
Cr^{4+}	$^{(4)}0.41$	$^{(6)}0.55$					
Cr^{5+}	$^{(4)}0.345$	$^{(6)}0.49$	$^{(8)}0.57$				
Cr^{6+}	$^{(4)}0.26$	$^{(6)}0.44$					
Cs^{+}	$^{(6)}1.67$	$^{(8)}1.74$	$^{(9)}1.78$	$^{(10)}1.81$	$^{(11)}1.85$	$^{(12)}1.88$	
Cu^{+}	$^{(2)}0.46$	$^{(4)}0.60$	$^{(6)}0.77$				
Cu^{2+}	$^{(4)}0.57$	$^{(4,sq)}0.57$	$^{(5)}0.65$	$^{(6)}0.73$			
Cu^{3+}	$^{(6,ls)}0.54$						
D^{+}	$^{(2)}-0.10$						
Dy^{2+}	$^{(6)}1.07$	$^{(7)}1.13$	$^{(8)}1.19$				

continued on next page

Tab. 1.1 (continued)

Ion	$^{\text{(coordination number)}}r_{\text{eff}}$ (Å)						
Dy^{3+}	$^{(6)}0.912$	$^{(7)}0.97$	$^{(8)}1.027$	$^{(9)}1.083$			
Er^{3+}	$^{(6)}0.890$	$^{(7)}0.945$	$^{(8)}1.004$	$^{(9)}1.062$			
Eu^{2+}	$^{(6)}1.17$	$^{(7)}1.20$	$^{(8)}1.25$	$^{(9)}1.30$	$^{(10)}1.35$		
Eu^{3+}	$^{(6)}0.947$	$^{(7)}1.01$	$^{(8)}1.066$	$^{(9)}1.120$			
F^{-}	$^{(2)}1.285$	$^{(3)}1.30$	$^{(4)}1.31$	$^{(6)}1.33$			
F^{7+}	$^{(6)}0.08$						
Fe^{2+}	$^{(4,\mathrm{hs})}0.63$	$^{(4,\mathrm{sq},\mathrm{hs})}0.64$	$^{(6,\mathrm{ls})}0.61$	$^{(6,\mathrm{hs})}0.78$	$^{(8,\mathrm{hs})}0.92$		
Fe^{3+}	$^{(4,\mathrm{hs})}0.49$	$^{(5)}0.58$	$^{(6,\mathrm{ls})}0.55$	$^{(6,\mathrm{hs})}0.645$	$^{(8,\mathrm{hs})}0.78$		
Fe^{4+}	$^{(6)}0.585$						
Fe^{6+}	$^{(4)}0.25$						
Fr^{+}	$^{(6)}1.80$						
Ga^{3+}	$^{(4)}0.47$	$^{(5)}0.55$	$^{(6)}0.620$				
Gd^{3+}	$^{(6)}0.938$	$^{(7)}1.00$	$^{(8)}1.053$	$^{(9)}1.107$			
Ge^{2+}	$^{(6)}0.73$						
Ge^{4+}	$^{(4)}0.390$	$^{(6)}0.530$					
H^{+}	$^{(1)}-0.38$	$^{(2)}-0.18$					
Hf^{4+}	$^{(4)}0.58$	$^{(6)}0.71$	$^{(7)}0.76$	$^{(8)}0.83$			
Hg^{+}	$^{(3)}0.97$	$^{(6)}1.19$					
Hg^{2+}	$^{(2)}0.69$	$^{(4)}0.96$	$^{(6)}1.02$	$^{(8)}1.14$			
Ho^{3+}	$^{(6)}0.901$	$^{(8)}1.015$	$^{(9)}1.072$	$^{(10)}1.12$			
