In recent years there has been an explosion of interest in the study of molecular crystals and their applications in optics and electronics. This advanced textbook describes their chemical and physical structure, their optical and electronic properties, and the reactions between neighbouring molecules in crystals. The author has taken into account research areas which have undergone extremely rapid development since the first edition was published in 1987. For instance, it features the applications of molecular materials in high-technology devices. There is also an entirely new chapter on C_{60} and organic non-linear optic materials. The level of treatment is aimed at first-year postgraduates or workers in industrial research laboratories wishing to gain insights into organic solid-state materials. It is also suitable for special topics in final-year undergraduate courses in chemistry, physics and electronic engineering.

Molecular crystals

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SECOND EDITION

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Preface to second edition

Since this text was first published there have been significant advances in the applications of molecular crystalline materials, and the whole area of C_{60} chemistry has developed on an enormous scale. The major features of this second edition are a significantly increased coverage of these areas. In the case of non-linear optic materials and C_{60}, special-topic chapters have been added at the end of the text. Both these areas draw heavily on material already described in several of the existing chapters. They therefore form excellent examples of the value of this background material. Other molecular electronics applications covered include high-technology applications of organic dyes (e.g. WORM optical data storage devices, colour microfilters for liquid crystal displays), the use of organic materials in electrophotography (photocopiers and laser printers), electroluminescent displays and photovoltaic solar cells. Significantly, much of the necessary background in ideas and materials was already covered, and these sections cross-reference many of the chapters of the first edition.

There have also been useful advances in techniques, and scanning probe microscopies are now included in chapter 4, while positron annihilation is now described more concisely, reflecting its diminishing use. Mention is also made of the growing use of crystallographic databases to establish structural trends and to identify structure-determining interactions. The application of this improved understanding of the interactions determining molecular assembly to the design of self-assembling molecules is also discussed in chapter 3, and examples of the use of these ideas are included in the discussions of gas-sensor and non-linear optical materials.

Apart from correction of minor errors, I have resisted the temptation to expand the bulk of the material from the first edition in the interests of retaining a concise format which provides a broad introduction to the

subject. Although it has been argued that it is simply not possible to convey such a wide field adequately in such a concise manner, evidence from both academic staff and students from many institutions has suggested that this approach is useful to gain a foothold in the subject which is not provided by larger, more comprehensive volumes. Similarly, line drawings of crystal structures etc. continue to be used rather than the excellent computer-generated molecular graphics which are now widely available, since students have some chance of sketching an approximation to the line drawings themselves to illustrate a point. The more advanced the graphics, the less likely it is that students will attempt this.

I thank the many colleagues and students who have provided helpful feedback contributing to this edition, and look forward to the continuation of this valuable source of new insights.

John D. Wright
January 1994

Preface to first edition

Many of the physical and chemical properties of molecular crystals are very different from those of other solid-state materials. There are also extensive possibilities for varying these properties by altering the electronic and geometric structure of the molecules using the synthetic skills developed by organic chemists. The exploitation of these possibilites in new material applications is entering a rapid-growth phase, supported by a very strong research base world-wide. However, in the teaching of solid-state chemistry and physics, molecular crystals are seriously neglected. Most of the current solid-state chemistry and physics textbooks at the level of final-year undergraduate/first-year postgraduate studies scarcely mention molecular crystals. There are several excellent advanced texts, but these cover limited areas of the subject and by their detailed nature tend to be difficult for newcomers, as well as expensive. This situation hinders the effective training of the growing number of scientists who wish to work with molecular crystalline materials. My objective in writing this book has been to fill this gap.

The range of material covered in the book is very wide, as is the range of inherent difficulty of the underlying concepts, and there are several places where details of experimental methods or of mathematical developments of theories (e.g. of exciton theory) would have made the text inordinately long or complex. In these cases the supporting references provided with each chapter should be particularly useful. These references are representative but by no means exhaustive. To have referenced all the elegant examples from the research literature would be impossible in a text of this level, and I apologise to those whose work is not cited. Omissions and variations in level of treatment are inevitable but not deliberate.

The book is based on over ten years of teaching an undergraduate course

on molecular crystals to final-year students, and I would like to acknowledge the challenging and perceptive questioning of these students, which has often forced me to examine and clarify my own thinking. I would also like to express my thanks to scientific colleagues from many countries for their contribution to my understanding of this field, to my research students and my family for their forbearance during my preoccupation with writing the book, and to John Couves for his helpful and critical comments, as a first-year postgraduate, on the manuscript.

November 1986

The publication of the paperback edition (1988) realised my original objective of a text accessible to students for their own libraries.

The citation of original references wherever possible has led to the omission of any reference to the following advanced texts: M. Pope and C.E. Swenberg, *Electronic Processes in Organic Crystals*, Oxford: Clarendon Press, 1982; H. Meier, *Organic Semiconductors*, Weinheim: Verlag Chemie, 1974; E.A. Silinsh, *Organic Molecular Crystals: Their Electronic States*, Berlin: Springer, 1980; K.C. Kao and W. Hwang, *Electrical Transport in Solids*, Oxford: Pergamon, 1981. These texts have had a significant influence on my own perceptions of the subject and can be strongly recommended for those wishing to extend their reading, in addition to those texts covering related areas which are cited in their own contexts.

1988
John D. Wright