R. A. LAUDISE

The Growth of Single Crystals

SOLID STATE PHYSICAL ELECTRONICS SERIES

THE GROWTH OF SINGLE CRYSTALS

R. A. Laudise

Bell Telephone Laboratories
Murray Hill, New Jersey

Prentice-Hall, Inc.

Englewood Cliffs, New Jersey

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Englewood Cliffs, N.J.

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Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

13-365320-X

Library of Congress Catalog Card No. 77-104173

Printed in the United States of America

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PREFACE

This book is intended for all those who want to grow crystals. It is intended both for those who consider crystal growth their principal professional activity and for those who want crystals in order to study their properties and find that they must grow them themselves. Background through a first course in physical chemistry is assumed but is not essential particularly if the reader devotes special attention to Chapters 2 and 3 and the references contained therein.

The book is intended to be used in several ways:

1. As a text or collateral reading in a senior level or graduate level course in a materials science curriculum where the contents, if presented with an appropriate laboratory or research problem, can be used to train that rare and greatly needed individual, the professional crystal grower.

2. As a professional crystal grower's *vade mecum*. Chapters 1, 2, and 3 summarize material on means of determining crystallinity, thermodynamics and kinetics not readily available in a form useful for the grower elsewhere, and the remaining chapters discuss each of the major methods and are arranged in a manner to assist the grower in a logical choice of growth method and to view each method in as logical a theoretical framework as is presently possible.

3. As a source book about particular growth methods and the growth of particular materials. Each of the major methods is related to theory, equipment is described (suppliers of unusual equipment are mentioned),

procedures are discussed and accounts of the growth of representative crystals are given.

If the reader does not elect to read the book cover to cover, it is suggested that he read or at least scan the introductory material in the chapter where the method or crystal he is especially interested in is described.

This book is not encyclopedic. Brevity, critical evaluation, the inclusion of background material and an attempt to present crystal growth techniques as a logical, coherent body of knowledge, have caused the author to abandon attempts to list every crystal ever grown, although most materials of present-day development and research importance have been included. Nevertheless, a search of the periodical literature before beginning experimental work is imperative.

Chapters 1, 2, and 3 are written from the viewpoint of the crystal *grower's* needs. If your interests are primarily perfection studies, thermodynamics or theory of crystallization, then entire works devoted to these subjects should be consulted.

Any work is largely a product of the environment in which it is produced. This book is especially the product of more than a decade's association with the preparation of single crystals for research and development at Bell Telephone Laboratories. Representative materials and illustrative procedures have in the main been chosen from this experience. In making this choice, I regret that a lack of familiarity with much good work in other laboratories may have, in some cases, caused its omission. No value judgment is intended. Similarly, the author is not a historian of science. Lengthy historical sections have been omitted unless they served a valid tutorial purpose. References are meant mainly to lead the reader to good recent expositions of material which could not be adequately covered in the text and not as unmitigated priority judgments.

Parts of the book have been critically reviewed by several of my colleagues whose suggestions were invaluable. I would particularly like to thank R. L. Barns, J. R. Carruthers, W. C. Ellis, K. A. Jackson, K. Nassau, J. W. Nielsen, W. G. Pfann, C. D. Thurmond, and J. H. Wernick for their suggestions on the manuscript. Some of the material was developed for courses delivered at the Hebrew University, Jerusalem, The University of California at Los Angeles, and the Massachusetts Institute of Technology. Professor Michael Schieber of Hebrew University and Professor Harry Gatos of M.I.T. are especially thanked for making these opportunities available to the author. I have learned much from day-by-day association with colleagues not mentioned above and would especially like to mention A. A. Ballman, J. G. Bergman, G. T. Kohman, E. D. Kolb, J. P. Remeika and L. G. Van Uitert, in this respect. Miss Kathleen Donnelly ably carried out the prodigious amount of secretarial work involved; my wife, Joyce Laudise, lent constant encouragement and many hours of time in literature work. A. G.

Chynoweth, J. H. Scaff, and N. B. Hannay have often been sources of advice and encouragement. What is good in this work is due in large measure to these friends; the faults are the author's.

The following publishers and publications are to be thanked for permission to reproduce the illustrations used: American Chemical Society; American Institute of Physics; The American Mineralogist; Electrochemical Society, Inc.; Interscience Publishers, Inc.; John Wiley & Sons, Inc.; Journal of the American Ceramic Society; Journal of Physics and Chemistry of Solids; Macmillan (Journals) Ltd.; McGraw-Hill Book Company; The Royal Society; Van Nostrand Reinhold Company; W. H. Freeman and Company and *Zeitschrift für Naturforschung*.

R. A. Laudise

Murray Hill, N.J.

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1

SINGLE CRYSTALS

Crystals have interested man because of their beauty and rarity since prehistoric times, but their large-scale use has been brought about mainly by the demands of solid-state physics for materials for research and devices.

