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Symmetry in Crystallography

Understanding the International Tables

PAOLO G. RADAELLI

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Symmetry in Crystallography

Understanding the International Tables

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To Jacopo, Sofia (she spotted the pattern on page 47!) and Anna.

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Preface

The purpose of this book is to provide a basic introduction to crystallographic symmetry, up to the point where understanding and using the *International Tables for Crystallography* (hereafter referred to as ITC) becomes possible. The ITC are an essential tool for understanding the literature and carrying out original research in the subfields of solid-state physics, chemistry and structural biology dealing with crystalline materials. Since their first edition, published in two volumes in 1935 under the title *Internationale Tabellen zur Bestimmung von Kristallstrukturen* with Carl Hermann as editor (Hermann, 1935), the ITC have steadily grown into eight ponderous volumes, to become the true "bible" of crystallographers. Over the years, the ITC have become progressively more general, from the initial topic of crystal structure determination by X-ray diffraction towards the recently stated purpose of covering all the subjects that may be of interest for crystallographers. Of course, information about crystal symmetry is central to the ITC, but subjects such as the properties of radiations used in crystallography, the physical properties of crystals and the proper format for crystallographic software are also covered. The ITC are a collective enterprise, each volume having one or more editors and many different contributors. As a consequence, although a remarkable effort has been made to provide a consistent notation and clear explanations, the perception of what is important and how it is best explained can vary from one section to the next, generating a significant amount of duplication and making the approach to the ITC a daunting task for the non-initiated. Here, I have collected a subset of topics regarding crystal symmetry, which I believe are most useful for physicists, chemists and biologists who deal with crystalline materials. The concepts are introduced gradually, with an emphasis on graphical rather than algebraic notation. This may seem somewhat surprising, but my experience over the years has been that manipulating operator "graphs" together with a schematic representation of the crystal structures is the clearest way to visualize symmetry and symmetry reduction through phase transitions. Once the basic concepts are firmly established, the necessary generation of atomic coordinates and their transformations, according to the different conventions, can be easily accomplished by one of the many crystallographic software programs now available on the market or in the public domain.

The approach I follow differs somewhat from the conventional way of teaching crystallography, which starts by establishing coordinate systems to locate atoms and then develops algebraic relations between the coordinates of symmetry-equivalent atoms; for an excellent book on general crystallography, including some elements of symmetry, see Giacovazzo *et al*. (2002). Here, I begin by examining simple patterns, as found in architecture, art, graphic design, etc., and develop a graphical notation to describe their symmetry and to combine symmetry operators. A minimal but reasonably rigorous set of group theoretical concepts, such as composition and the "multiplication table", will be introduced to enable the manipulations of these symbols. As the dimensionality and complexity of the patterns increase from symmetry around a fixed point to quasi-1D (frieze patterns) to 2D (plane or "wallpaper" patterns), so will the set of graphical symbols we become familiar with. I will also introduce in a graphical way concepts such as site symmetry, multiplicity and special positions (denoted using Wyckoff letters), group–subgroup relations, etc.

Only at this point will I introduce coordinate systems to locate points on the patterns. Initially I will use simple Cartesian coordinates, which will be later extended to linear but non-orthogonal coordinates. These will enable the symmetry operators to be expressed in matrix form and the effect of coordinate transformations on the operators to be deduced. At the end of this part, the reader should be capable of constructing graphically the 17 planar "wallpaper" groups from their Hermann–Mauguin symbols (Hermann and Mauguin, 1935) and to understand all the entries in the ITC related to them (Volume A, pages 91–111), with the exception of the reflection conditions. A significant amount of space will be subsequently devoted to the 230 space groups and their various settings, but only minimal additions to the concepts and notation already introduced will be needed. The final part of the book will be devoted to a brief overview of symmetry in reciprocal space, with particular reference to the deduction of the reflection conditions.

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Figure acknowledgements

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