I^{-}	$^{(6)}2.20$						
I^{5+}	$^{(3,\mathrm{py})}0.44$	$^{(6)}0.95$					
I^{7+}	$^{(4)}0.42$	$^{(6)}0.53$					
In^{3+}	$^{(4)}0.62$	$^{(6)}0.800$	$^{(8)}0.92$				
Ir^{3+}	$^{(6)}0.68$						
Ir^{4+}	$^{(6)}0.625$						
Ir^{5+}	$^{(6)}0.57$						
K^{+}	$^{(4)}1.37$	$^{(6)}1.38$	$^{(7)}1.46$	$^{(8)}1.51$	$^{(9)}1.55$	$^{(10)}1.59$	$^{(12)}1.64$
La^{3+}	$^{(6)}1.032$	$^{(7)}1.10$	$^{(8)}1.160$	$^{(9)}1.216$	$^{(10)}1.27$	$^{(12)}1.36$	
Li^{+}	$^{(4)}0.590$	$^{(6)}0.76$	$^{(8)}0.92$				
Lu^{3+}	$^{(6)}0.861$	$^{(8)}0.977$	$^{(9)}1.032$				
Mg^{2+}	$^{(4)}0.57$	$^{(5)}0.66$	$^{(6)}0.720$	$^{(8)}0.89$			
Mn^{2+}	$^{(4,\mathrm{hs})}0.66$	$^{(5,\mathrm{hs})}0.75$	$^{(6,\mathrm{ls})}0.67$	$^{(6,\mathrm{hs})}0.83$	$^{(7,\mathrm{hs})}0.90$	$^{(8)}0.96$	
Mn^{3+}	$^{(5)}0.58$	$^{(6,\mathrm{ls})}0.58$	$^{(6,\mathrm{hs})}0.645$				
Mn^{4+}	$^{(4)}0.39$	$^{(6)}0.53$					
Mn^{5+}	$^{(4)}0.33$						
Mn^{6+}	$^{(4)}0.255$						
Mn^{7+}	$^{(4)}0.25$	$^{(6)}0.46$					
Mo^{3+}	$^{(6)}0.69$						
Mo^{4+}	$^{(6)}0.650$						
Mo^{5+}	$^{(4)}0.46$	$^{(6)}0.61$					
Mo^{6+}	$^{(4)}0.41$	$^{(5)}0.50$	$^{(6)}0.59$	$^{(7)}0.73$			
N^{3-}	$^{(4)}1.46$						
N^{3+}	$^{(6)}0.16$						
N^{5+}	$^{(3)}-0.104$	$^{(6)}0.13$					
Na^{+}	$^{(4)}0.99$	$^{(5)}1.00$	$^{(6)}1.02$	$^{(7)}1.12$	$^{(8)}1.18$	$^{(9)}1.24$	$^{(12)}1.39$
Nb^{3+}	$^{(6)}0.72$						
Nb^{4+}	$^{(6)}0.68$	$^{(8)}0.79$					
Nb^{5+}	$^{(4)}0.48$	$^{(6)}0.64$	$^{(7)}0.69$	$^{(8)}0.74$			
Nd^{2+}	$^{(8)}1.29$	$^{(9)}1.35$					
Nd^{3+}	$^{(6)}0.983$	$^{(8)}1.109$	$^{(9)}1.163$	$^{(12)}1.27$			
Ni^{2+}	$^{(4)}0.55$	$^{(4,\mathrm{sq})}0.49$	$^{(5)}0.63$	$^{(6)}0.690$			
Ni^{3+}	$^{(6,\mathrm{ls})}0.56$	$^{(6,\mathrm{hs})}0.60$					

