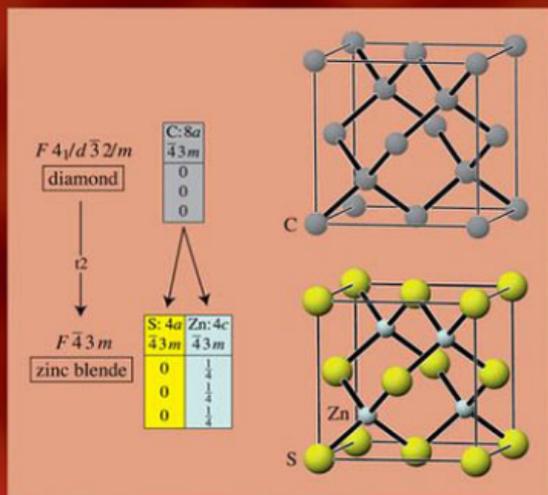


Symmetry

Relationships between Crystal Structures

Applications of Crystallographic
Group Theory in Crystal Chemistry

ULRICH MÜLLER



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Symmetry Relationships between Crystal Structures

Applications of Crystallographic Group Theory in
Crystal Chemistry

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with texts adapted from

Hans Wondratschek and Hartmut Bärnighausen

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permission of the *International Union of Crystallography*, together with
some accompanying text written by the author of this book

Dedicated to

Hartmut Bärnighausen

and

Hans Wondratschek

Hartmut Bärnighausen was Professor of Inorganic Chemistry at the University of Karlsruhe from 1967 to 1998. His article Group–subgroup relations between space groups: a useful tool in crystal chemistry, published in 1980, showed the way to the application of crystallographic group theory in crystal chemistry. The present book is based on this article and on his manuscripts for several courses on this topic.



Hans Wondratschek was Professor of Crystallography at the University of Karlsruhe from 1964 to 1991. He contributed to the derivation of the space groups of four-dimensional space and to the complete listing of the subgroups of the three-dimensional space groups. These were then published in International Tables for Crystallography, Volume A1.



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Preface

Crystal-structure analysis has become one of the most essential tools in chemistry and related disciplines. Several hundreds of thousands of crystal structures have been determined in the course of the years. The results obtained from 1931 to 1990 were published year by year in *Strukturbericht* [1], later *Structure Reports* [2]. Nowadays, crystal structures are deposited in several large databases [3–8]. However, the mere accumulation of data is only of restricted value if it lacks a systematic order and if the scientific interpretation of the data leaves much to be desired.

Shortly after the discovery of X-ray diffraction from crystals by MAX VON LAUE, WALTHER FRIEDRICH, and PAUL KNIPPING (1912) and the subsequent pioneering work by father WILLIAM HENRY BRAGG and son WILLIAM LAWRENCE BRAGG, efforts set in to order the crystal structures found. By 1926 the number of crystal structures was already large enough for VIKTOR MORITZ GOLDSCHMIDT to formulate the basic principles of packing of atoms and ions in inorganic solids [9]. In 1928 LINUS PAULING set forth a number of structural principles, essentially for ionic crystals, which he later repeated in his famous book *The Nature of the Chemical Bond*, first published in 1938 [10]. Quite a few other approaches to show relationships between crystal structures and to bring order into the constantly increasing amount of data were presented and developed quite successfully over time. Most of these approaches, however, have one peculiarity in common: they make no or nearly no use of the symmetry of the crystal structures.

The importance of symmetry relations in phase transitions in the solid state was realized in 1937 by LEW LANDAU [11]. Around 1968 HARTMUT BÄRNIGHAUSEN developed a procedure to work out relationships between crystal structures with the aid of symmetry relations [12]. Since then, chemists have become more and more aware of the value of these symmetry relations. Symmetry relations can be formulated mathematically. This offers a secure foundation for their application and makes it possible to develop algorithms to make use of computers.

The symmetry of crystals is presented in *International Tables for Crystallography*, Volume A [13], by diagrams and with the aid of analytical geometry. The methods of analytical geometry can be applied universally; they are based on the techniques of matrix calculus and make use of the results of elementary group theory. Since 2004, the supplementary volume A1 of *International Tables for Crystallography* has been available [14]. For the first time they contain a complete listing of the subgroups of the space groups. This book shows how to make use of these tables.

Part I of this book presents the necessary mathematical tools: the fundamentals of crystallography, especially of symmetry, the theory of crystallographic groups, and the formalisms for the necessary crystallographic calculations. As often in the natural sciences, these tools may appear difficult as long as one is not accustomed to their use. However, the presented calculation techniques are nothing more than applications of simple theorems of algebra and group theory.

Group theory has profound foundations. For its application, however, the profoundness is not needed. The mathematical foundations are contained in the presented formalisms. Calculations can be performed and consequences can be drawn with these formalisms, without the need to duplicate their mathematical background.

Those who have some familiarity with the symmetry of crystals, i.e. who have worked with space groups, are acquainted with Hermann–Mauguin symbols, know how to handle atomic coordinates, etc., may take a first look at Part II to obtain an impression of the results that follow from the mathematical relations. However, it is not recommended to skip the chapters of Part I. Don't be mistaken: crystallographic group theory and symbolism does have pitfalls, and calculations are susceptible to errors if they are not performed strictly in accordance with the rules.

Part II of the book gives an insight into the application to problems in crystal chemistry. Numerous examples show how crystallographic group theory can be used to disclose relations between crystal structures, to maintain order among the enormous number of crystal structures, to predict possible crystal-structure types, to analyse phase transitions, to understand the phenomenon of domain formation and twinning in crystals, and to avoid errors in crystal-structure determinations.

Appendix A deals with peculiarities of a certain kind of subgroup of the space groups, the isomorphic subgroups, and discloses cross-connections to number theory. Another appendix gives some insight into a few physico-chemical aspects referring to phase transitions and to the theory of phase transitions.

A broad range of end-of-chapter exercises offers the possibility to apply the learned material. Worked-out solutions to the exercises can be found in Appendix D.

In the Glossary one can look up the meanings of special terms used in the field.

One topic of group theory is not addressed in this book: representation theory. Crystallographic symmetry does not deal with time. Representation theory is needed to cover the symmetry properties of time-dependent phenomena (such as vibrations). This is dealt with in numerous books and articles; we could only repeat their content (see, e.g. [15–22]). However, some remarks can be found in Chapter 15 and in Appendix C.

The book has many predecessors. It is based on earlier lectures and on courses that were taught repeatedly since 1975 in Germany, Italy, France, Czechia, Bulgaria, Russia, and South Africa. Lecturers of these courses were first of all H. BÄRNIGHAUSEN (Karlsruhe), TH. HAHN (Aachen), and H. WONDRATSCHEK (Karlsruhe), and, in addition, M. AROYO (Sofia, later Bil-

bao), G. CHAPUIS (Lausanne), W. E. KLEE (Karlsruhe), R. PÖTTGEN (Münster), and myself.

The text of Chapters 2–7 is due to H. WONDRATSCHEK, who allowed me to use his material; he also revised these chapters after I had appended figures, examples, exercises, and a few paragraphs. These chapters partly reflect lecture notes by W. E. KLEE. Chapters 1, 10, 11, 15, and 16 essentially go back to H. BÄRNIGHAUSEN and contain text by him; he also critically checked drafts of these chapters. Parts of a script by R. PÖTTGEN, R.-D. HOFFMANN, and U. RODEWALD were included in Chapter 17. I am especially grateful to all of them. Without their manuscripts and without their consent to make use of their texts this book could not have come into being.

