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Introduction

Research in many areas of materials science requires a thorough knowledge of crystalline solid-state systems on an atomic scale. These systems may represent real materials such as complex semiconductors or may act as meaningful models, for example, simulating reactive sites of catalysts. Here, physical and chemical insight depends very much on details of the geometry of local environments around atoms and of possible periodic atom arrangements inside the crystal and at its surface. As examples we mention that

- *chemical binding* between atoms inside a crystal and at its surface strongly depends, apart from atomic parameters, on local geometry [1, 2]. This is very often expressed by local *coordination* describing the number and arrangement of nearest-neighbor atoms with respect to the binding atom. For example, metal atoms in a bulk metal crystal are usually characterized by a large number of nearest neighbors, 8 or 12, yielding metallic binding. At surfaces, the changed chemical binding due to different coordination, compared to that in the bulk, is closely connected with local geometry that can be expressed by relaxation and reconstruction. Furthermore, atoms or molecules can adsorb at specific sites of crystalline substrates, where the adsorption geometry is essential to an understanding of local binding behavior.
- *electronic* properties at surfaces of single crystals can differ substantially from those of the corresponding bulk. For example, the existence of a surface can induce additional electronic states, surface states, that have been found in experiments and studied theoretically some time ago [3]. Here, the detailed surface geometry determines both the existence and the energetic behavior of the states. Further, electronic interband transitions in silicon nanowires and nanodots are found to cause photoluminescence that does not occur in silicon bulk crystals [4]. The difference is explained by both the spatial confinement of the nanoparticles and the changed geometric properties of their atom arrangement. Finally, it has been claimed from experiment that semiconducting bulk silicon shows metallicity at its (7×7) reconstructed (1 1 1) surface [5], and metallicity is also found in theoretical studies on silicon nanowires [6].

- *magnetism* of crystalline bulk material and its surfaces depends on the crystal structure and local coordination. For example, vanadium sesquioxide (V_2O_3) in its monoclinic crystal structure at low temperatures is antiferromagnetic, whereas its high-temperature phase is described by a trigonal corundum lattice and is paramagnetic [7]. Vanadium crystals with a body-centered cubic lattice are found to be paramagnetic in their bulk volume but ferromagnetic at their surfaces [8]. Other examples are thin iron films grown on top of copper single crystal surfaces where, as a function of film thickness, their crystal geometry changes and, as a consequence, so do their magnetic properties [9].
- *anisotropic electrical conductivity* is often connected with dense atom packing along specific directions inside crystals. An example is given by trigonal $LiCoO_2$ crystals that form the most common lithium storage material for rechargeable batteries. Here, the electrical conductivity is greatly enhanced along densely packed Co and Li planes while it is much smaller perpendicular to the planes [10].
- *catalytic surface reactions* depend crucially on geometric properties of the surfaces of crystalline catalyst materials [11, 12] and are needed for understanding the heterogeneous catalysis at an atomic scale. The atomic surface geometry determines possible adsorption and reaction sites for molecules, which can support specific catalytic reactions but also can exclude others (structure–reactivity relationship [11]). For example, catalytic CO oxidation happens at single crystal surfaces of platinum with different efficiency depending on the surface orientation [13], where the surface geometry determines the type and density of reactive sites.

In addition to bulk crystals and their surfaces, crystalline *nanoparticles* [14, 15] have become a new exciting field of research. This includes nanotubes [16], nanowires [14], or compact particles of finite size, such as atom clusters [17], fullerenes [18], or quantum dots [19], which show novel physical and chemical properties deviating from those of corresponding bulk material. Examples are carbon nanotubes providing substrate material to yield new active catalysts [20] or silicon nanowires whose visible photoluminescence is determined by their size [21]. Furthermore, nanosize quantum dots at semiconductor surfaces are found to yield quite powerful light emitting diodes (LEDs) of technological relevance [19].

These nanosystems are described as *atom aggregates* of finite size in one or more dimensions, where their local geometric arrangement can still be close to that of extended bulk crystals. Likewise, their spatial confinement with corresponding surfaces and interfaces can be considered analogous to that appearing at bulk crystal surfaces. Therefore, surface crystallography, initially developed to describe geometric properties at single crystal surfaces, also forms a sound basis for characterizing geometry of nanoparticle surfaces. This is particularly interesting since the relative number of atoms positioned at nanoparticle surfaces compared to those of their inner volume is always larger than that of extended macroscopic single crystals. Thus, atoms at *nanoparticle surfaces* are expected to play a more important role in determining physical properties than corresponding atoms at single crystal surfaces. In addition, nanoparticles can possess symmetry and geometric properties that do not

appear in single crystals or at their surfaces. Examples are curved nanoparticle surfaces that originate from bending single crystal sections, where in this book *nanotubes* will be discussed as examples.