continued on next page

Tab. 1.1 (continued)

Ion	**$^{\text{(coordination number)}}r_{\text{eff}}$ (Å)**							
Ni^{4+}	$^{(6,\text{ls})}$0.48							
No^{2+}	$^{(6)}$1.1							
Np^{2+}	$^{(6)}$1.10							
Np^{3+}	$^{(6)}$1.01							
Np^{4+}	$^{(6)}$0.87	$^{(8)}$0.98						
Np^{5+}	$^{(6)}$0.75							
Np^{6+}	$^{(6)}$0.72							
Np^{7+}	$^{(6)}$0.71							
O^{2-}	$^{(2)}$1.35	$^{(3)}$1.36	$^{(4)}$1.38	$^{(6)}$1.40	$^{(8)}$1.42			
OH^{-}	$^{(2)}$1.32	$^{(3)}$1.34	$^{(4)}$1.35	$^{(6)}$1.37				
Os^{4+}	$^{(6)}$0.630							
Os^{5+}	$^{(6)}$0.575							
Os^{6+}	$^{(5)}$0.49	$^{(6)}$0.545						
Os^{7+}	$^{(6)}$0.525							
Os^{8+}	$^{(4)}$0.39							
P^{3+}	$^{(6)}$0.44							
P^{5+}	$^{(4)}$0.17	$^{(5)}$0.29	$^{(6)}$0.38					
Pa^{3+}	$^{(6)}$1.04							
Pa^{4+}	$^{(6)}$0.90	$^{(8)}$1.01						
Pa^{5+}	$^{(6)}$0.78	$^{(8)}$0.91	$^{(9)}$0.95					
Pb^{2+}	$^{(4,\text{py})}$0.98	$^{(6)}$1.19	$^{(7)}$1.23	$^{(8)}$1.29	$^{(9)}$1.35	$^{(10)}$1.40	$^{(11)}$1.45	$^{(12)}$1.49
Pb^{4+}	$^{(4)}$0.65	$^{(5)}$0.73	$^{(6)}$0.775	$^{(8)}$0.94				
Pd^{+}	$^{(2)}$0.59							
Pd^{2+}	$^{(4,\text{sq})}$0.64	$^{(6)}$0.86						
Pd^{3+}	$^{(6)}$0.76							
Pd^{4+}	$^{(6)}$0.615							
Pm^{3+}	$^{(6)}$0.97	$^{(8)}$1.093	$^{(9)}$1.144					
Po^{4+}	$^{(6)}$0.94	$^{(8)}$1.08						
Po^{6+}	$^{(6)}$0.67							
Pr^{3+}	$^{(6)}$0.99	$^{(8)}$1.126	$^{(9)}$1.179					
Pr^{4+}	$^{(6)}$0.85	$^{(8)}$0.96						
Pt^{2+}	$^{(4,\text{sq})}$0.60	$^{(6)}$0.80						
Pt^{4+}	$^{(6)}$0.625							
Pt^{5+}	$^{(6)}$0.57							
Pu^{3+}	$^{(6)}$1.00							
Pu^{4+}	$^{(6)}$0.86	$^{(8)}$0.96						
Pu^{5+}	$^{(6)}$0.74							
Pu^{6+}	$^{(6)}$0.71							
Ra^{2+}	$^{(8)}$1.48	$^{(12)}$1.70						
Rb^{+}	$^{(6)}$1.52	$^{(7)}$1.56	$^{(8)}$1.61	$^{(9)}$1.63	$^{(10)}$1.66	$^{(11)}$1.69	$^{(12)}$1.72	$^{(14)}$1.83
Re^{4+}	$^{(6)}$0.63							
Re^{5+}	$^{(6)}$0.58							
Re^{6+}	$^{(6)}$0.55							
Re^{7+}	$^{(4)}$0.38	$^{(6)}$0.53						
Rh^{3+}	$^{(6)}$0.665							
Rh^{4+}	$^{(6)}$0.60							
Rh^{5+}	$^{(6)}$0.55							
Ru^{3+}	$^{(6)}$0.68							
Ru^{4+}	$^{(6)}$0.620							
Ru^{5+}	$^{(6)}$0.565							
Ru^{7+}	$^{(4)}$0.38							
Ru^{8+}	$^{(4)}$0.36							
S^{2-}	$^{(6)}$1.84							

continued on next page

Tab. 1.1 (continued)