Indirect contributors are G. NEBE (mathematician, Aachen), J. NEUBÜSER (mathematician, Aachen), and V. JANOVEC (physicist, Liberec) by their suggestions, and numerous discussions with H. WONDRATSCHEK. In addition, I am grateful to further unnamed colleagues for suggestions and discussions.

Ulrich Müller

Marburg, Germany, November 2012

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Contents

List of symbols	xvi
1 Introduction	1
1.1 The symmetry principle in crystal chemistry	2
1.2 Introductory examples	4
I Crystallographic Foundations	9
2 Basics of crystallography, part 1	11
2.1 Introductory remarks	11
2.2 Crystals and lattices	11
2.3 Appropriate coordinate systems, crystal coordinates	13
2.4 Lattice directions, net planes, and reciprocal lattice	15
2.5 Calculation of distances and angles	16
3 Mappings	19
3.1 Mappings in crystallography	19
3.1.1 An example	19
3.1.2 Symmetry operations	19
3.2 Affine mappings	20
3.3 Application of $(n + 1) \times (n + 1)$ matrices	23
3.4 Affine mappings of vectors	24
3.5 Isometries	25
3.6 Types of isometries	27
3.7 Changes of the coordinate system	30
3.7.1 Origin shift	30
3.7.2 Basis change	31
3.7.3 General transformation of the coordinate system	32
3.7.4 The effect of coordinate transformations on mappings	33
3.7.5 Several consecutive transformations of the coordinate system	36
3.7.6 Calculation of origin shifts from coordinate transformations	38
3.7.7 Transformation of further crystallographic quantities	39
Exercises	40

4	Basics of crystallography, part 2	41
4.1	The description of crystal symmetry in International Tables A: Positions	41
4.2	Crystallographic symmetry operations	41
4.3	Geometric interpretation of the matrix–column pair (W, w) of a crystallographic symmetry operation	45
4.4	Derivation of the matrix–column pair of an isometry	47
	Exercises	48
5	Group theory	49
5.1	Two examples of groups	49
5.2	Basics of group theory	51
5.3	Coset decomposition of a group	53
5.4	Conjugation	56
5.5	Factor groups and homomorphisms	57
5.6	Action of a group on a set	59
	Exercises	61
6	Basics of crystallography, part 3	63
6.1	Space groups and point groups	63
6.1.1	Molecular symmetry	63
6.1.2	The space group and its point group	66
6.1.3	Classification of the space groups	67
6.2	The lattice of a space group	69
6.3	Space-group symbols	70
6.3.1	Hermann–Mauguin symbols	70
6.3.2	Schoenflies symbols	74
6.4	Description of space-group symmetry in International Tables A	76
6.4.1	Diagrams of the symmetry elements	76
6.4.2	Lists of the Wyckoff positions	79
6.4.3	Symmetry operations of the general position	80
6.4.4	Diagrams of the general positions	80
6.5	General and special positions of the space groups	81
6.5.1	The general position of a space group	82
6.5.2	The special positions of a space group	83
6.6	The difference between space group and space-group type	84
	Exercises	85
7	Subgroups and supergroups of point and space groups	87
7.1	Subgroups of the point groups of molecules	87
7.2	Subgroups of the space groups	89
7.2.1	Maximal <i>translationengleiche</i> subgroups	91
7.2.2	Maximal non-isomorphic <i>klassengleiche</i> subgroups	93
7.2.3	Maximal isomorphic subgroups	93
7.3	Minimal supergroups of the space groups	94
7.4	Layer groups and rod groups	96
	Exercises	99

8	Conjugate subgroups, normalizers and equivalent descriptions of crystal structures	101
8.1	Conjugate subgroups of space groups	101
8.2	Normalizers of space groups	103
8.3	The number of conjugate subgroups. Subgroups on a par	106
8.4	Standardized description of crystal structures	110
8.5	Equivalent descriptions of crystal structures	110
8.6	Chirality	113
8.7	Wrongly assigned space groups	115
8.8	Isotypism	117
	Exercises	119
9	How to handle space groups	121
9.1	Wyckoff positions of space groups	121
9.2	Relations between the Wyckoff positions in group–subgroup relations	122
9.3	Non-conventional settings of space groups	123
9.3.1	Orthorhombic space groups	123
9.3.2	Monoclinic space groups	125
9.3.3	Tetragonal space groups	127
9.3.4	Rhombohedral space groups	129
9.3.5	Hexagonal space groups	129
	Exercises	130
II	Symmetry Relations between Space Groups as a Tool to Disclose Connections between Crystal Structures	131
10	The group-theoretical presentation of crystal-chemical relationships	133
11	Symmetry relations between related crystal structures	137
11.1	The space group of a structure is a <i>translationengleiche</i> maximal subgroup of the space group of another structure	137
11.2	The maximal subgroup is <i>klassengleiche</i>	141
11.3	The maximal subgroup is isomorphic	145
11.4	The subgroup is neither <i>translationengleiche</i> nor <i>klassengleiche</i>	148
11.5	The space groups of two structures have a common supergroup	149
11.6	Large families of structures	151
	Exercises	156
12	Pitfalls when setting up group–subgroup relations	159
12.1	Origin shifts	160
12.2	Subgroups on a par	162
12.3	Wrong cell transformations	162
12.4	Different paths of symmetry reduction	163
12.5	Forbidden addition of symmetry operations	165
	Exercises	166

13 Derivation of crystal structures from closest packings of spheres	167
13.1 Occupation of interstices in closest packings of spheres	167
13.2 Occupation of octahedral interstices in the hexagonal-closest packing of spheres	168
13.2.1 Rhombohedral hettotypes	168
13.2.2 Hexagonal and trigonal hettotypes of the hexagonal-closest packing of spheres	174
13.3 Occupation of octahedral and tetrahedral interstices in the cubic-closest packing of spheres	178
13.3.1 Hettotypes of the NaCl type with doubled unit cell	178
13.3.2 Hettotypes of the CaF ₂ type with doubled unit cell	180
Exercises	183
14 Crystal structures of molecular compounds	185
14.1 Symmetry reduction due to reduced point symmetry of building blocks	186
14.2 Molecular packings after the pattern of sphere packings	187
14.3 The packing in tetraphenylphosphonium salts	191
Exercises	195
15 Symmetry relations at phase transitions	197
15.1 Phase transitions in the solid state	197
15.1.1 First- and second-order phase transitions	198
15.1.2 Structural classification of phase transitions	199
15.2 On the theory of phase transitions	200
15.2.1 Lattice vibrations	200
15.2.2 The Landau theory of continuous phase transitions	202
15.3 Domains and twinned crystals	205
15.4 Can a reconstructive phase transition proceed via a common subgroup?	207
15.5 Growth and transformation twins	210
15.6 Antiphase domains	211
Exercises	214
16 Topotactic reactions	217
16.1 Symmetry relations among topotactic reactions	218
16.2 Topotactic reactions among lanthanoid halides	220
Exercises	224
17 Group–subgroup relations as an aid for structure determination	227
17.1 What space group should be chosen?	228
17.2 Solving the phase problem of protein structures	228
17.3 Superstructure reflections, suspicious structural features	229
17.4 Detection of twinned crystals	230
Exercises	233