This book is intended to tell how to grow crystals and presents the necessary background concerning the perfection of crystalline materials, thermodynamics, kinetics of crystallization processes, and theory of the various methods to make one effective as a crystal grower.

Chapter 1 is devoted to the question of recognizing crystallinity in a material and determining the perfection of crystals. Chapters 2 and 3 discuss thermodynamics and kinetics of crystallization and the remaining chapters discuss in detail the various growth methods and the growth of specific materials.

1.1 What Is a Crystal?

Matter may exist in three states of aggregation—*solid*, *liquid*, or *gas*. In the gaseous state, the molecules are separated by comparatively large distances (about 30 Å at 1 atm). This large separation results in comparatively negligible interactions between the molecules and the molecules are thus free to move in any direction. Therefore, a gas has a very low viscosity and expands to fill completely a containing vessel of any size or shape. The arrangement

of molecules in a gas is essentially completely disordered. In the liquid state the molecules (or atoms) are separated by about 1 Å, and their interactions are consequently much stronger than in a gas. Thus a liquid exhibits higher viscosity and does not expand to fill completely its container. There is short-range order in a liquid, but it does not persist more than a few atomic diameters from a given atom. In the solid state, the atomic separation is about the same as in a liquid, but the interactions between atoms are stronger. Thus the atoms are able to move only in vibrations of extremely low amplitude about fixed positions relative to one another. As a result, solids have rigidity, fixed shape, and mechanical strength. In addition, a *crystalline* solid is characterized by long-range order extending over many atom diameters. Upon increasing the internal energy in a crystalline solid by heating it, melting occurs at a fixed temperature for a given pressure or in a few cases sublimation to the gaseous state occurs. A further increase in internal energy will volatilize the material. At every temperature, gas or vapor of a material will exist in equilibrium with the material at a definite pressure. Thus in terms of internal energy for a particular material, the internal energy of the gaseous state $>$ the internal energy of the liquid state $>$ the internal energy of the solid state.

There is another class of materials often called *amorphous solids*, including glasses, waxes, and pitches, that possess such a high viscosity as to behave essentially as solids. Such materials do not have fixed melting points, and they exhibit the short-range order characteristic of liquids. It is often convenient to think of these substances as supercooled liquids. Figure 1.1 shows schematic representations of a gas, a liquid, and a solid. The representation of an amorphous solid would be identical to that of the liquid. A useful means of illustrating the difference between a crystalline solid and a liquid is shown in Fig. 1.2. Figure 1.2 shows the radial-distribution function, that is, the number of atoms encountered as a function of distance from a given atom for solid (crystalline) and for liquid potassium. A high degree of order even at

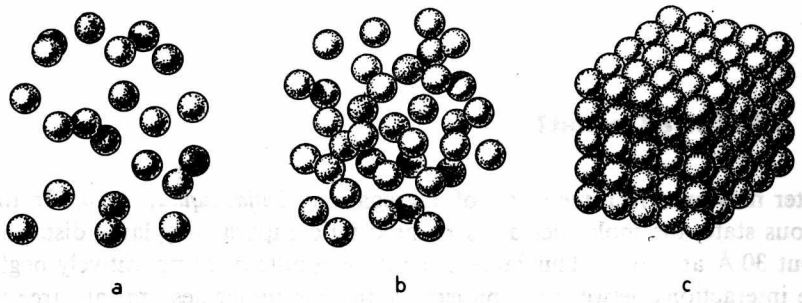

Fig. 1.1 Schematic representations of a gas (a), a liquid (b), and a solid (c).

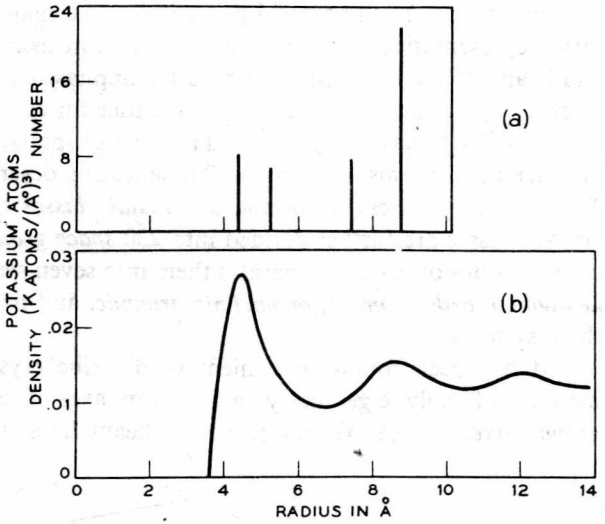

Fig. 1.2 Radial distribution function for (a) crystalline and (b) liquid potassium (after Thomas and Gingrich, 1938).

distances longer than those shown would occur in the crystal, while, as can be seen, the order in the liquid (or the amorphous solid) is short-range.