Ion	**$^{\text{(coordination number)}}r_{\text{eff}}$ (Å)**					
S^{4+}	$^{(6)}0.37$					
S^{6+}	$^{(4)}0.12$	$^{(6)}0.29$				
Sb^{3+}	$^{(4,py)}0.76$	$^{(5)}0.80$	$^{(6)}0.76$			
Sb^{5+}	$^{(6)}0.60$					
Sc^{3+}	$^{(6)}0.745$	$^{(8)}0.870$				
Se^{2-}	$^{(6)}1.98$					
Se^{4+}	$^{(6)}0.50$					
Se^{6+}	$^{(4)}0.28$	$^{(6)}0.42$				
Si^{4+}	$^{(4)}0.26$	$^{(6)}0.400$				
Sm^{2+}	$^{(7)}1.22$	$^{(8)}1.27$	$^{(9)}1.32$			
Sm^{3+}	$^{(6)}0.958$	$^{(7)}1.02$	$^{(8)}1.079$	$^{(9)}1.132$	$^{(12)}1.24$	
Sn^{4+}	$^{(4)}0.55$	$^{(5)}0.62$	$^{(6)}0.690$	$^{(7)}0.75$	$^{(8)}0.81$	
Sr^{2+}	$^{(6)}1.18$	$^{(7)}1.21$	$^{(8)}1.26$	$^{(9)}1.31$	$^{(10)}1.36$	$^{(12)}1.44$
Ta^{3+}	$^{(6)}0.72$					
Ta^{4+}	$^{(6)}0.68$					
Ta^{5+}	$^{(6)}0.64$	$^{(7)}0.69$	$^{(8)}0.74$			
Tb^{3+}	$^{(6)}0.923$	$^{(7)}0.98$	$^{(8)}1.040$	$^{(9)}1.095$		
Tb^{4+}	$^{(6)}0.76$	$^{(8)}0.88$				
Tc^{4+}	$^{(6)}0.645$					
Tc^{5+}	$^{(6)}0.60$					
Tc^{7+}	$^{(4)}0.37$	$^{(6)}0.56$				
Te^{2-}	$^{(6)}2.21$					
Te^{4+}	$^{(3)}0.52$	$^{(4)}0.66$	$^{(6)}0.97$			
Te^{6+}	$^{(4)}0.43$	$^{(6)}0.56$				
Th^{4+}	$^{(6)}0.94$	$^{(8)}1.05$	$^{(9)}1.09$	$^{(10)}1.13$	$^{(11)}1.18$	$^{(12)}1.21$
Ti^{2+}	$^{(6)}0.86$					
Ti^{3+}	$^{(6)}0.670$					
Ti^{4+}	$^{(4)}0.42$	$^{(5)}0.51$	$^{(6)}0.605$	$^{(8)}0.74$		
Tl^{+}	$^{(6)}1.50$	$^{(8)}1.59$	$^{(12)}1.70$			
Tl^{3+}	$^{(4)}0.75$	$^{(6)}0.885$	$^{(8)}0.98$			
Tm^{2+}	$^{(6)}1.03$	$^{(7)}1.09$				
Tm^{3+}	$^{(6)}0.880$	$^{(8)}0.994$	$^{(9)}1.052$			
U^{3+}	$^{(6)}1.025$					
U^{4+}	$^{(6)}0.89$	$^{(7)}0.95$	$^{(8)}1.00$	$^{(9)}1.05$	$^{(12)}1.17$	
U^{5+}	$^{(6)}0.76$	$^{(7)}0.84$				
U^{6+}	$^{(2)}0.45$	$^{(4)}0.52$	$^{(6)}0.73$	$^{(7)}0.81$	$^{(8)}0.86$	
V^{2+}	$^{(6)}0.79$					
V^{3+}	$^{(6)}0.640$					
V^{4+}	$^{(5)}0.53$	$^{(6)}0.58$	$^{(8)}0.72$			
V^{5+}	$^{(4)}0.355$	$^{(5)}0.46$	$^{(6)}0.54$			
W^{4+}	$^{(6)}0.66$					
W^{5+}	$^{(6)}0.62$					
W^{6+}	$^{(4)}0.42$	$^{(5)}0.51$	$^{(6)}0.60$			
Xe^{8+}	$^{(4)}0.40$	$^{(6)}0.48$				
Y^{3+}	$^{(6)}0.900$	$^{(7)}0.96$	$^{(8)}1.019$	$^{(9)}1.075$		
Yb^{2+}	$^{(6)}1.02$	$^{(7)}1.08$	$^{(8)}1.14$			
Yb^{3+}	$^{(6)}0.868$	$^{(7)}0.925$	$^{(8)}0.985$	$^{(9)}1.042$		
Zn^{2+}	$^{(4)}0.60$	$^{(5)}0.68$	$^{(6)}0.740$	$^{(8)}0.90$		
Zr^{4+}	$^{(4)}0.59$	$^{(5)}0.66$	$^{(6)}0.72$	$^{(7)}0.78$	$^{(8)}0.84$	$^{(9)}0.89$

A nice feature of Shannon's radii – dubbed *effective* ionic radii by himself – is that the complete set is *additive*, such that experimental cation–anion distances are, in most cases, correctly reproduced. To allow for this, a few ions must have *negative* radii but such an unphysical property does not bother the brave crystal chemist.[4] Second, because of the popularity of Pauling's radii, the size of O^{2-} in six-fold coordination is also fixed to 1.40 Å, such that traditionalists of ionic radii do not have to rethink. Nonetheless, an alternative, likewise additive, set of *crystal* radii – not to be confused with Pauling's crystal radii! – is generated from Shannon's effective radii by subtracting 0.14 Å from all anionic radii and adding this 0.14 Å to all the cationic radii (see below).