18 Prediction of possible structure types	235
18.1 Derivation of hypothetical structure types with the aid of group–subgroup relations	235
18.2 Enumeration of possible structure types	239
18.2.1 The total number of possible structures	239
18.2.2 The number of possible structures depending on symmetry	241
18.3 Combinatorial computation of distributions of atoms among given positions	245
18.4 Derivation of possible crystal structure types for a given molecular structure	249
Exercises	253
19 Historical remarks	255
Appendices	259
A Isomorphic subgroups	261
Exercises	267
B On the theory of phase transitions	269
B.1 Thermodynamic aspects concerning phase transitions	269
B.2 About Landau theory	271
B.3 Renormalization-group theory	274
B.4 Discontinuous phase transitions	276
C Symmetry species	279
D Solutions to the exercises	281
References	301
Glossary	323
Index	327

Introduction



Crystallography is the science of crystals. The inner (atomic and electronic) structure of crystalline solids as well as their physical properties are of central interest. This includes the methods of structure determination and of measurement of properties. A well-founded theoretical treatment is of special importance to understand the connections and to find applications. In part, the theories are strongly influenced by mathematics. Due to its strong interrelation with mathematics, physics, chemistry, mineralogy, materials sciences, biochemistry, molecular biology, pharmaceuticals, and metrology, crystallography is more multidisciplinary than hardly any other field of science.

The *theory of symmetry* is of special importance among the theories in crystallography. The symmetry of crystals, which also has influence on the physical properties, is specified with the aid of *space groups*.

Crystal chemistry is the branch of chemistry that deals with the structures, properties, and other chemical aspects of crystalline solids. Geometric considerations relating to the structures attract much attention in this discipline. In this context it is a main objective to disclose relationships between different crystal structures and to document the corresponding results in a concise but also informative way. To this end, different approaches were presented over time, which demonstrate the similarities and the differences of distinct structures from different points of view. For example, the main attention can be directed to the coordination polyhedra and the joining of these polyhedra, or to the relative size of ions, or to the kind of chemical bonding, or to similar physical or chemical properties.

Symmetry has received attention for a long time in the description of single structures—this is familiar to anyone who has been engaged in work with crystal structures. However, concerning the comparison of structures, symmetry considerations have for a long time been the exception. For certain, there exist diverse reasons for this astonishing unbalanced development of crystal chemistry. The main reason is likely to be that related crystal structures often have different space groups so that their relationship becomes apparent only by consideration of the group–subgroup relations between their space groups. An essential part of the necessary group-theoretical material, namely a listing of the subgroups of the space groups, became available in a useful form rather late.

Aspects of space-group theory important to crystal chemistry were indeed solved around 1930 by C. HERMANN and H. HEESCH and were included in the 1935 edition of *International Tables for the Determination of Crystal Structures* [23]; this comprised lists of the subgroups of the space groups. However, in the following edition of 1952 [24] they were excluded. In addition, in the

1.1 The symmetry principle in crystal chemistry	2
1.2 Introductory examples	4

edition of 1935 only a certain kind of subgroup was mentioned, namely the *translationengleiche* subgroups, called *zellengleiche* subgroups at that time. A broad application was thus hardly possible. For crystal-chemical applications another kind of subgroup, the *klassengleiche* subgroups, are at least as important. A compilation of the *klassengleiche* subgroups of the space groups was presented by J. NEUBÜSER and H. WONDRATSCHEK as much as 53 years after the discovery of X-ray diffraction [25], and the *isomorphic* subgroups, which are a special category of *klassengleiche* subgroups, were then derived by E. BERTAUT and Y. BILLIET [26].

For 18 years this material existed only as a collection of copied sheets of paper and was distributed this way among interested scientists. Finally, the subgroups of the space groups were included in the 1983 edition of Volume A of *International Tables for Crystallography* [13]. And yet, the listing of the subgroups in the 1st to the 5th edition of Volume A (1983–2005) has been incomplete. Beginning with the 6th edition (approx. 2013) the subgroups of the space groups will no longer be included in Volume A.

Instead, a finally complete listing of all subgroups of the space groups has existed since 2004 in the supplementary Volume A1 of *International Tables for Crystallography* [14]. This includes the corresponding axes and coordinate transformations as well as the relations that exist between the Wyckoff positions of a space group and the Wyckoff positions of its subgroups. This information, which is essential for group-theoretical considerations, can indeed also be derived from the data of Volume A; that, however, is cumbersome and prone to errors. In addition, since 1999 the *Bilbao Crystallographic Server* has been in operation; it is accessible free of charge by internet, <www.cryst.ehu.es>. It offers access to computer programs that display the subgroups and supergroups of space groups as well as the corresponding Wyckoff-position relations and other things [27–29].

International Tables for Crystallography, Volumes A and A1, will be henceforth referred to as *International Tables A* and *International Tables A1*. *International Tables* are available in printed and in electronic form, <<http://it.iucr.org>>.

In this book it is shown that symmetry relations between the space groups are a useful tool for the clear derivation and the concise presentation of facts in the field of crystal chemistry. The presented examples will speak for themselves. However, it should be mentioned why the abstract framework of group theory is so successful: it is due to the so-called symmetry principle in crystal chemistry.

1.1 The symmetry principle in crystal chemistry

The symmetry principle is an old principle based on experience that has been worded during its long history in rather different ways, such that a common root is hardly discernible at first glance (see Chapter 19 for the historical development). In view of crystal chemistry, BÄRNIGHAUSEN summarized the symmetry principle in the following way, pointing out three important partial aspects [12]:

- (1) In crystal structures the arrangement of atoms reveals a pronounced tendency towards the highest possible symmetry.
- (2) Counteracting factors due to special properties of the atoms or atom aggregates may prevent the attainment of the highest possible symmetry. However, in many cases the deviations from ideal symmetry are only small (key word: *pseudosymmetry*).
- (3) During phase transitions and solid-state reactions which result in products of lower symmetry, the higher symmetry of the starting material is often indirectly preserved by the formation of oriented domains.

Aspect 1 is due to the tendency of atoms of the same kind to occupy equivalent positions in a crystal, as stated by BRUNNER [30]. This has physical reasons:

Depending on the given conditions, such as chemical composition, the kind of chemical bonding, electron configurations of the atoms, relative size of the atoms, pressure, temperature, etc., there exists *one* energetically most favourable surrounding for atoms of a given species that all of these atoms strive to attain. The same surrounding of atoms in a crystal is ensured only if they are symmetry equivalent.

Aspect 2 of the symmetry principle is exploited extensively in Part II of this book. Factors that counteract the attainment of the highest symmetry include:

- stereochemically active lone electron pairs;
- distortions caused by the Jahn–Teller effect;
- Peierls distortions;
- covalent bonds, hydrogen bonds and other bonding interactions between atoms;
- electronic effects between atoms, such as spin interactions;
- ordering of atoms in a disordered structure;
- freezing (condensation) of lattice vibrations (soft modes) giving rise to phase transitions;
- ordered occupancy of originally equivalent sites by different kinds of atoms (substitution derivatives);
- partial vacation of atomic positions;
- partial occupancy of voids in a packing of atoms.

