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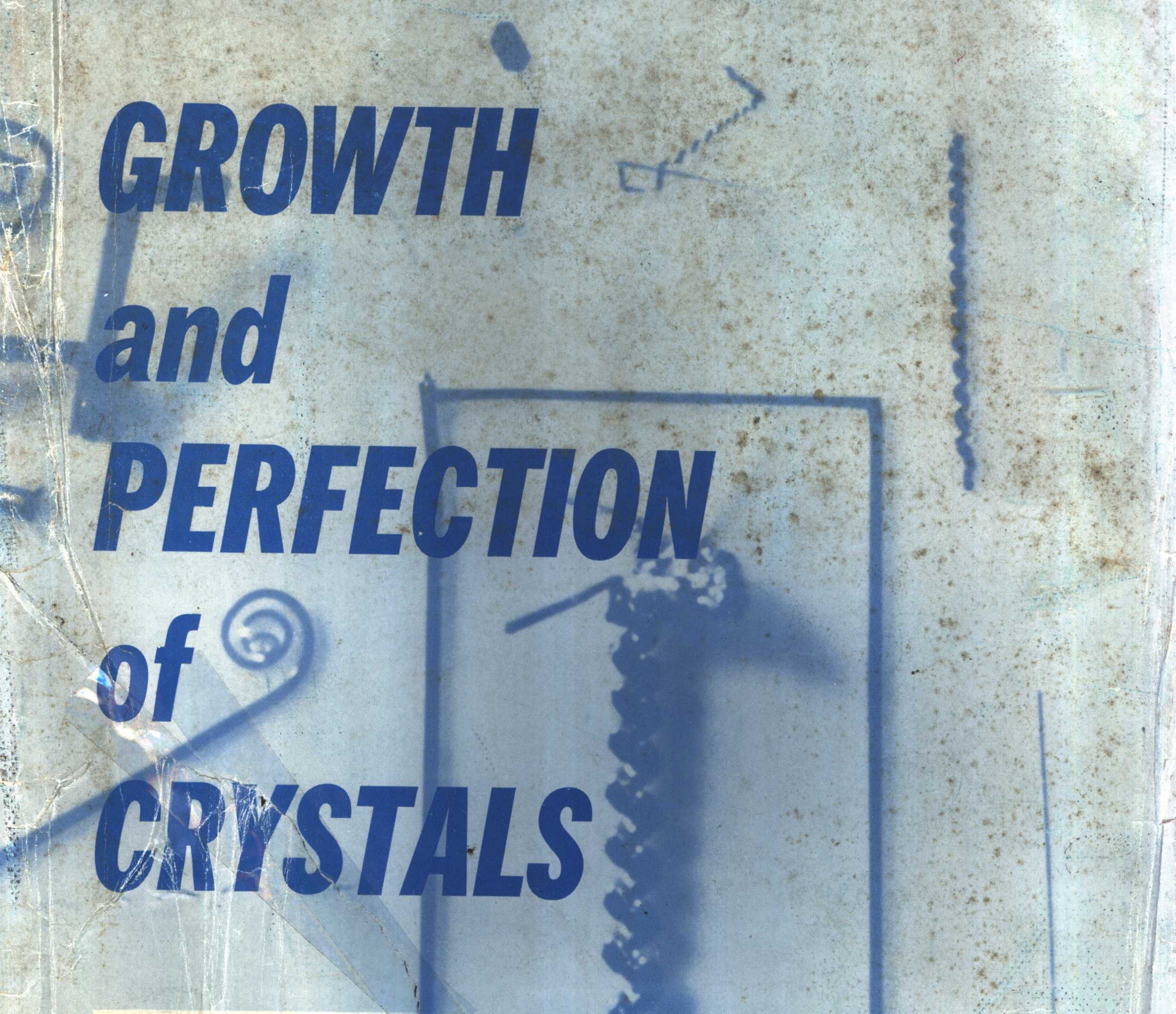
R. H. Doremus • B. W. Roberts • David Turnbull



GROWTH and PERFECTION of CRYSTALS

International conference reports on recent research in crystal morphology, whiskers, and polymer crystallization

Sponsored by the Air Force Office of Scientific Research, Air Research and Development Command; and the General Electric Research Laboratory, Schenectady, New York

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Edited by..

