INTERNATIONAL CONFERENCE ON CRYSTAL GROWTH

A Report by ***David Turnbull***

ALTHOUGH crystallization is a very familiar phenomenon the mechanisms whereby it occurs have proved to be subtle and difficult to establish. For this reason the subject has held great interest, both scientifically and technologically, for a long time.

Several years ago one of the key problems was: how can crystals bounded by low-index crystallographic planes grow at sensible rates in fluids at low supersaturation? At an earlier conference on crystal growth about a decade ago, Frank proposed as a solution to this problem his screw dislocation theory of growth. Frank's theory stimulated much experimental and theoretical activity and apparently was vindicated by many experiments. At the present time it is generally, though not unanimously, agreed that the theory does explain what it was supposed to explain.

More recently much of the activity in the crystal-growth field has focused on the following problems: the mechanism of growth of crystals into concentrated solutions and melts; the role of impurities in crystal growth; how do dislocations arise in crystal growth and how can dislocation-free crystals be grown; and the mechanism of crystallization of very complex molecules such as polymers. It seemed that the time was opportune for an international conference in which the main topics would be these and other crystal-growth problems. Therefore the US Air Force Office of Scientific Research, Air Research and Development Com-

David Turnbull, research associate at the General Electric Company's Research Laboratory in Schenectady, N. Y., is a co-editor, with R. H. Doremus and B. W. Roberts, of the promptly completed proceedings of the International Conference on Crystal Growth, which were published in the latter part of November by John Wiley & Sons, Inc., New York, under the title, *Growth and Perfection of Crystals* (609 pp., $12.50). Dr. Turnbull is also co-editor, with F. Seitz, of the widely known series of review volumes, *Solid State Physics*, published by Academic Press Inc.

Participants in 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
25. 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. M. 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

mand, and the General Electric Research Laboratory decided to sponsor such a conference jointly.

The conference was held August 27–29, 1958, at the Otesaga Hotel, Cooperstown, New York. The program was developed by a committee consisting of N. Cabrera, B. Chalmers, P. J. Flory, D. A. Vermilyea, and the writer. While the writer was on leave at Cambridge University during the period September 1957 to April 1958 the main tasks of carrying out the committee's recommendations were performed by Vermilyea. The Air Force representative, C. F. Yost, and B. W. Roberts gave valuable assistance on many arrangements.

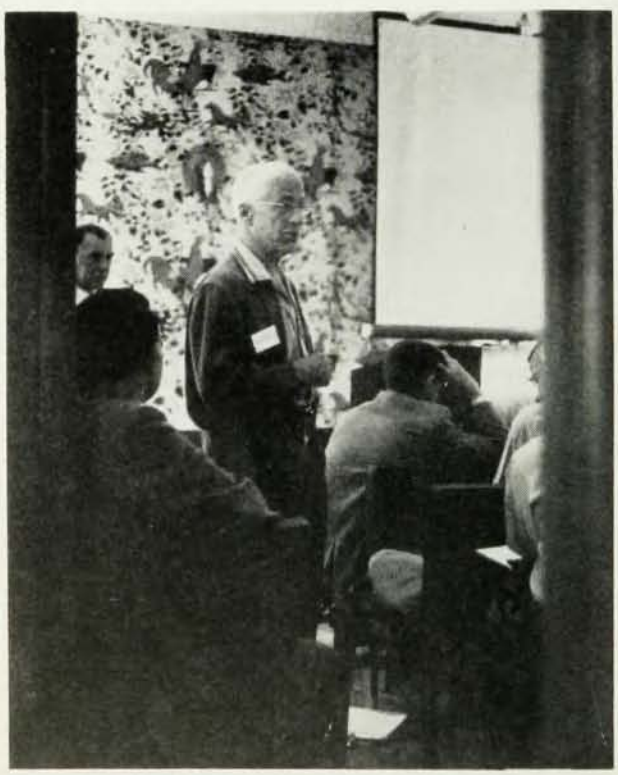
Participation in the conference was by invitation of the committee. Sixty-three scientists, including fifteen from overseas, actually attended.

In outline the program was as follows: I. Introductory Lecture (F. C. Frank); II. Growth of Whiskers; III. Properties of Whiskers and Crystal Imperfections; IV. Growth of Crystals of the Solvent Phase; V. Growth of Crystals of the Solute Phase; and VI. Crystallization of Polymers.

After Frank's introductory lecture each of the above main subjects was discussed in turn at a conference session (with the exception that two sessions were required for III). Each subject was introduced by a specially invited review paper (there were two such reviews on Crystallization of Polymers). Following each review a number of shorter papers describing, primarily, new results were presented. There was discussion following each presentation.

What follows is a summary of the personal impressions I gained from the papers and discussions about the status of important crystal-growth problems.

Above (left to right): J. W. Mitchell of the University of Bristol, D. A. Vermilyea of the GE Research Laboratory, and N. Cabrera of the University of Virginia.



J. H. Hildebrand, University of California at Berkeley, discussing a point on theory of liquids.

IT is especially appropriate 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 gave an account of the historical development of this subject leading up to our current understanding of it.

In connection with the perfection of crystals, relative to dislocations, there is great interest currently in the growth and properties of crystal whiskers (filamentary single crystals). A large number of papers and two and one-half conference sessions were devoted to this subject. Nabarro and Jackson presented a comprehensive review of the phenomena and theories of whisker growth. They pointed out that the existence of crystal whiskers has been known for centuries. However, it was only after the recent discovery at Bell Telephone Laboratories that some have mechanical strengths near those expected for perfect crystals that their unique properties came to be appreciated widely.