Aspect 3 of the symmetry principle has its origin in an observation by J. D. BERNAL. He noted that in the solid-state reaction $\text{Mn}(\text{OH})_2 \rightarrow \text{MnOOH} \rightarrow \text{MnO}_2$ the initial and the product crystal had the same orientation [31]. Such reactions are called *topotactic reactions* after F. K. LOTGERING [32] (for a more exact definition see [33]). In a paper by J. D. BERNAL and A. L. MACKAY we find the sentences [34]:

‘One of the controlling factors of topotactic reactions is, of course, symmetry. This can be treated at various levels of sophistication, ranging from Lyubarskii’s to ours, where we find that the simple concept of Buridan’s ass illumines most cases.’

According to the metaphor ascribed to the French philosopher JEAN BURIDAN (died *circa* 1358), the ass starves to death between two equal and equidistant piles of hay because it cannot decide between them. Referred to crystals, such asinine behaviour would correspond to an absence of phase transitions or solid-state reactions if there are two or more energetically equivalent orientations of the domains of the product. Crystals, of course, do not behave like the ass; they take both.

1.2 Introductory examples

To get an impression for the kind of considerations that will be treated in more detail in later chapters, we present a few simple examples. Many crystal structures can be related to a few simple, highly symmetrical crystal-structure types. Zinc blende (sphalerite, ZnS) has the same structural principle as diamond; alternating zinc and sulfur atoms take the positions of the carbon atoms. Both structures have the same kind of cubic unit cell, the atoms in the cell occupy the same positions, and they are bonded with one another in the same way. Whereas all atoms in diamond are symmetrically equivalent, there must be two symmetrically independent atomic positions in zinc blende, one for zinc and one for sulfur. Zinc blende cannot have the same symmetry as diamond; its space group is a subgroup of the space group of diamond. The relation is depicted in Fig. 1.1 in a way that we will make use of in later chapters and which is explained more exactly in Chapter 10.

In Fig. 1.1 a small ‘family tree’ is shown to the left; at its top the symmetry of diamond is mentioned, marked by the symbol of its space group $F4_1/d\bar{3}2/m$. An arrow pointing downwards indicates the symmetry reduction to a subgroup. The subgroup has the space-group symbol $F\bar{4}3m$; it has a reduced number of symmetry operations. In particular, no symmetry operation of diamond may be

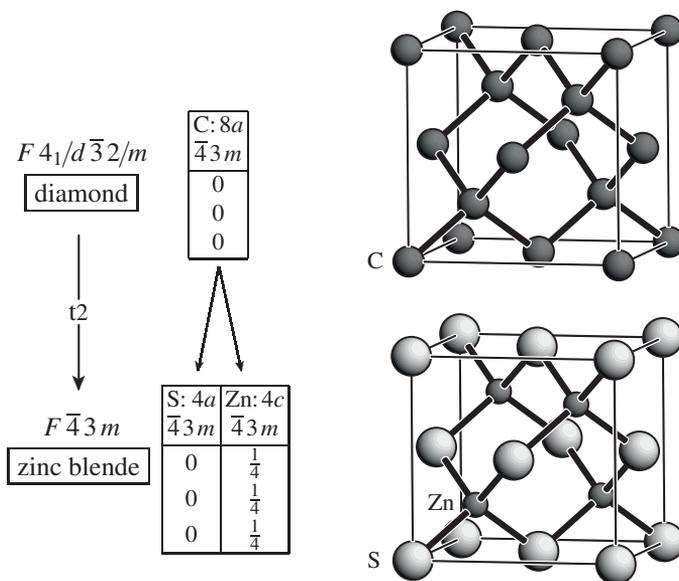


Fig. 1.1 The relation between diamond and zinc blende. The numbers in the boxes are the atomic coordinates.

retained that would convert a zinc position to a sulfur position. The *multiplicity* of the C atoms in diamond is 8, i.e. the unit cell of diamond contains eight symmetrically equivalent C atoms. Their position is expressed by the *Wyckoff symbol* 8a. The 8 marks this multiplicity, and the a is an alphabetical label according to which the positions are numbered in *International Tables A* [13]. Due to the symmetry reduction this position 8a splits into two independent positions 4a and 4c in the subgroup. The point symmetry of the mentioned atomic positions remains tetrahedral, symbol $\bar{4}3m$.

The ‘family tree’ in Fig. 1.1 is rather small; it comprises only one ‘mother’ and one ‘daughter’. As will be shown later, larger ‘family trees’ can be used to depict relations among numerous crystal structures, with many ‘daughters’ and ‘grandchildren’. This notion harmonizes with the term *family of structures* in the rather strict sense according to H. D. MEGAW [35]. For the most symmetrical structure in the family of structures MEGAW coined the term *aristotype*.¹ The derived structures are called, again after MEGAW, *hettotypes*.² These terms correspond to the terms *basic structure* and *derivative structure* after BUERGER [36, 37].

¹greek *aristos* = the best, the highest

²greek *hetto* = weaker, inferior

Trees of group–subgroup relations as shown in Fig. 1.1 are called *Bärnig-hausen trees*.

In reality it is impossible to substitute Zn and S atoms for C atoms in a diamond crystal. The substitution takes place only in one’s imagination. Nevertheless, this kind of approach is very helpful to trace back the large number of known structures to a few simple and well-known structure types and to thus obtain a general view.

On the other hand, the case that the symmetry reduction actually takes place in a sample does occur, namely in phase transitions as well as in chemical reactions in the solid state. An example is the phase transition of CaCl₂ that takes place at 217 °C [38–40]. It involves a mutual rotation of the coordination octahedra about *c*, which is expressed by slightly altered atomic coordinates of the Cl atoms (Fig. 1.2). Contrary to the diamond–zinc blende relation, the calcium as well as the chlorine atoms remain symmetry equivalent; no atomic position splits into several independent positions. Instead, their point symmetries are reduced. Phase transitions of this kind are linked to changes of the physical properties that depend on crystal symmetry. For example, CaCl₂ is ferroelastic at temperatures below 217 °C.³

³Ferroelastic: The domains in a crystal differ in spontaneous strain and can be shifted by a mechanical force.

In the literature in physics the aristotype is often called the *prototype* or *parent phase*, and the hettotype the *daughter phase* or *distorted structure*. These terms are only applicable to phase transitions, i.e. to processes in which one solid phase is converted to another one with the same chemical composition, with a change of symmetry.

Calcium chloride forms twinned crystals in the course of the phase transition from the high- to the low-temperature modification. The reason for this can be perceived in the images of the structures in Fig. 1.2. If the octahedron in the middle of the cell is rotated clockwise (as depicted), the tetragonal high-temperature form ($a = b$) transforms to the orthorhombic low-temperature form with decreased *a* and increased *b* axis. The same structure is obtained by counter-clockwise rotation, but with an increased *a* and a decreased *b* axis (Fig. 1.3). In the initial tetragonal crystal the formation of the orthorhombic