R. H. DOREMUS

B. W. ROBERTS

DAVID TURNBULL

GROWTH AND PERFECTION OF CRYSTALS

Proceedings of
an International Conference on Crystal Growth
held at Cooperstown, New York
on August 27-29, 1958.

Sponsored by

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FOREWORD

This book consists of the papers and discussion presented at an International Conference held at Cooperstown, New York, August 27 - 29, 1958.

The Conference was sponsored jointly by the U.S. Air Force Office of Scientific Research, Air Research and Development Command, and the General Electric Research Laboratory.

The program of the Conference was developed by a committee consisting of:

N. Cabrera	University of Virginia
B. Chalmers	Harvard University
P. J. Flory	Mellon Institute
D. Turnbull (Chairman)	General Electric Research Laboratory
D. A. Vermilyea	General Electric Research Laboratory

While the writer was on leave at Cambridge University during the period September 1957 to April 1958 the main burden of implementing of the Committee's recommendations fell upon D. A. Vermilyea, who also served as Committee Chairman during this period.

The Committee benefited greatly from the enthusiastic help and cooperation of the Air Force representative, C. F. Yost. We are also deeply indebted to B. W. Roberts for his splendid work in discharging his responsibilities for the physical arrangements for the Conference.

Participation in the conference was by invitation from the Committee. The list of participants, including fifteen scientists from overseas, is given on page xi

The Table of Contents is divided into sections corresponding to the main subjects discussed at the conference. After Frank's introductory lecture each of these subjects was discussed in turn at a conference session. At the beginning of each session a specially invited paper (and in the polymer session two papers) reviewing the topic of the session was presented. The review paper was followed by a number of shorter papers which primarily described recent results and ideas. Each presentation was followed by a discussion, which was recorded. The transcription of this discussion, as edited by the participants, is published after each paper. Also included are some written discussions submitted by conferees but not actually presented at the conference.

In order to facilitate rapid publication, the text of this book was prepared on IBM Executive typewriters and the figures and photographs were immediately added after necessary size adjustments. These pages were then photographed and a reduction of 90 per cent was introduced to prepare for the photo-offset printing process.

The niceties of complete editing which yield uniformity in equation structure, word usage and conventions throughout a book have been partially foregone in this attempt to make available to the scientific community an accurate text as soon as practicable.

DAVID TURNBULL
Schenectady, New York
September, 1958

PREFACE

Crystallization is a very common phenomenon but the mechanisms whereby it occurs have proved to be quite elusive. Consequently the subject of crystal growth and morphology has held a high level of interest, both scientifically and technologically, for a very long period. One of the central problems was: why is it that crystals bounded by molecularly densely packed faces usually grow at sensible rates in dilute fluids at low supersaturation? A plausible solution for this, the screw dislocation theory, was proposed by F. C. Frank at an earlier conference on crystal growth about a decade ago. Since then the Frank theory has had a great influence on both the experimental and theoretical activity in the crystal growth field. Now it is usually accepted that the theory does explain what it was intended to explain.

However many important problems remained. For example: the mechanism of growth of crystals into concentrated solutions and melts; the role of impurities in crystal growth; and the mechanism of crystallization of very complex molecules such as polymers. Recently great interest has also developed in the origin of line imperfections in crystals and their control by growth techniques. The somewhat analagous problem of controlling the impurity level in crystals and growing ultra-pure crystals was solved in part at least by the development of zone melting techniques.

It seemed that the time was opportune for a conference discussing the unresolved problems in crystal growth mentioned above. Also it was believed that such a conference might promote useful exchanges of views between scientists studying polymer crystallization and those investigating the crystallization of simpler molecules. To these ends the conference that gave rise to this book was organized.

It is especially fitting that the conference was opened with an invited lecture by F. C. Frank. He pointed out that the central connecting subject of the conference was crystal morphology and reviewed the historical development of this field leading to the present state of our understanding of it.

A large number of papers are directed to the problem of the origin and control of line imperfections in crystal growth. In this connection the growth and properties (see Sections II and III) of crystal whiskers (filamentary single crystals) are very important. As Nabarro and Jackson emphasized the existence of crystal whiskers has been known for centuries. However, it was only following the recent discovery at

Bell Laboratories, that some have mechanical strengths near that expected for dislocation free crystals, that their importance was recognized. It is surprising that this recognition came so late, but it may be significant that it immediately followed major developments which vindicated the dislocation theories for various aspects of crystal behavior.

