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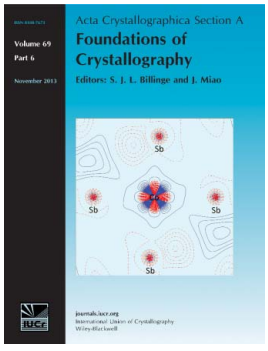

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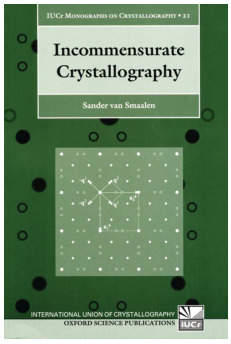

Incommensurate Crystallography. By Sander van Smaalen. IUCr Monographs on Crystallography, No. 21. Oxford University Press, 2012. Pp. 284. Price (paperback) GBP 37.50. ISBN 978-0-19-965923-4.

This book is a slightly revised paperback edition of the hardcover edition that first appeared in 2007 in the series of monographs published by the IUCr. The availability of a paperback edition is certainly welcome, reducing thus by a half the cost of the book.

Incommensurate crystallography is now a mature subject and is well established among specialists dedicated to the structural studies of crystalline matter. The award of the Nobel Prize in Chemistry to Dan Shechtman in 2011 for the discovery of quasicrystals is another confirmation of the importance and significance of the field of aperiodic crystallography, a generic term encompassing both incommensurate and quasicrystals.

Sander van Smaalen's book covers the field of incommensurate crystallography starting from a general introduction of the subject and ending with methods for the solution of incommensurate structures. It is divided into eleven chapters and covers first all the theoretical aspects of the superspace concept including symmetry and diffraction properties. Methods and specific features of structure solution are then described with numerous examples and illustrations. Finally, a description of the crystal–chemical aspects of incommensurate structures is presented, giving an overview of the field.

In the following, we shall analyse in more detail the general content of the individual chapters.

The introductory chapter gives an overview of the concept of aperiodic structures, paying specific attention to modulated structures, incommensurate composite crystals and quasicrystals. The diffraction aspects of periodic crystals are generalized in order to include the properties of modulated crystals. The consequences of modulations in a structure appear in a diffraction pattern as so-called satellite reflections, the characteristics of which are described in the last part of the chapter.

The second chapter is a thorough description of the superspace concept, which is now very well established for the description of incommensurately modulated structures. Just as a diffraction pattern of modulated structures can best be described in higher-dimensional reciprocal space in order to benefit from integer indices for the diffraction spots, the description of the corresponding crystal structure is best described in a higher-dimensional space of the same dimension in order to retain the fundamental property of spatial periodicity. Superspace describes specifically this higher-dimensional space in which all the translational properties of atomic structures are maintained. This would not be possible if we were to confine the description of modulated structures to three-dimensional space. In a series of steps, the author illustrates nicely how the description of modulated structures can be extended in superspace in order to recover periodicity. It is also shown how the point-like aspect of atoms in three-dimensional space has to be generalized in superspace, becoming thus a string or even a more elaborate form in icosahedral quasicrystals. The notion of *t*-plots is also introduced in this chapter for the description of the crystal–chemical properties of the structure under consideration. Finally, the chapter concludes by introducing the structure factor for all possible incommensurate structures, including displacive and occupational modulation functions.

The third chapter concerns one of the most important aspects of modulated structures, namely their symmetry properties. Starting from the concept of a space group in three dimensions, the author shows how the symmetry properties can be extended for the description of modulated structures. Like space groups, superspace groups are tabulated and are conveniently described by symbols from which many characteristics can be deduced. The consequence of symmetry on the diffraction pattern is also extensively described and illustrated with a few examples. The systematic absences of reflections in superspace, which are fundamental for the modelling and determination of incommensurate structures, are also described in detail in this book. The very useful notion of equivalent settings of superspace groups is treated at the end of the chapter in order to assist the reader and to provide them with the tools for dealing with specific cases. This is necessary, as tables of superspace groups are limited in size and only list the most standard settings.

Chapter 4 discusses incommensurate composite crystals, a subject which is close to the heart of the author. Composites structures can be interpreted as intergrowths of modulated structures. The treatment of the structure factors, the symmetry of composites and the interpretation of the results require specific treatment, which is described in detail.