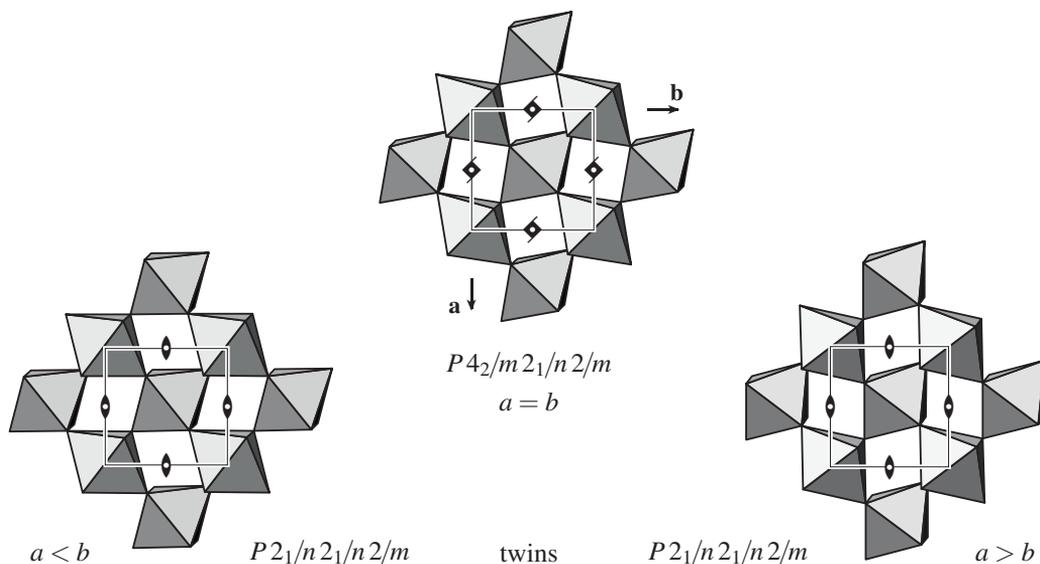
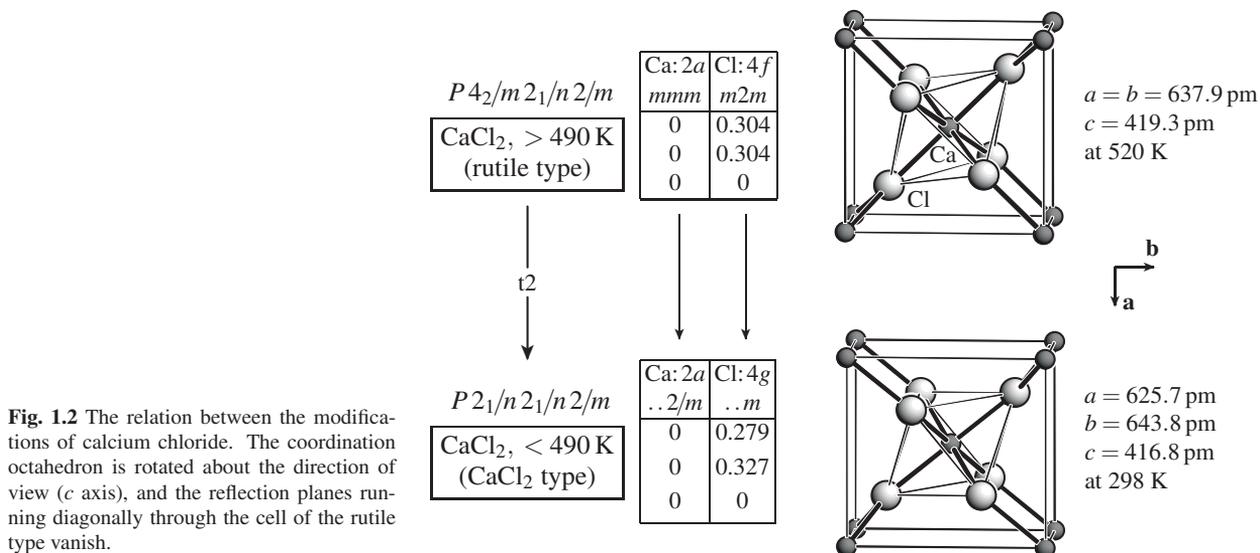


Fig. 1.3 The orientation of the coordination octahedra in the modifications of CaCl_2 and the relative orientation of the unit cells of the twin domains of the low-temperature modification. The marked fourfold axes of the tetragonal modification are converted to twofold axes in the orthorhombic modification.

crystals sets in in different regions, statistically with the one or the other orientation. At the end the whole crystal consists of intergrown twin domains. The symmetry elements being lost during the phase transition, for example the reflection planes running diagonally through the cell of the high-temperature form, are indirectly preserved by the relative orientation of the twin domains. More details concerning this phase transition are dealt with in Chapter 15; there it is also explained that the kind of group-subgroup relation immediately shows that the formation of twinned crystals is to be expected in this case.

The occurrence of twinned crystals is a widespread phenomenon. They can severely hamper crystal-structure determination. Their existence cannot al-

ways be detected on X-ray diffraction diagrams, and systematic superposition of X-ray reflections can cause the deduction of a false space group and even a false unit cell. In spite of the false space group, often a seemingly plausible structural model can be obtained, which may even be refined. Unfortunately, faulty crystal-structure determinations are not uncommon, and undetected twins are one of the causes. The most common consequences are slight to severe errors of interatomic distances; but even wrong coordination numbers and polyhedra up to a false chemical composition may be the result. Applications that rely on certain physical properties such as the piezoelectric effect can be impeded if twinned crystals are employed. Knowledge of the group-theoretical relations can help to avoid such errors.

Another kind of phase transformation occurs when statistically distributed atoms become ordered. This is a common observation among intermetallic compounds, but it is not restricted to this class of substances. Cu_3Au offers an example. Above 390°C the copper and gold atoms are statistically distributed among all atomic positions of a face-centred cubic packing of spheres (space group $F4/m\bar{3}2/m$; Fig. 1.4). Upon cooling an ordering process sets in; the Au atoms now take the vertices of the unit cell whereas the Cu atoms take the centres of the faces. This is a symmetry reduction because the unit cell is no longer centred. The F of the space group symbol, meaning face-centred, is replaced by a P for primitive (space group $P4/m\bar{3}2/m$).

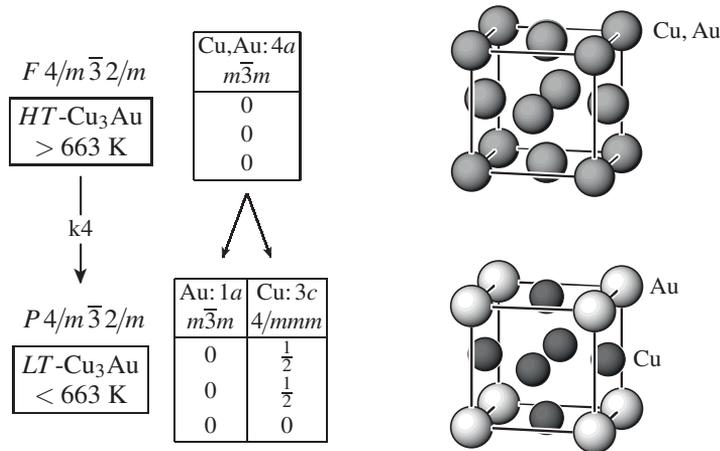


Fig. 1.4 The relation between misordered and ordered Cu_3Au . See margin note No. 2 in Section 15.1.2 (page 199) for a remark referring to the term 'misorder'.

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Part I

**Crystallographic
Foundations**

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Basics of crystallography, part 1

2

2.1 Introductory remarks

Matter consists of atoms of diverse elements. These atoms do not occur as isolated particles, but in organized arrays: Finite arrays of interest are *molecules* (N_2 , H_2O , CH_4 , NH_3 , C_6H_6 , ...); large arrays are *crystals* that consist of equal parts that are periodically repeated in (nearly) any number.

Molecules and crystals are two kinds of appearance of matter. Molecules can assemble to crystals. However, crystals do not necessarily consist of molecules; the crystal components may be simple ions like Na^+ and Cl^- , complex ions like CO_3^{2-} and NH_4^+ , and many others. Henceforth, molecules and other such components will be called building blocks if they are components of crystals.