It is interesting to point out that there is a class of materials called liquid crystals (Brown and Shaw, 1957) whose properties are intermediate between those of liquids and crystals. These materials exhibit the flow behavior of liquids but are not isotropic in all of their properties, as is the case with true liquids. One way of viewing liquid crystals is to consider that they have one- or at most two-dimensional order, while true crystals exhibit three-dimensional order.

Let us examine the nature of the ordered array of atoms in a crystal. We will give here only a brief outline. Texts such as Buerger (1942) and Lipson and Cochran (1966) should be consulted for details. We may describe a crystal in terms of the pattern or arrangement of its constituent atoms. This pattern is often described in terms of the *unit cell*, which is an imaginary parallelepiped containing atoms of the crystal that, if moved or translated and repeated over and over again, will reconstruct the pattern of all of the atoms in the crystal. Repetition by translation is a kind of movement that can be represented by a vector. The origin of the vector describing the translation may be taken as any point within the crystal convenient for the problem at hand. If it is taken as some arbitrary reference point in the pattern to be repeated, the repetitive action of the translation obviously reproduces this reference point (as well as all the others in the system) as a three-dimensional pattern of points in space. This pattern is a *point-space lattice*. The grid, or

line lattice, can be indicated by specifying the magnitude and direction of three representative grid lines, that is, the dimensions or *lattice parameters* and shape of the unit cell. It should be emphasized that the point lattice is given us by nature; we choose the line lattice for convenience. It is geometrically possible to have only a limited number of spatial arrangements of points in space or of atoms in a crystal. These can be described in terms of the 14 *Bravais space lattices* or of the 32 *crystal classes* or *point groups*. The 32 crystal classes are further divided into 230 *space groups*. One of the simplest classifications of crystals separates them into seven systems: *cubic*, *tetragonal*, *hexagonal*, *orthorhombic*, *monoclinic*, *triclinic*, and *trigonal*. Figure 1.3 shows these systems.

It has been found convenient to describe crystals by the use of the methods of analytic geometry and to adopt axes of reference called *crystallographic axes*. These axes are shown as heavy lines in Fig. 1.3. The axes are

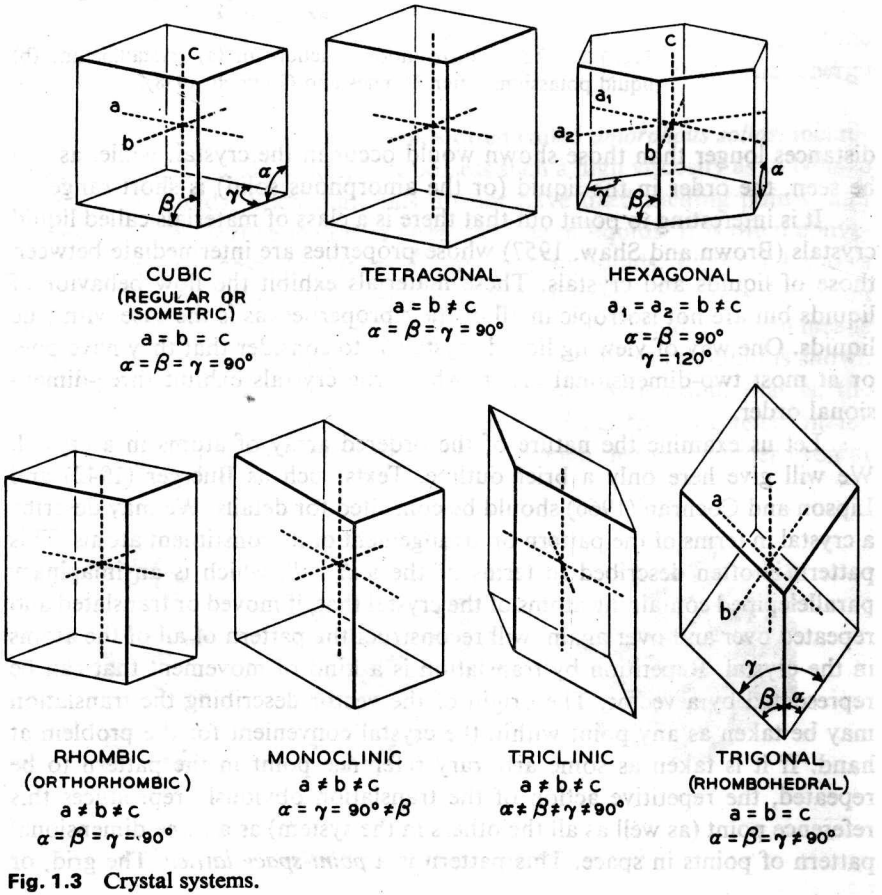

Fig. 1.3 Crystal systems.

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