# 1
Introduction

Research in many areas of materials science requires detailed knowledge about crystalline solids on an atomic scale. These systems may represent real materials such as complex semiconductors, or may act as meaningful models, for example, by simulating reactive sites of catalysts. Here, physical and chemical insight depends very much on the details of the geometric structure of local environments of atoms and of the possible periodic atom arrangements inside the crystal as well as at its surface. As examples we mention the following:

- *Chemical binding* between atoms inside a crystal but also at its surfaces depends, apart from atomic parameters, strongly on local geometry [1, 2]. This is very often expressed by local **coordination** that describes the number and arrangement of nearest neighbor atoms with respect to the binding atom. As an example, metal atoms inside a bulk metal crystal are usually characterized by a large number of nearest neighbors, 8 or 12, yielding metallic binding. At surfaces, the change in chemical binding due to different coordination, compared with that inside the bulk, is tightly connected with local structure, which can be expressed by relaxation and reconstruction. Further, atoms or molecules can adsorb at specific sites of crystalline substrates, where the adsorption geometry is essential for understanding their 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, so-called surface states, that have been found in experiments and studied theoretically for some time [3]. Here, the detailed surface structure determines the existence as well as 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 also by changes in geometric properties of their atom arrangement. Finally, it has been claimed from experiments 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 as well as of its surfaces depends on the crystal structure and local coordination. For example, vanadium sesquioxide, V_2O_3, in its monoclinic crystal structure is antiferromagnetic at low temperatures, whereas its high-temperature phase, described by a trigonal corundum lattice, 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 structure changes and, as a consequence, their magnetic properties [9].
- *Anisotropic electrical conductivity* is often connected with dense atom packing along specific directions inside a crystal. 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 structural properties of the surfaces of crystalline catalyst materials at an atomic scale [11, 12]. The atomic surface structure determines possible adsorption and reaction sites for molecules, which can support specific catalytic reactions but can also exclude others known as *structure−reactivity relationships* [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 structure determines the type and density of reactive sites.

In addition to bulk crystals and their surfaces, studies on crystalline **nanoparticles** [14, 15] have become an 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 the 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]. Further, nanosize quantum dots at semiconductor surfaces are found to yield quite powerful light emitting diodes (LEDs) of technological relevance [19].

These nanoparticle systems 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 structural properties at single crystal surfaces, also forms a sound basis by which the structure of nanoparticle surfaces can be characterized. This is particularly interesting since the relative number of atoms positioned at nanoparticle surfaces compared with those of their inner volume is always larger than that of extended macroscopic single crystals. Thus, the relative importance of atoms at **nanoparticle surfaces** in determining physical properties is expected to be greater than that of atoms at single crystal surfaces. In addition, nanoparticles
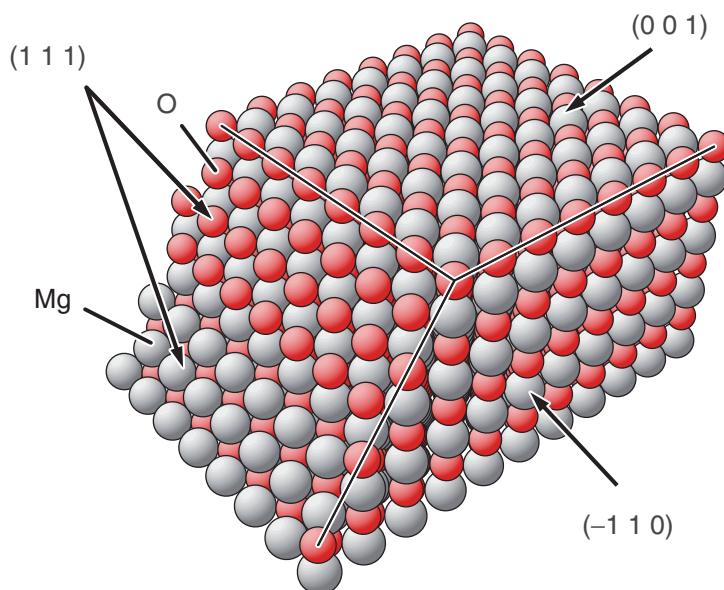
Figure 1.1 Section of an MgO crystal (NaCl lattice). The atoms are shown as shaded balls of different color and labeled accordingly. The section is enclosed by nonpolar (0 0 1), (−1 1 0), and by polar (1 1 1) oriented surfaces.

can possess symmetry and geometric properties that do not appear in single crystals or at their surfaces. Examples are icosahedral clusters or 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 as **ideal single crystals** with a well-defined atomic composition and an unperturbed three-dimensional periodicity. In addition, planar surfaces of single crystals are often assumed to be bulk-terminated and of unperturbed two-dimensional periodicity. With this approximation in mind a rigorous mathematical description of all structural parameters becomes possible and is one of the basic subjects of classical crystallography. As an illustration, Figure 1.1 shows the structure 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 the following chapters of this book we will discuss the basic elements as well as the **mathematical methods** used in crystallography to evaluate structural 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-dimensional space groups. Next, we discuss details of the deviation of atomic structures at surfaces due to changes in surface binding compared with that in the bulk. This is usually described by surface relaxation and reconstruction, where we consider different schemes. In addition, structural behavior during growth processes is discussed. Then we deal with the crystallographic aspects of commensurate, high-order commensurate, and incommensurate adsorbate systems as special cases of surface reconstruction. Here also the different structure notations used in the literature will 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. Further, formal requirements of complete quantitative surface structure databases will be considered. Finally, we describe the 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 mentioned above, and demonstrate that crystallographic methods can also be applied to these systems in order to account for their structural properties. Finally, the book concludes with appendices spelling out further details of the mathematical methods used in the different sections, with tabulations of typical surface sites, and with compilations of structural parameters of crystals.

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 documented in the 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 questions to small research projects, and are meant to stimulate the discussion on the different subjects and to contribute to their clarification. Some of the exercises may require **visualization tools** for crystals, such as **Balsac** [26] or **Survis** [27] or the like.

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

A few illustrations are included as **stereo pictures** for an enhanced three-dimensional impression. These pictures may be viewed either by 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.

Clearly, the present book cannot cover all aspects of the field and may, in some cases, be quite brief. Further, the selection of topics as well as their presentation is, to some degree, determined by the author's personal preferences. However, the interested reader is referred to the extensive crystallographic literature, see for example, [28–33], to the surface science literature, see for example, [34–39], or to the solid state physics literature, see for example, [1, 2, 40], to explore additional details.