Other forms of appearance of matter, such as gases, liquids, glasses, partially ordered structures, modulated structures, or quasicrystals will not be considered.

2.2 Crystals and lattices

Crystals are distinguished by the property that a shift called *translation* results in a perfect superposition of all building blocks of the crystal.

Naturally occurring crystals (quartz, rock salt, garnet, ...) and synthetically produced crystals (sugar, SrTiO_3 , silicon, ...) can be regarded as finite blocks from infinite periodic structures. Replacement of the finite real crystal by the corresponding periodic, infinite array usually allows an excellent description of the real conditions and, therefore, is of great value, even though the infinitely extended ideal crystal does not exist. The *crystal structure* is the spatial distribution of the atoms in a crystal; usually, it is described with the model of the infinite crystal pattern. Hereafter, when we address a crystal structure, we always assume this kind of description.

Definition 2.1 The infinite, three-dimensional periodic array corresponding to a crystal is called the *crystal pattern* (or infinite ideal crystal). The lengths of the periodicities of this array may not be arbitrarily small.

The periodicity of a crystal structure implies that it comes to coincidence with itself after having been shifted in certain directions by certain distances.

2.1 Introductory remarks	11
2.2 Crystals and lattices	11
2.3 Appropriate coordinate systems, crystal coordinates	13
2.4 Lattice directions, net planes, and reciprocal lattice	15
2.5 Calculation of distances and angles	16

¹Only the patterns are two dimensional; tilings, brick walls, etc. themselves are three-dimensional bodies; their symmetries are layer groups (Section 7.4).

The dimension $d = 3$ can be generalized to $d = 1, 2, 3, \dots$. This way, planar arrangements ($d = 2$) can be included: periodic patterns of wall paper, tilings, brick walls, tiled roofs,¹ cross-sections and projections of three-dimensional crystals, etc. Dimensions $d = 4, 5, 6, \dots$ serve to formally describe incommensurate crystal structures and quasicrystals in higher-dimensional spaces ('superspaces').

The condition that periodicity lengths may not be arbitrarily small excludes homogeneous continua among crystal structures. Due to the finite size of the building blocks in real crystals there always exists a lower limit of the periodicity distances (>0.1 nanometres).

The building blocks of the crystal structure may not only be points, figures, tiles, atoms, molecules, ions, etc., but also continuous functions such as electron density.

A *macroscopic (ideal) crystal* is a finite block out of a crystal pattern. Macroscopic crystals do not really exist. A *real crystal* not only has, like the macroscopic (ideal) crystal, a finite size, but is also defective. In addition, the atoms are not located at the exact positions like in the macroscopic crystal, but perform vibrational motions about these positions. The periodic pattern of atoms of the macroscopic crystal is fulfilled only by the positions of equilibrium of the vibrations.

Definition 2.2 A shift which brings a crystal structure to superposition with itself is called a *symmetry translation* (or simply *translation*) of this crystal structure. The corresponding shift vector is a *translation vector*.

Due to the periodicity, all integral multiples of a translation vector are also translation vectors. With two non-parallel translation vectors \mathbf{t}_1 and \mathbf{t}_2 all integral linear combinations are translation vectors:

$$\mathbf{t} = q\mathbf{t}_1 + r\mathbf{t}_2 \quad q, r = \text{integers}$$

Definition 2.3 The infinite set of all translation vectors \mathbf{t}_i of a crystal pattern is its *vector lattice* \mathbf{T} . The translation vectors are called *lattice vectors*.

The vector lattice is often simply called the *lattice*. In chemistry (not in crystallography) the expression 'crystal lattice' is common. Frequently, the term 'lattice' has been used as a synonym for 'structure' (e.g. diamond lattice instead of diamond structure). Here we distinguish, as in *International Tables*, between 'lattice' and 'structure', and 'lattice' is something different from 'point lattice' and 'particle lattice', as defined in the next paragraph.² Two-dimensional lattices are sometimes called *nets* in crystallography (not in chemistry).

The vector lattice \mathbf{T} of a crystal structure is an infinite set of vectors \mathbf{t}_i . With the aid of the vector lattice \mathbf{T} it is possible to construct other more expressive lattices. Choose a starting point X_o with the positional vector \mathbf{x}_o (vector pointing from a selected origin to X_o). The endpoints X_i of all vectors $\mathbf{x}_i = \mathbf{x}_o + \mathbf{t}_i$ make up the *point lattice* belonging to X_o and \mathbf{T} . The points of the point lattice have a periodic order, they are all equal and they all have the same surroundings. If the centres of gravity of particles are situated at the points of a point lattice, this is a *particle lattice*. All particles of the particle lattice are of the same kind.

²The terms 'lattice' and 'structure' should not be mixed up either. Do not say 'lattice structure' when you mean a framework structure consisting of atoms linked in three dimensions.

An infinity of point lattices exists for every (vector) lattice, because any arbitrary starting point X_o can be combined with the lattice vectors \mathbf{t}_i . The lattice vectors may not be arbitrarily short according to Definition 2.1.

Definition 2.4 Points or particles that are transferred one to the other by a translation of the crystal structure are called *translation equivalent*.

Avoid terms like ‘identical points’, which can often be found in the literature, when ‘translation-equivalent points’ are meant. Identical means ‘the very same’. Two translation-equivalent points are equal, but they are not the very same point.

2.3 Appropriate coordinate systems, crystal coordinates

To describe the geometric facts in space analytically, one introduces a coordinate system, consisting of an origin and a *basis* of three linearly independent, i.e. not coplanar *basis vectors* $\mathbf{a}, \mathbf{b}, \mathbf{c}$ or $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$. Referred to this coordinate system, each point in space can be specified by three coordinates (a coordinate triplet). The origin has the coordinates 0,0,0. An arbitrary point P has coordinates x, y, z or x_1, x_2, x_3 , the vector \vec{OP} (the position vector) being:

$$\vec{OP} = \mathbf{x} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c} = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3$$

In the plane, points P have coordinates x, y or x_1, x_2 referred to an origin (0, 0) and the basis \mathbf{a}, \mathbf{b} or $\mathbf{a}_1, \mathbf{a}_2$.

Often a *Cartesian coordinate system* is suitable, in which the basis vectors are mutually perpendicular and have the length of 1 (*orthonormal basis*). Commonly, the angles between \mathbf{a}, \mathbf{b} , and \mathbf{c} are denominated by α (between \mathbf{b} and \mathbf{c}), β (between \mathbf{c} and \mathbf{a}), and γ (between \mathbf{a} and \mathbf{b}) or correspondingly by $\alpha_1, \alpha_2, \alpha_3$. With an orthonormal basis we then have

$$a = |\mathbf{a}| = b = |\mathbf{b}| = c = |\mathbf{c}| = 1; \quad \alpha = \beta = \gamma = 90^\circ$$

or $|\mathbf{a}_i| = 1$ and angles $(\mathbf{a}_i, \mathbf{a}_k) = 90^\circ$ for $i, k = 1, 2, 3$ and $i \neq k$.

Generally, as far as the description of crystals is concerned, Cartesian coordinate systems are not the most convenient. For crystallographic purposes, it is more convenient to use a coordinate system that is adapted to the periodic structure of a crystal. Therefore, lattice vectors are chosen as basis vectors. With any other basis the description of the lattice of a crystal structure would be more complicated.