The next chapter deals with an important aspect of the nature of modulations. They can be either commensurate or incommensurate, and many examples appear in temperature- or pressure-induced phase transitions. It is not always possible to distinguish between an incommensurate value of the modulation periodicity and a rational approximation. Therefore, many so-called superstructures can be described as commensurately modulated structures. The advantage of this

approach is that it is better adapted to the solution, refinement and description of the structure than the classical treatment. This is illustrated with examples from the family of compounds A_2BX_4.

Chapter 6 deals with some quantitative aspects of diffraction by aperiodic crystals, in particular the problem of overlapping reflections and twinning, which is particularly acute in this field. Atomic vibrations giving rise to phonons and phasons are also treated in conjunction with the Debye–Waller factor for aperiodic crystals. The last part of the chapter deals with the probability distributions of the structure-factor amplitudes of incommensurate structures, which show a behaviour very similar to conventional crystals.

The refinement of incommensurate structures is treated next. Use of the superspace model requires more care than conventional structure refinement. In most cases, special modulation functions like sawtooth or step functions are applied in order to match the experimental data. These functions request specific mathematical treatment and must be orthogonalized before being applied. The author pays special attention to the constraints imposed by superspace symmetry on the model variables. The rigid-body treatment of incommensurate organic structures is explained well. The last section of the chapter is dedicated to the refinement of incommensurate structures from powder-diffraction data by the Rietveld method. The refinement of incommensurate structures from synchrotron powder-diffraction data is frequent, owing to the superior quality of the data as compared those from a laboratory diffractometer.

Chapter 9 is dedicated to electron density in superspace, and includes the exploitation of the maximum-entropy principle in order to extract the best possible information from the electron-density maps. Here the reader can benefit from the expertise of the author, who has contributed greatly to the spread of this method in the field of incommensurate structures.

The next two chapters are dedicated to the determination of superspace groups and the methods of structure solution. Systematic absences are specific for each superspace group. The difference to conventional space groups is that, in general, the absences concern more than three indices. The methods of structure solution used in conventional crystals (trial and error, Patterson, direct methods, charge flipping) are also used for the solution of structures in superspace. The author describes each method in detail and shows how they can be adapted and extended in order to deal with the special characteristics of incommensurate structures.

The last chapter discusses systematic crystal chemistry. For example, many elements exhibit some incommensurate characteristics under high pressure or at low temperatures. An important part of the chapter is dedicated to series of homologous compounds, where the concept of superspace has the great ability to characterise each member, sometimes using a single composition-dependent parameter. It is to be noted that the series can contain both commensurate and incommensurate members as well as only commensurate members. A section of this chapter is also dedicated to the treatment of atomic valences in aperiodic crystals.

The book concludes with two appendices. The first is dedicated to special software for data collection, data treatment and refinement of incommensurate structures. A glossary of all the symbols and terms used in the book is given in the second appendix.

The scope of this textbook is quite broad and covers all the aspects required firstly to obtain a deep understanding of the field of incommensurate structures and secondly to acquire a good understanding of the concept of superspace in order to solve their structures using diffraction data. It is clear that the reader must have a good knowledge of classical crystallography before exploring this new subject. The primary target of the textbook is PhD students in physics, material sciences, chemistry or mineralogy interested in solving incommensurate structures. At the postdoctoral level, this textbook will give a general introduction to the subject for scientists interested in discovering the field of incommensurate materials and the complexity of crystalline matter. The teacher of an advanced course on incommensurate structures or in a specialized doctoral school will surely find this book very useful for the preparation of their lecture.

One may wonder if some topics have been omitted in the book or if some chapters are incomplete. One of my first remarks when introducing the subject in a lecture on incommensurate structures is to assert that the work of the crystallographer starts when their structure is solved. In other words, the knowledge of the structure must contribute to a better understanding of some physical properties or of the chemical interactions giving rise to the incommensurability. In a future edition of the textbook, the relations between structural properties of incommensurate structures and the corresponding physical properties should perhaps be more emphasized. The power of superspace to explore and design new materials with specific properties should also be stressed, in order to convince material scientists of the great potential still to be discovered within the superspace paradigm.

In conclusion, I warmly recommend this textbook, which is written by a very experienced and knowledgeable specialist in the field of incommensurate structures.

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