It will be seen from the papers published here that fairly plausible mechanisms have been developed for whisker growth under various conditions. However critical experimental tests of these mechanisms are still lacking excepting in a few instances.

There was much discussion of the question: are whiskers indeed free of dislocations, as might be inferred from their perfect-crystal-like behavior, or do they contain dislocations which somehow do not react to some of the stimuli that normally show them to be present ? Considerable direct evidence bearing on the dislocation content of whiskers was presented. It seems that some contain no dislocations, some have a single axial screw dislocation and others, usually the larger whiskers, may contain many dislocations. There is some suggestion that the unique characteristics of whiskers may be due to surface rather than internal perfection. However it is also brought out that the properties of whiskers vary widely from specimen to specimen. This points to the need to use the same specimens for the perfection and property studies.

Several of the papers describe mechanisms by which dislocations may be introduced into crystals. Hirsch and Silcox (Section III) reviewed experiments which established that dislocation loops in metals can form from the precipitation of vacancies. Tiller and Washburn (Section IV) showed how dislocations may form in crystals during crystallization from the melt.

Recently it was discovered that very large crystals of some substances can be grown which are apparently entirely free of dislocations. Methods for doing this are described in the papers of Dash and Mitchell (Section IV).

A somewhat better definition of the problem of crystal growth from the melt may have been achieved as a result of the discussions and papers published in Section IV. Understanding of the nature of the liquid state and of the liquid-solid interface is, no doubt, the key to this problem. As Frank pointed out, if the liquid-solid interface is "singular" (i.e. there is a cusp in the Wulff plot of surface free energy at the interface orientation), a screw dislocation mechanism would be necessary for growth at small undercooling. If no such cusp exists (i.e. the interface is nonsingular) a dislocation mechanism should not be required even though the cusp is replaced by a shallow minimum. The evidence now indicates that, depending on the system and conditions, either situation (i.e. singular or nonsingular interface growth) may be encountered in crystallization from the melt.

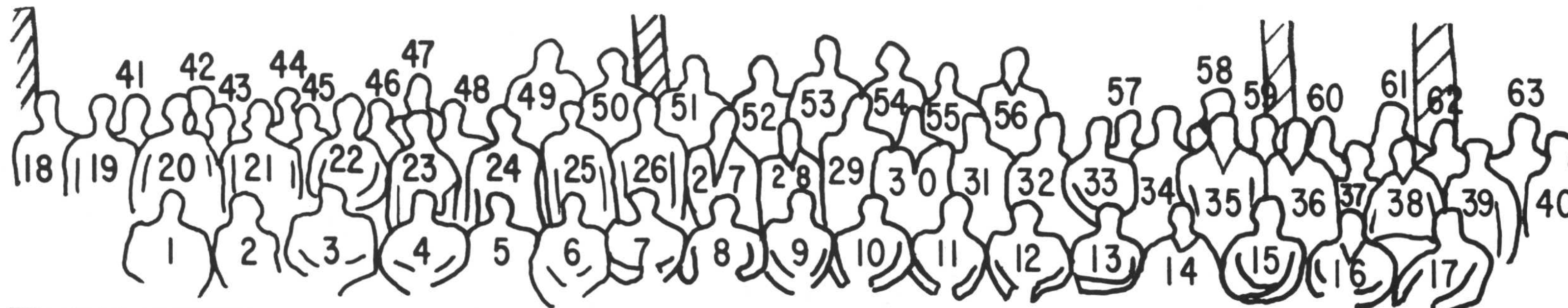
The old problem of dendrite formation was discussed. Hille, Rau and Schlipf and Frank advanced plausible explanations (Section IV) for the crystallography of dendrites. However the mechanism of branching is still obscure.

It has long been recognized that traces of certain impurities can have remarkable effects on both the rate of growth and morphology of crystals, but there was little knowledge of the reasons for this. However it appears (Section V) that very significant beginnings have been made toward more quantitative theories for impurity effects. Warning was given in the discussion that we are a long way from complete understanding of the problem. Nevertheless there is good reason to hope that we are on the threshold of additional important developments in this field.