In many experimental and theoretical studies, real crystalline systems are, for the sake of simplicity, approximately described by *ideal single crystals* with a well-defined atomic composition and an unperturbed three-dimensional periodicity. In addition, surfaces of the single crystals are assumed to be bulk-terminated and of unperturbed two-dimensional periodicity. With this approximation in mind, a rigorous mathematical description of all geometric parameters becomes possible and is one of the basic subjects of classical crystallography. As an illustration, Figure 1.1 shows the geometry of a section of an ideal single crystal of magnesium oxide (MgO) with its perfect three-dimensional periodic arrangement of atoms. Here, sections of ideal planar surfaces, originating from bulk truncation, become visible and demonstrate the variety of surface types for the same crystal depending on the crystal cut.

In this book, we will discuss basic elements and *mathematical methods* used in crystallography to evaluate geometric parameters of single crystals with particular emphasis on their surfaces. We start with ideal bulk crystals of three-dimensional periodicity, where classical bulk crystallography provides a quantitative description. Then, we introduce ideal two-dimensional surfaces as a result of bulk truncation along specific directions including high-density, vicinal, stepped, kinked, and chiral surfaces. We give a detailed account of their two-dimensional symmetry behavior following the crystallographic classification scheme of Bravais lattices and two-
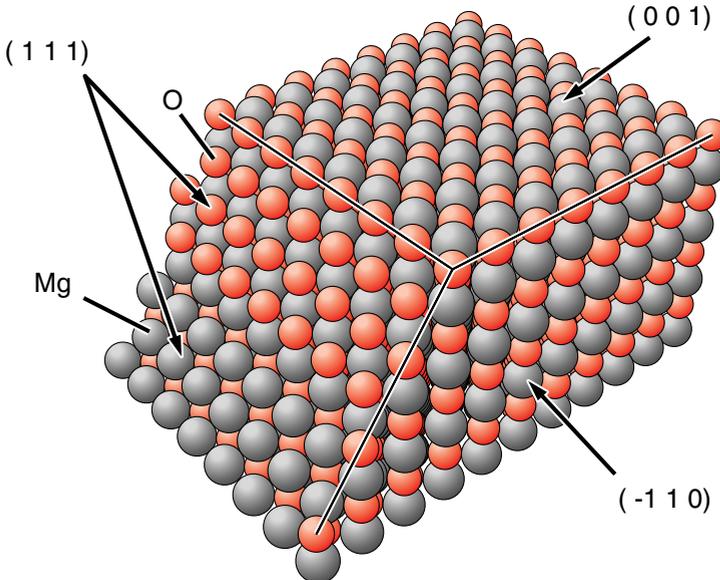
Figure 1.1 Section of an MgO crystal (NaCl lattice). The atoms are shown as colored balls and labeled accordingly. The section is enclosed by nonpolar (0 0 1), (−1 1 0) and by polar (1 1 1) oriented surfaces.

dimensional space groups. Next, we discuss in detail the deviation of atom geometry at surfaces due to changed surface binding compared to the bulk. This is usually described by surface relaxation and reconstruction, where we consider different schemes. After that, we mention crystallographic aspects of commensurate and incommensurate adsorbate systems as special cases of surface reconstruction, where the different notations used in the literature will also be described. The discussion of surface structure will be completed by an overview of the surfaces that have been analyzed quantitatively at an atomic level in scattering, diffraction, imaging, or spectroscopic experiments. Finally, we describe theoretical aspects and structural details of nanotubes of different element composition as special cases of rolled sections of crystal monolayers. These nanotubes are examples of a larger class of crystalline materials, nanoparticles, and demonstrate that crystallographic methods can also be applied to these systems in order to account for their geometric properties. The book concludes with appendices providing details of the mathematical methods used in different chapters.

The theoretical concepts treated in this book will be illustrated by example applications for further understanding, which include results from *measured* real single crystal surfaces that are documented in the NIST Surface Structure Database (SSD) [22–24] or its earlier version SCIS (Surface Crystallographic Information Service) [25]. In addition, each chapter of the book concludes with a set of *exercises*. These exercises are of varying difficulty, ranging from simple problems to small research projects, and are meant to stimulate questions and answers about the different subjects. Some of the exercises may require a *visualization tool* for crystals, such as Balsac [26], or Survis, the visualization part of the SSDIN package [27] or the like.

For the theoretical treatment of some geometric properties of ideal single crystals, we will apply *number theoretical methods*, dealing with relations between integer numbers. While this approach is not commonly used in textbooks on surface science or crystallography, it can considerably simplify the formal treatment. Examples are solutions of linear and quadratic Diophantine equations that facilitate the discussion of netplanes or of atom neighbor shells in crystals. Therefore, number theoretical methods will be introduced briefly as required, and further details are provided in Appendix C.

A few illustrations are included as *stereo pictures* for an enhanced three-dimensional impression. These pictures may be viewed by either using optical stereo glasses (available separately) or by cross-eyed viewing without glasses. In the latter case, viewing for an extended time may overstrain the eyes and should be avoided.

Obviously, the present book cannot cover all aspects of the field and may, in some cases, be quite brief. Furthermore, the selection of topics, as well as their presentation, is, to some degree, determined by the author's personal preferences. However, the interested reader may consult the extensive crystallographic literature, for example, Refs. [28–32], or the solid-state physics literature, for example, Refs. [1, 2], to explore additional details.