Definition 2.5 A basis which consists of three lattice vectors of a crystal pattern is called a *crystallographic basis* or a *lattice basis* of this crystal structure.³

Referred to a crystallographic basis, each lattice vector $\mathbf{t} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2 + t_3\mathbf{a}_3$ is a linear combination of the basis vectors with *rational coefficients* t_i . Every vector with *integral* t_i is a lattice vector. One can even select bases such that the coefficients of all lattice vectors are integers.

³The term ‘basis’ was used erstwhile with another meaning, namely in the sense of ‘cell contents’.

Among the infinity of crystallographic bases of a crystal structure, some permit a particularly simple description and thus have turned out to be the most convenient. Such bases are the foundation for the description of the space groups in *International Tables A*. These bases are selected whenever there is no special reason for another choice.

Definition 2.6 The crystallographic bases used in *International Tables A* are called *conventional bases*.

Definition 2.7 A crystallographic basis $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ of a vector lattice is called a *primitive (crystallographic) basis* if its basis vectors are lattice vectors and if every lattice vector \mathbf{t} can be expressed as a linear combination with *integral* coefficients t_i :

$$\mathbf{t} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2 + t_3\mathbf{a}_3 \quad (2.1)$$

For any vector lattice there exist an infinite number of primitive bases.

One could always choose a primitive basis. However, this would not be convenient for many applications. Therefore, the chosen conventional crystallographic basis is often not primitive, but such that as many as possible of the angles between the basis vectors amount to 90° ; the coefficients t_i in eqn (2.1) can then also be certain fractional numbers (mostly multiples of $\frac{1}{2}$). Frequently, the lattice is called primitive if the conventional basis of the lattice is primitive; if it is not primitive, it is called a *centred lattice*, or one says ‘*the setting is centred*’.⁴ Well-known examples are the face-centred cubic lattice *cF* as in the cubic-closest packing of spheres (copper type) and the body-centred cubic lattice *cI* of the tungsten type. Lattice types are treated in Section 6.2.

After having selected a crystallographic basis and an origin, it is easy to describe a crystal structure. To this end one defines:

Definition 2.8 The parallelepiped in which the coordinates of all points are

$$0 \leq x, y, z < 1$$

is called a *unit cell* of the crystal structure.

The selection of a basis and an origin implies the selection of a unit cell. Every point in this unit cell has three coordinates $0 \leq x, y, z < 1$. By addition or subtraction of integral numbers to the coordinates one obtains the coordinates of translation-equivalent points which are located in other cells. The transformation of numerical values to values $0 \leq x, y, z < 1$ is called *standardization*. We can now construct a crystal structure in two different ways:

- (1) One takes a unit cell and adds or subtracts integral numbers to the coordinates of its contents. This corresponds to a shift of the unit cell by lattice vectors. In this way the complete crystal structure is built up systematically by joining (an infinity of) blocks, all with the same contents.
- (2) One takes the centre of gravity of a particle in the unit cell and adds equal particles in the points of the corresponding (infinite) point lattice. If there are more particles to be considered, one takes the centre of gravity of one of the remaining particles together with its point lattice, etc. Due to the minimum distances between particles in the finite size of the cell,

⁴For the sake of precise terminology, the term ‘centred’ should not be misused with a different meaning; do not call a cluster of atoms a ‘centred cluster’ if you mean a cluster of atoms with an embedded atom, nor say, ‘the F_6 octahedron of the PF_6^- ion is centred by the P atom’.

the number of particles to be considered is finite. In this way one obtains a finite number of interlaced particle lattices that make up the crystal structure.

In the first case, the structure is composed of an infinity of finite cells. In the second case, the structure is composed by interlacing a finite number of particle lattices which have an infinite extension. Both kinds of composition are useful. A third kind of composition is presented in Section 6.5 on page 82.

A crystal structure can now easily be described completely by specifying the metrics of the unit cell (lengths of the basis vectors and the angles between them) and the contents of the cell (kind of particles and their coordinates within one unit cell).

In order to be able to compare different or similar structures, their descriptions have to refer to equal or similar cells. The conditions for conventional cell choices are often not sufficient to warrant this. Methods to obtain a uniquely defined cell from an arbitrarily chosen cell are called reduction methods. Common methods are:

- (1) derivation of the *reduced cell*, see Section 8.4 (page 110) and *International Tables A*, Chapter 9.2 [13];
- (2) the Delaunay reduction, see *Zeitschrift für Kristallographie* **84** (1933) page 109; *International Tables for X-ray Crystallography*, Volume I (1952), pages 530–535 [24].

The cells obtained by these methods may or may not be identical. Therefore, the method of reduction should be specified.

The geometric invariants of a crystal structure, for example, the distances between particles and the bond angles, are independent of the chosen coordinate system (basis and origin). How atoms are bonded with each other is manifested in these quantities. In addition, these data are useful for the direct comparison of different particles in the same crystal structure or of corresponding particles in different crystal structures.

2.4 Lattice directions, net planes, and reciprocal lattice

A *lattice direction* is the direction parallel to a lattice vector \mathbf{t} . It is designated by the symbol $[uvw]$, u, v, w being the smallest integral coefficients of the lattice vector in this direction; u, v , and w have no common divisor. $[100]$, $[010]$ and $[001]$ correspond to the directions of \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 , respectively; $[\bar{1}10]$ is the direction of the vector $-\mathbf{a}_1 + \mathbf{a}_2$.

A net plane running through points of a point lattice is one out of a set of equidistant, parallel planes. The net plane is designated by the symbol (hkl) in parentheses; h, k, l are the integral *Miller indices*. From the set of planes, that one is selected which is closest to the origin without running itself through the origin. It intersects the coordinate axes at distances of a_1/h , a_2/k , a_3/l from the origin (Fig. 2.1). A plane running parallel to a basis vector obtains a 0 for this direction.

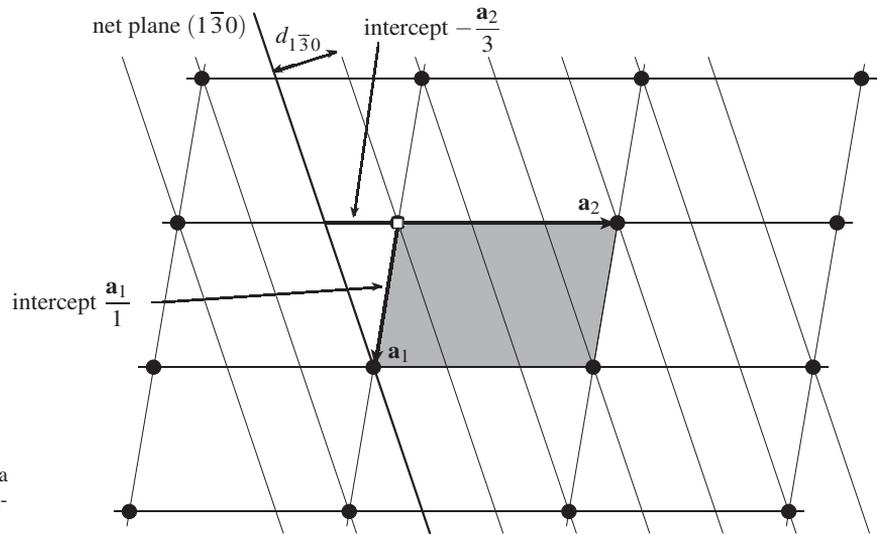


Fig. 2.1 A set of planes running through a point lattice. The third basis vector is perpendicular to the plane of the paper.