Why do we need two sets of Shannon radii? Knowing that LiI also adopts the sodium chloride structure type, we might predict (see again Figure 1.1(b)) the experimental LiI lattice parameter (6.00 Å) either by twice the *effective* ionic radii of Li^+ and I^-, that is, $2 \times (0.76\ Å + 2.20\ Å) = 5.92\ Å$, or by twice their *crystal* radii, namely $2 \times (0.90\ Å + 2.06\ Å) = 5.92\ Å$. If we think in terms of packings of anions, however, a close-packing of I^- anions with $r(I^-) = 2.20$ Å and Li^+ in octahedral holes will come closer to the volume of the unit cell (almost 83%), thus favoring the *effective* ionic radii which are closer to Pauling's radii.

Shannon's *crystal* radii, however, better match the experimentally found electron density distribution mentioned at the beginning. For example, modern X-ray data show that the minimum electron density for LiF ([NaCl] type) corresponds to $r(Li^+) = 0.92$ Å and $r(F^-) = 1.08$ Å. This reflects a significantly larger/smaller lithium/fluorine ion than Pauling's (0.60/1.36 Å), Goldschmidt's (0.78/1.33 Å) and also Shannon's effective ionic radii (0.76/1.33 Å), but it is already quite close to Shannon's crystal radii (0.90/1.19 Å). Summarizing, *effective* ionic radii correspond to the idea of closely packed anions but *crystal* radii are closer to the real sizes of anions *and* cations.

The purpose of ionic radii, as presented so far, can be understood as to predict or at least "rationalize" interionic distances and also lattice parameters when the crystal structure type adopted is already known. One is tempted to go somewhat further and try to use ionic radii for the prediction of the crystal structure itself. Let us illustrate this from the simple examples of AB-type structures, depicted in Figure 1.1. For example, the [NaCl] type (b) is usually derived by assuming that the larger anions adopt the elemental fcc structure and the smaller cations just fill up all octahedral sites; indeed, the visual comparison of the fcc type (Figure 1.2(b)) and the [NaCl] type shows that the latter is composed of two fcc structures (by Na^+ and Cl^-) which have been shifted against each other by half the lattice parameter. Despite this elegant

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[4] The most extreme example is the fate of the H^+ ion which, because the O^{2-} ion is larger than the OH^- ion, is considered to have a strongly negative ionic radius; the reader should not be too concerned about this.

derivation, it seems somewhat strange to assume that both anions and cations should strive for close packing because that is where the anion–anion and cation–cation repulsion is maximized! Neglecting this internal inconsistency for the moment, the AB structure prediction usually proceeds as follows:

No matter what kind of interaction exists between A and B in, for example, the zinc-blende structure type with a coordination number of four (see Figure 1.1(c)), the atoms (or ions) can be expected to minimize their interatomic A–B distance because of energy optimization; so shorter distances should indicate stronger interaction. For a purely electrostatic one (see Section 1.2), this is particularly easy to calculate; the distance between A and B can then be approximated by the sum of the ionic radii of the cation and anion, r_c and r_a.

If we further imagine the cation radius r_c to grow, the A–B distance will also become larger so that the A–B interaction should weaken. Then, however, A might already be so large that six instead of four B partners may coordinate A; in electrostatic terms, the weakening of the A–B interaction is partly overridden by a larger electrostatic field as indicated by the larger Madelung constant for coordination number six (see Section 1.2). Thus, the sodium chloride type will be more favorable than the zinc-blende type for a sufficiently large cation radius or, more generally, for a critical ratio r_c/r_a. The same argument holds true for the change from the sodium chloride to the caesium chloride type (eight-fold coordination) such that, in general, a large radius ratio points towards an enlarged coordination number. This seems logical.

