

## Preface

It was several years ago that an extremely intricate relation between the substructure and superstructure of a mineral pligionite  $5\text{PbS}\cdot 4\text{Sb}_2\text{S}_3$  was successfully visualized with the aid of computer graphics. The result revealed that the homologous series  $x\text{PbS}\cdot 4\text{Sb}_2\text{S}_3$  with  $x = 3, 5, 7$  or  $9$  provides a new example based on tropochemical cell-twinning (TCT), the concept of which was introduced by the writer in 1978 as a crystallographic mechanism of building complex structures. A preliminary account of the result was presented to the XVth Congress of the International Union of Crystallography held at Bordeaux in 1990. The large number of drawings necessary to convey the process of the analysis, however, kept the writer from publishing a full account of the study in a current journal.

Meanwhile, a survey of literature in the past decade has brought out that considerable progress has been made on the structural study of minerals and inorganic phases known to be based on the TCT mechanism. It seemed to be worthwhile to review the crystallochemical aspects of these materials in light of the new knowledge. A decision was then made to prepare such a review, combine it with the new findings and dare to publish them in the form of a book. The aim of this book is principally to discuss the structural details of the homologous series characterized by the TCT mechanism.

Although this small book, thus undertaken, covers only a limited topical field, discussions herein have been extended to certain basic structures of silicates, sulfides and borates. One will find that they are of vital importance in understanding the complex structures appearing in this book. In crystal chemistry, in general, the problem often arises on how to decide the coordination number of an atom when the environment of the atom is irregular. In relation to a distorted coordination polyhedron which is described in Chapter 5, a concept of geometrically characterizing coordination polyhedra is given in the Appendices. Several sets of new structure data, which were made available for certain phases discussed in this book, are also supplemented in the Appendices. It is anticipated that the discussions incorporated in this volume would throw at least a little light on the study of derivative structures, including, in general, the structures of non-stoichiometric compounds such as those characterized by crystallographic slips.

I would like to take this opportunity of recording my gratitude to Professors Tei-ichi Ito, who guided me into the beloved science of crystallography, Martin J. Buerger, with whom I have been accorded the privilege of spending two years in study, for kindly suggesting the word "tropochemical", which has been used in the main title of this book, and Werner Nowacki, for introducing me to the crystal chemistry of sulfosalts, many having structures of fascinating complexity. Without the influence of these outstanding crystallographers, this book would not have

appeared. I also wish to express my sincere gratitude to Professor R. Sadanaga, M.J.A. for his continued interest and encouragement throughout the course of my studies.

To Professor B. J. Wuensch, Massachusetts Institute of Technology, I am indebted for his stimulating discussion on the relationship between the subcell and the true cell of plagioclite. The present work eventually started with this discussion. My special thanks are due to M. A. Richard C. Erd, U.S. Geological Survey, California, for kindly providing me with copies of many papers on borates, including that of unpublished manuscript by Dr. W. T. Schaller, and a number of specimens of pinakiole related minerals, to Professor F. Liebau, Universität Kiel, for suggesting me the expression "heterovalent vacancy coupled substitution", which has been used as the title for Chapter 2, to Professor E. Makovicky, University of Copenhagen, for extremely valuable comments on the terminology of "homologous series", and to Dr. A. Skowron, McMaster University, for her kindness in giving me electron micrographs of heyrovskyite recorded with a transmission electron microscopy and corresponding electron diffraction patterns.

I am indebted to the Royal Swedish Academy of Sciences and to Dr. A. Skowron for permission to reproduce Fig. 11(b) of Chapter 3 from the *Chemica Scripta*, Volume 26, 1986; Dr. Skowron kindly permitted me to borrow her original photo print for this figure.

I am also indebted to the International Union of Crystallography and Professor J.-O. Bovin for permission to reproduce Fig. 11 of Chapter 6 from the *Acta Crystallographica*, A37, 1981. I am deeply grateful to the *Acta Crystallographica* for permission to reproduce figures of my articles which originally appeared there. They include Figs. 13, 20, 24, 28, 29, 32, 33, 34, 35, 36, and 38 of Chapter 5.

I am grateful to the *Zeitschrift für Kristallographie* and Professor J.-O. Bovin for permission to reproduce Fig. 19 of Chapter 6. The *Zeitschrift für Kristallographie* has also kindly permitted me to reproduce Figs. 15, 16 and 18 of Chapter 3.

The Mineralogical Society of Japan and Prof. I. Kostov have also kindly permitted me to reproduce Fig. 1 of Chapter 7 from the *Mineralogical Journal*.

With the exception of the cuts acknowledged above, all other illustrations have been prepared especially for this book. Among them, those of crystal structures were mostly made with ATOMS written by E. Dowty, Shape Software, Tennessee. My drawing of those illustrations benefited greatly from the use of a set of computing system which my former students of the Nihon University presented to me on my seventieth birthday. It is a pleasure to acknowledge this great debt I owe to them.

Both Fig. 15 (Chapter 6) and Fig. 13 (Chapter 7) were made with KRISTAL which was originally written by M. Hirano (*J. Mineral. Soc. Japan*, 19, 1-7, 1989) and modified by K. Ohkubo (Y. Takéuchi: Report to the Ministry of Education, Science and Culture for a Grant-in-Aid for Scientific Research 62580043, 1989). The computer graphics procedure used for the work described in Chapter 7 was carried out with this program KRISTAL. I am indebted to Dr. Haruo Sawada, Mr. Koichi Ohkubo and Miss Maki Watanabe for their help in preparing certain of the diagrams.

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