It appears that the exchanges of views between the polymer and other crystal growth scientists were very useful (see Section VI). An intriguing question is: to what extent are the problems of polymer and ordinary crystallization similar? Certain special features of polymer crystallization resulting from the complexity of polymer molecules have been emphasized by Flory. However, as Mandelkern and Keller point out, polymer crystallization also has many characteristics similar to ordinary crystallization. For example both take place by a nucleation and growth mechanism and in both single crystals appear to grow in dilute solutions by a screw dislocation mechanism. However because of their molecular complexity polymers rarely grow as isolated single crystals but rather as spherulites (or hedrites) made up of aggregates of very small crystals. Further, polymer melts almost never can be crystallized completely. Nevertheless Keller explained that by careful application of the ordinary crystal growth techniques isolated thin polymer single crystals can sometimes be grown. In these crystals the chains are folded at intervals of about 70 carbon atoms into a pleated structure. Mandelkern showed that the activation energy for the growth of polymer spherulites is identical to that for their primary nucleation. Therefore the growth in polymer spherulites must, in contrast to ordinary crystal growth, be governed by a secondary or stimulated nucleation process. Thus there are important differences as well as points of similarity between polymer and ordinary crystallization.

In this brief summary of some of the main problems discussed I have not attempted to do justice to all the contributions individually. However all together they made for a lively and stimulating conference.

RH DOREMUS
BW ROBERTS
DAVID TURNBULL
Schenectady, New York
September, 1958



PARTICIPANTS OF THE INTERNATIONAL CONFERENCE ON CRYSTAL GROWTH
Cooperstown, N.Y., Aug. 27-29, 1958

1. R.L. Parker; 2. Mrs. Parker; 3. R.S. Bradley; 4. J.W. Mitchell; 5. W. Dekeyser; 6. B. Chalmers; 7. N. Cabrera; 8. F.C. Frank; 9. D. Turnbull; 10. P.J. Flory; 11. J.H. Hildebrand; 12. I.N. Stranski; 13. D.A. Vermilyea; 14. F.P. Price; 15. R.H. Doremus; 16. W.C. Dash; 17. W.A. Tiller; 18. D. Reynolds; 19. H.M. Strong; 20. K.A. Jackson; 21. W.B. Hillig; 22. H.D. Keith; 23. R.S. Stein; 24. A. Carlson; 24. P.H. Egli; 26. J. Washburn; 27. G.T. Kohman; 28. L. Himmel; 29. F.L. Vogel, Jr.; 30. R. Eisner; 31. W.J. Dunning; 32. P.B. Hirsch; 33. S.S. Brenner; 34. P.J. Shlichta; 35. W.P. Slichter; 36. L. Mandelkern; 37. K. Neumann; 38. F.R.N. Nabarro; 39. G.A. Wolff; 40. D.O. Niederhauser; 41. C. Pitha; 42. J.W. Nielsen; 43. D. Sweeney; 44. G.M. Pound; 45. J.E. Gordon; 46. R. Condit; 47. L.S. Darken; 48. S. Amelinckx; 49. C.F. Yost; 50. J. O'Conner; 51. R.E. Sellers; 52. W.C. Ellis; 53. R. Bacon; 54. R.A. Laudise; 55. R. Gomer; 56. C.F. Hammer; 57. W.W. Webb; 58. R.V. Coleman; 59. P.B. Price, Jr.; 60. A.J. Herzog; 61. G.S. Baker; 62. J.D. Eshelby; 63. A. Keller.