Textbooks of structural chemistry usually go to great lengths to reproduce Goldschmidt's (and also Pauling's) reasoning of how the critical radius ratio between cation and anion can be derived [5]. This elementary calculus will not be repeated here but is left to the reader as an exercise if time allows. Eventually, a critical radius ratio r_c/r_a of less than 0.414 favors four-fold coordination; the zinc-blende type. For larger cations (or smaller anions) which correspond to a radius ratio of between 0.414 and 0.732, six-fold coordination, the [NaCl] type, would be preferred.[5] For even larger ratios beyond 0.732, one should find the [CsCl] type with eight-fold coordination.

Regrettably, the world is not that simple. The corresponding test of the above hypothesis has been pursued by Burdett and coworkers [15] (unfortunately, only many years after the radius-ratio rule had become an essential part of general chemistry), and it is depicted in Figure 1.3.

The maximum coordination number (8) is indeed found for the largest radius ratios, calling for the [CsCl] structure type (open squares). A very large number of structures is of the [NaCl] type with a coordination number of six (shaded circles), and small radius ratios point towards a coordination num-

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[5] Another choice for six-fold coordination is given by the [NiAs] structure type, with an octahedral environment for Ni and a hexagonal prism for As. This structure type, usually not found for ionic solids, is therefore never considered.

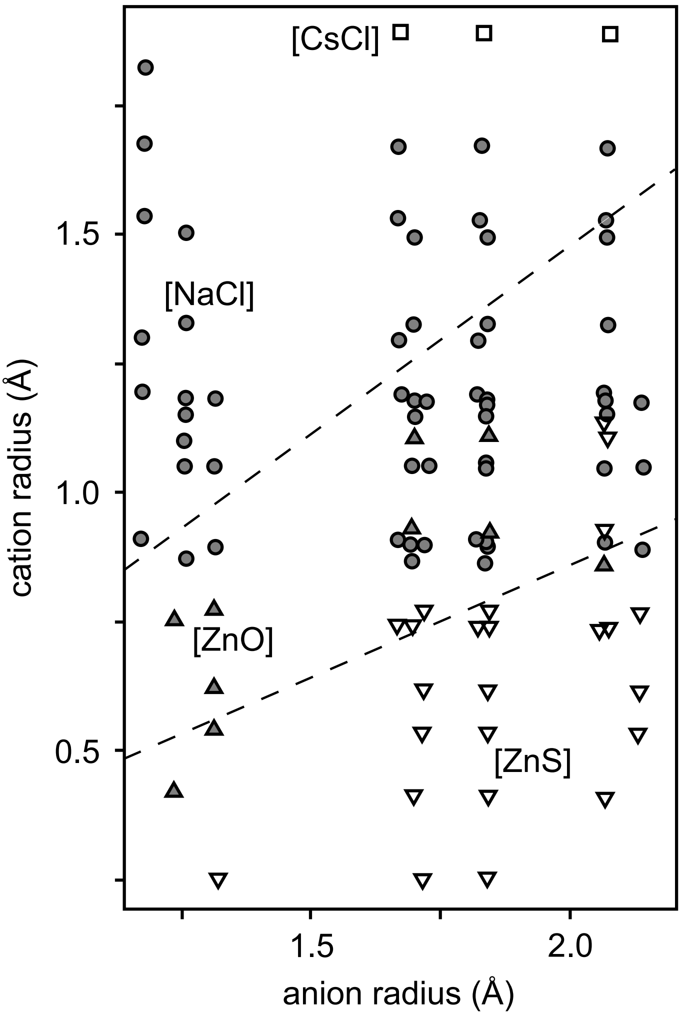

Fig. 1.3 Structure map of AB solids with noble-gas configuration for the ions as a function of cation and anion radii; the experimentally found structures are indicated. All entries above the upper dashed line should crystallize in the [CsCl] type, whereas all under the lower dashed line should adopt the [ZnS] type; the intermediate region is one of the [NaCl] type. For an anion radius of 1.0 Å, the upper and lower lines yield a cation radius of 0.732 and 0.414 Å.

ber of four and the [ZnS] or [ZnO] structure (open and shaded triangles). The disappointing part of the story is that, of the 95 AB-type compounds with supposedly ionic bonding, 37 – close to forty percent! – are incorrectly placed such that the *quantitative* predictive power of the radius ratios is almost imaginary; there must be some variability in these radii upon chemical bonding and the atoms do not behave as billiard balls. Nonetheless, the *qualitative* trend is fine, namely that larger/smaller cations/anions favor large coordination numbers for the cation. Quantitatively, the concept does not serve its purpose, however.