In order to facilitate the calculus with planes, it is convenient to represent each set of net planes by a vector $\mathbf{t}_{hkl}^* = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^*$ in the reciprocal lattice. The *reciprocal lattice* \mathbf{T}^* is a vector lattice with the reciprocal basis vectors $\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*$ (or $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$). \mathbf{t}_{hkl}^* is perpendicular to the net plane (hkl) and has the length $1/d_{hkl}$, d_{hkl} being the interplanar distance between neighbouring net planes. For more details see textbooks of crystal-structure analysis (e.g. [41–44]).

2.5 Calculation of distances and angles

Crystallographic bases are convenient for a simple description of crystals. However, the formulae for the computation of distances and angles in the crystal structure become less practical than with Cartesian coordinates.

Definition 2.9 The lengths a, b, c of the basis vectors and the angles α, β, γ between them are called the *lattice constants* or (better) the *lattice parameters* of the lattice.

Let Q and R be two points in a crystal structure having the coordinates x_q, y_q, z_q and x_r, y_r, z_r . Then the distance r_{qr} between Q and R is equal to the length of the vector $\mathbf{x}_r - \mathbf{x}_q = \overrightarrow{QR}$, where \mathbf{x}_q and \mathbf{x}_r are the position vectors (vectors from the origin) of Q and R . The length r_{qr} is the root of the scalar product of $\mathbf{x}_r - \mathbf{x}_q$ with itself:

$$\begin{aligned} r_{qr}^2 &= (\mathbf{x}_r - \mathbf{x}_q)^2 = [(x_r - x_q)\mathbf{a} + (y_r - y_q)\mathbf{b} + (z_r - z_q)\mathbf{c}]^2 \\ &= (x_r - x_q)^2 a^2 + (y_r - y_q)^2 b^2 + (z_r - z_q)^2 c^2 + 2(x_r - x_q)(y_r - y_q)ab \cos \gamma \\ &\quad + 2(z_r - z_q)(x_r - x_q)ac \cos \beta + 2(y_r - y_q)(z_r - z_q)bc \cos \alpha \end{aligned}$$

The (bond) angle ψ at the apex P between the connecting lines PQ and PR (Fig. 2.2) can be calculated with the following formula, using the scalar

product of the vectors $(\mathbf{x}_q - \mathbf{x}_p)$ and $(\mathbf{x}_r - \mathbf{x}_p)$ (\mathbf{x}_p is the position vector of P):

$$\begin{aligned} (\mathbf{x}_q - \mathbf{x}_p) \cdot (\mathbf{x}_r - \mathbf{x}_p) &= r_{pq} r_{pr} \cos \psi \\ &= (x_q - x_p)(x_r - x_p)a^2 + (y_q - y_p)(y_r - y_p)b^2 + (z_q - z_p)(z_r - z_p)c^2 \\ &\quad + [(x_q - x_p)(y_r - y_p) + (y_q - y_p)(x_r - x_p)] ab \cos \gamma \\ &\quad + [(z_q - z_p)(x_r - x_p) + (x_q - x_p)(z_r - z_p)] ac \cos \beta \\ &\quad + [(y_q - y_p)(z_r - z_p) + (z_q - z_p)(y_r - y_p)] bc \cos \alpha \end{aligned}$$

Every angle $\alpha_j = 90^\circ$ strongly simplifies the formula. This is an advantage of an orthonormal basis; for this reason it is commonly used in crystal physics. The simplified formula then is ($e =$ unit of length of the basis, e.g. $e = 1$ pm):

$$\begin{aligned} r_{qr}^2 &= [(x_r - x_q)^2 + (y_r - y_q)^2 + (z_r - z_q)^2] e^2 \\ \cos \psi &= r_{pq}^{-1} r_{pr}^{-1} [(x_q - x_p)(x_r - x_p) + (y_q - y_p)(y_r - y_p) + (z_q - z_p)(z_r - z_p)] e^2 \end{aligned}$$

The volume V of the unit cell is obtained from the formula:

$$V^2 = a^2 b^2 c^2 (1 + 2 \cos \alpha \cos \beta \cos \gamma - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma)$$

The lattice parameters $a, b, c, \alpha, \beta, \gamma$ appear in the combinations $g_{ii} = a_i^2$ or $g_{ik} = \mathbf{a}_i \cdot \mathbf{a}_k = a_i a_k \cos \alpha_j$, $i \neq j \neq k \neq i$.

For calculations, the specification of the shape of the cell by the g_{ik} values is more important than the usually quoted lattice parameters a_i and α_j , since the g_{ik} are needed for all calculations. From the a_i and α_j one can calculate all g_{ik} , conversely from the g_{ik} the a_i and α_j .

Definition 2.10 The complete set of the coefficients g_{ik} is called the *metric tensor*, formulated in the following way:

$$\mathbf{G} = \begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix} = \begin{pmatrix} a^2 & abc \cos \gamma & ac \cos \beta \\ ab \cos \gamma & b^2 & bc \cos \alpha \\ ac \cos \beta & bc \cos \alpha & c^2 \end{pmatrix}$$

$g_{ik} = g_{ki}$ holds, since $\mathbf{a}_i \cdot \mathbf{a}_k = \mathbf{a}_k \cdot \mathbf{a}_i$.

With p_i, q_i , and r_i , $i = 1, 2, 3$, as the coordinates of the points P, Q , and R one obtains the formulae:

- Distance $QR = r_{qr}$:
$$r_{qr}^2 = \sum_{i,k} g_{ik} (r_i - q_i)(r_k - q_k) \quad (2.2)$$

- Distance from the origin O : $OQ = r_q$;
$$r_q^2 = \sum_{i,k} g_{ik} q_i q_k$$

- Angle QPR (apex P):

$$\cos(QPR) = (r_{pq})^{-1} (r_{pr})^{-1} \sum_{i,k} g_{ik} (q_i - p_i)(r_k - p_k) \quad (2.3)$$

- Volume V of the unit cell:
$$V^2 = \det(\mathbf{G}) \quad (2.4)$$

Application of \mathbf{G} with the independent quantities g_{ik} instead of the six lattice parameters $a, b, c, \alpha, \beta, \gamma$ has the advantage that the g_{ik} are more homogeneous; for example, they all have the same unit \AA^2 or pm^2 .

The importance of the metric tensor \mathbf{G} is not restricted to the calculation of distances and angles:

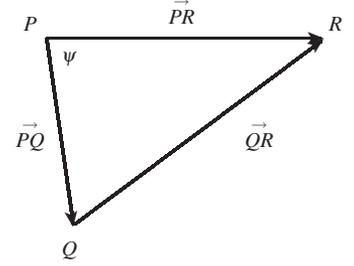


Fig. 2.2 Triangle of the points P, Q , and R with distances PQ, PR , and QR and angle ψ .

- With the aid of \mathbf{G} one can decide whether a given affine mapping leaves invariant all distances and angles, i.e. whether it is an isometry, see Section 3.5.
- If \mathbf{T}^* is the reciprocal lattice of the lattice \mathbf{T} , then $\mathbf{G}^*(\mathbf{T}^*) = \mathbf{G}^{-1}(\mathbf{T})$ is the inverse matrix of \mathbf{G} : The metric tensors of the lattice and the reciprocal lattice are mutually inverse.