LIST OF PARTICIPANTS

S. Amelinckx	University of Ghent, Ghent, Belgium
R. Bacon	National Carbon Company Research Laboratories, Cleveland, Ohio
G.S. Baker	Department of Physics, University of Utah, Salt Lake City, Utah
R.S. Bradley	School of Chemistry, The University, Leeds, England
S.S. Brenner	General Electric Research Laboratory, Schenectady, New York
N. Cabrera	Physics Department, University of Virginia, Charlottesville, Virginia
A. Carlson	Clevite Research Center, Cleveland, Ohio
B. Chalmers	Harvard University, Cambridge, Massachusetts
R.V. Coleman	General Motors Corporation, Detroit, Michigan
Ralph Condit	U.S. Air Force Office of Scientific Research, Washington, D.C.
L.S. Darken	U.S. Steel Corporation, Monroeville, Pennsylvania
W.C. Dash	General Electric Research Laboratory, Schenectady, New York
W. Dekeyser	University of Ghent, Ghent, Belgium
R.H. Doremus	General Electric Research Laboratory, Schenectady, New York
W.J. Dunning	Department of Chemistry, University of Bristol, Bristol, England
P.H. Egli	Naval Research Laboratory, Washington, D.C.
W.C. Ellis	Bell Telephone Laboratories, Murray Hill, New Jersey
R. Eisner	Westinghouse Electric Corporation Research Laboratories, Pittsburgh, Pennsylvania
J.D. Eshelby	University of Birmingham, Edgbaston, Birmingham, England
P.J. Flory	Mellon Institute, Pittsburgh, Pennsylvania
F.C. Frank	University of Bristol, Bristol, England
R. Gomer	Institute for the Study of Metals, University of Chicago, Chicago, Illinois
J.E. Gordon	Tube Investments Research Laboratories, Essex, England
C.F. Hammer	E.I. DuPont de Nemours and Company Research Division, Wilmington, Delaware
A.J. Herzog	Wright Air Development Center, Dayton, Ohio
J.H. Hildebrand	Department of Chemistry, University of California, Berkeley, California
W.B. Hillig	General Electric Research Laboratory, Schenectady, New York

L. Himmel	Office of Naval Research, Washington, D.C.
P.B. Hirsch	University of Cambridge, Cambridge, England
K.A. Jackson	Harvard University, Cambridge, Massachusetts
H.D. Keith	American Viscose Corporation, Marcus Hook, Pennsylvania
A. Keller	University of Bristol, Bristol, England
G.T. Kohman	Bell Telephone Laboratories, Murray Hill, New Jersey
R.A. Laudise	Bell Telephone Laboratories, Murray Hill, New Jersey
L. Mandelkern	National Bureau of Standards, Washington, D.C.
J.W. Mitchell	University of Bristol, Bristol, England
F.R.N. Nabarro	University of the Witwatersrand, Johannesburg, South Africa
K. Neumann	Physikalisch-Chemisches Institut der Justus Liebig Universität Giessen, Giessen, Germany
D.O. Niederhauser	E.I. DuPont de Nemours and Company, Wilmington, Delaware
J.W. Nielsen	Bell Telephone Laboratories, Murray Hill, New Jersey
J. O'Connor	Air Force Cambridge Research Center, Bedford, Massachusetts
R.L. Parker	National Bureau of Standards, Washington, D.C.
C. Pitha	Air Force Cambridge Research Center, Bedford, Massachusetts
G.M. Pound	Carnegie Institute of Technology, Pittsburgh, Pennsylvania
F.P. Price	General Electric Research Laboratory, Schenectady, New York
P.B. Price	University of Virginia, Charlottesville, Virginia
D. Reynolds	Wright Air Development Center, Dayton, Ohio
D.S. Rodbell	General Electric Research Laboratory, Schenectady, New York
F. Seitz	University of Illinois, Urbana, Illinois
R.E. Sellers	U.S. Air Force Office of Scientific Research, Washington, D.C.
P.J. Shlichta	California Institute of Technology, Pasadena, California
W.P. Slichter	Bell Telephone Laboratories, Murray Hill, New Jersey
R.S. Stein	University of Massachusetts, Amherst, Massachusetts
I.N. Stranski	Technische Universität Berlin-Charlottenburg, Berlin-Charlottenburg, Germany
D.M. Sweeney	Bellarmine College, Louisville, Kentucky
W.A. Tiller	Westinghouse Electric Corporation Research Laboratories, Pittsburgh, Pennsylvania
D. Turnbull	General Electric Research Laboratory, Schenectady, New York

D.A. Vermilyea	General Electric Research Laboratory, Schenectady, New York
F.L. Vogel, Jr.	Bell Telephone Laboratories, Murray Hill, New Jersey
J. Washburn	University of California, Berkeley, California
W.W. Webb	Electro Metallurgical Company, Niagara Falls, New York
G.A. Wolff	U.S. Army Signal Research and Development Laboratory, Ft. Monmouth, New Jersey
C.F. Yost	U.S. Air Force Office Scientific Research, Washington, D.C.

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INTRODUCTORY LECTURE