There have been other attempts to derive such structure-sorting maps, with considerable success. One of the most influential strategies is the one by Mooser and Pearson [16] who used the average principal quantum number and electronegativity differences as corresponding indices. Nonetheless, it *is* possible to quantitatively consider atomic size for the derivation of structure-sorting maps [17], but only by a quantum-chemical derivation in the form of *pseudopotential* radii (see Section 2.15.2). The latter express atomic size by the extent of which the outer valence electrons are expelled by the inner core electrons, through the Pauli principle. Thus, the classical idea may be kept but only by transcending it into the realm of quantum chemistry.

Yet another, entirely phenomenological, approach for arriving at structure-sorting maps goes back to the work of Pettifor who used the periodic table of the elements as a starting point [18]. When all atomic numbers are exchanged by Mendeléev numbers M – this effectively corresponds to a total renumbering of the whole periodic table – a structural separation of many binary compounds AB_x may be achieved by using these Mendeléev numbers of the constituent atoms, M^A and M^B, as the axes of the coordinate systems. Why this works – as it often does – is a mystery to me.

1.2
Electrostatics

Amongst the various solid-state materials with either insulating, semiconducting or metallic properties, electric insulators were probably the first to have been studied by theoretical, albeit classical, approaches. Indeed, there is definitely no book on solid-state chemistry which does not, at least qualitatively or unconsciously, mention the "ionic model" of chemical bonding in solids. Let us do that here, too.

A moment's reflection on the possibility of a *gaseous* sodium chloride species based upon experimental energetic data immediately reveals that such a molecular $NaCl_{(g)}$ is unlikely to form if ionic bonding would be involved. The electron loss of Na to form Na^+ will cost an ionization energy I of about 496 kJ/mol, and the capture of the electron by Cl to form Cl^- will gain an electron affinity A of merely -361 kJ/mol such that the system is unstable by 496 kJ/mol $-$ 361 kJ/mol = 135 kJ/mol. Generally, experimental evidence proves that there is no such combination of metals and nonmetals where the electron affinity exceeds the ionization energy; thus, the ionic bonding we always refer to is bound to the condensed matter, period.

This has been known for a long time, and the correct energetic calculus for the formation of solid sodium chloride (we will stay with this example for simplicity) is given by the so-called Born–Haber cycle, depicted in Figure 1.4.

$$\begin{tikzcd}
Na_{(s)} + {}^{1}/_{2}\, Cl_{2(g)} \arrow[r, "\Delta H_{subl} + {}^{1}/_{2}\, \Delta H_{diss}"] \arrow[d, "\Delta H_{R}"] & Na_{(g)} \arrow[d, "I"] & + & Cl_{(g)} \arrow[d, "A"] \\
NaCl_{(s)} & Na^{+}_{(g)} \arrow[l, "-U_{L}"'] & + & Cl^{-}_{(g)}
\end{tikzcd}$$

Fig. 1.4 Schematic Born–Haber cycle for the formation of solid NaCl; the energetic data (kJ/mol) are: Na sublimation enthalpy ΔH_{subl} = 100.5; $\frac{1}{2} \times Cl_2$ dissociation enthalpy ΔH_{diss} = 121.4; Na ionization energy I = 495.7; Cl electron affinity A = -360.5; experimental reaction enthalpy ΔH_{R} = -411.1.

Summing up all atomic energetic data in the above figure, namely ΔH_{subl}(Na) + $\frac{1}{2} \times \Delta H_{\mathrm{diss}}(\mathrm{Cl}_2)$ + I(Na) + A(Cl), yields that the formation of gaseous ions needs a total energy of 357.1 kJ/mol (on the right side); on the other hand, the experimental reaction enthalpy is -411.1 kJ/mol (left side) such that, and this is the important result, the ionic solid is more stable than the isolated ions by 357.1 kJ/mol $-(-411.1)$ kJ/mol = 768.2 kJ/mol. It is common practice to call this energy the *lattice energy* U_{L} of the solid, needed to evaporate the ionic solid into gaseous *ions* – not atoms – and it carries a positive sign by definition.[6] Whether or not the isolated ions exist in the gas phase is another matter (see below).

Because the lattice energy defined as such alludes to structural stability, its theoretical calculation (as opposed to its experimental determination by means of the above Born–Haber cycle) was investigated at an early stage. We might, for example, define the lattice energy to be composed of an electrostatic interaction between the ions which we may approximate by a simple Coulomb expression, augmented by a repulsive part U_{rep} such that the ionic lattice cannot collapse into a singularity, and also account for weak covalent bonding contributions U_{cov}, even weaker van der Waals (dispersive) attractions U_{vdW} and also the zero-point vibration U_{zero}, namely

$$U_{\mathrm{L}} \equiv U_{\mathrm{Coulomb}} + U_{\mathrm{rep}} + U_{\mathrm{cov}} + U_{\mathrm{vdW}} + U_{\mathrm{zero}}, \tag{1.3}$$

but it transpires that the three latter terms, being of quantum-mechanical origin and indeed relatively small in size, may be safely ignored for the remain-

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[6] In the English-speaking world, however, U_{L} is sometimes found with a negative sign because then one considers the energy which is gained when the ions form the crystal.

ing part of the discussion. This leaves us with an approximate two-particle lattice energy

$$U_{\mathrm{L}} \approx U_{\mathrm{Coulomb}} + U_{\mathrm{rep}} = \frac{1}{4\pi\epsilon_0}\frac{z_1 z_2 e^2}{r} + U_{\mathrm{rep}}, \tag{1.4}$$

where the Coulomb part goes back to the interaction between point charges (+1 and -1 for the case of NaCl) and e is the elementary charge; the repulsion term still needs to be specified. Interestingly, this repulsion term is also of quantum-mechanical origin, and it simply shows that it is impossible to push atoms into each other. The reason, as one might expect, is the exchange interaction between the electrons such that, simply speaking, it is the Pauli principle (see Section 2.9) which forbids the too-close encounter of atoms, when their associated orbitals have already been completely filled; we can always expect such a scenario for the inner shells of any kind of atom. The same reason is responsible for the fact that there is no covalently bonded He_2 molecule (see Section 2.1). One may envisage different ways to describe this quantum effect classically but a simple exponential expression [19],

$$U_{\mathrm{rep}} \approx b e^{-r/\rho}, \tag{1.5}$$

with empirical scaling parameters b and ρ, is a very good approximation since it imitates the exponential decay of the atomic orbitals (see Section 2.2). In practice, a parameter of, say, $\rho = 0.345$ Å does a fine job but ρ may also be

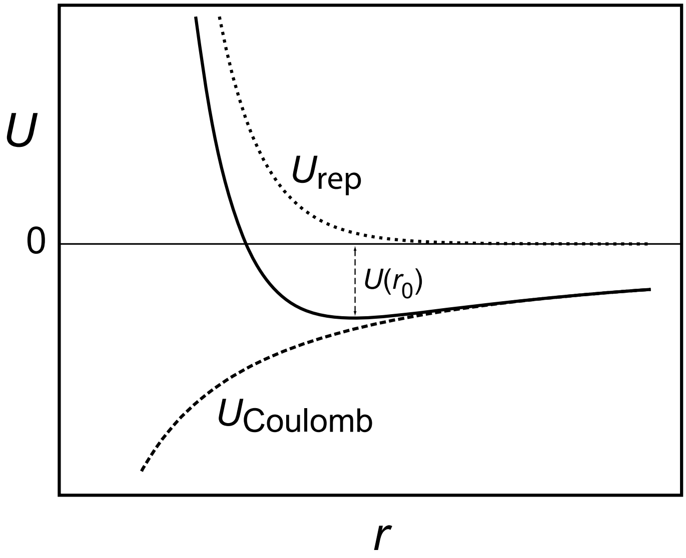

Fig. 1.5 Schematic drawing of Coulomb, repulsive and total energies of a cation–anion pair.