Whiskers can be formed in a variety of ways and plausible mechanisms have now been proposed for most of them. Most of these mechanisms have not yet been subjected to critical experimental tests. However, Gomer described field-emission microscopic studies that seemed to confirm for mercury the Sears mechanism, that whiskers grow from the vapor by the operation of a single-axial screw dislocation. Ellis, Gibbons, and Treuting described a new recrystallization mechanism for the formation of spontaneously extruded (from the surface of bulk material) whiskers.

Whiskers of a wide variety of materials (organic compounds, ceramics, salts, covalent crystals, and metals) now have been grown and studied. Irrespective of material type, certain specimens, usually those having a small diameter, exhibit exceptional mechanical strength. J. E. Gordon reported that alkali halide whiskers sometimes exhibit surprising ductility (up to 35% elongation) in tension at room temperature. S. S. Brenner pointed out in his review paper that, in addition to their remarkable mechanical properties, whiskers are often unique in other ways, such as in their magnetic, electrical, and surface behavior. For example, C. P. Bean and R. W. DeBlois have shown that the magnetic field required to reverse magnetic domains in certain regions of iron whiskers is within 10 percent of the theoretical value of ~ 560 oersteds and more than 500 times larger than the value for ordinary iron.

There was much discussion and some controversy on the question: are whiskers indeed free of dislocations, as might be inferred from their perfect crystal-like behavior, or do they contain dislocations that somehow do not react in the normal way to mechanical stimuli? The application of etch-pit, decoration, and x-ray techniques to the detection of dislocations in whiskers was described in several papers. From the results it appears that the dislocation content of whiskers is widely variable. Some whiskers apparently are free of dislocations, some have a single axial screw dislocation, and many, particularly the larger ones,

In photograph at left, Bruce Chalmers of Harvard University discusses growth from the melt; lecturer at right is K. A. Jackson, also of Harvard.

contain several dislocations. Just what is the connection between the dislocation content of a particular whisker and its properties is still far from clear. Some evidence was presented which indicates that the unique characteristics of whiskers are due to surface condition or perfection rather than to internal perfection. However, it was brought out that the properties of whiskers vary widely from specimen to specimen; thus the question of the relation between dislocation content and properties can only be settled by using the *same* specimen for perfection and property studies. Results of this kind are still too limited to permit any clear conclusion.

Several papers described mechanisms for the introduction of dislocations into crystals. Hirsch and Silcox described recent experiments in which dislocation loops, presumably formed by the precipitation of lattice vacancies from supersaturated solutions, were identified in aluminum and copper by means of electron microscopy. Mechanisms by which dislocations are produced in crystals during growth from the melt were presented in papers by W. A. Tiller and J. Washburn.

Recently methods have been developed for growing very large crystals of certain materials that are apparently entirely free from dislocations. W. C. Dash described methods of growing large (e.g., 5 cm long, 1 cm diameter) dislocation-free silicon crystals from the melt. Dash stated that ultrapurity does not seem to be a necessary condition for the success of the technique. J. W. Mitchell described a technique for producing large dislocation-free regions in silver chloride crystals. These regions are formed by strain energy motivated grain boundary migration.

There was much discussion and considerable controversy on the mechanism of crystal growth from the melt. The key to the problem is the nature of the liquid state and of the liquid-solid interface. In his review paper Chalmers stressed the similarities between the solid and the liquid states in the case of metals. However Hildebrand maintained that some important properties of liquids, particularly their kinetic behavior, are incompatible with the "latticelike" concept of the liquid state.

Frank pointed out that if the liquid-solid interface is "singular" (that is, there is a cusp in the Wulff surface-free energy diagram at the interface orientation) a screw dislocation mechanism should be necessary for its advance at small undercooling. If there is no cusp or even if it is replaced by a shallow minimum the interface is said to be nonsingular and screw dislocations should not be required for its movement. There is some evidence 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 mechanism of dendrite formation was discussed. The crystallography of dendrites seems fairly well understood; however the mechanism of branching is still obscure. Stranski reported on work of Hille, Rau, and Schlipf which showed variations in the crystallographic orientation of dendrite axes in salt crystals with supersaturation. These results were consistent with predictions based on the theory of nucleation of crystal monolayers.

Frank presented a new theory for crystal-growth forms resulting from dissolution. He used a mathematical treatment for the retreat of crystal steps during dissolution analogous to that used by Lighthill and Whitham to describe traffic flow. The dissolution forms of germanium are consistent with the predictions of the theory. Lighthill and Whitham's mathematics also was used by Cabrera and Vermilyea in treating the growth and dissolution of crystals in the presence of impurities.

One of the principal topics discussed in the session on "Growth of Crystals of the Solute Phase" was the role of impurities in crystal growth. It is well known that traces of certain impurities can have remarkable effects on both the growth rate and morphology of crystals. However, these effects usually were not specified

C. F. Yost (left) presents a "Cooperstown Gavel" to Conference Chairman David Turnbull. Seated (left to right) are P. J. Flory, Bruce Chalmers, and D. A. Vermilyea.

R. S. Bradley (University of Leeds), R. A. Laudise (Bell Telephone Labs), J. E. Gordon (Tube Investment Labs, England), P. J. Shlichta (Caltech), and D. M. Sweeney.

Above (left to right): D. Turnbull, D. A. Vermilyea, N. Cabrera, F. R. N. Nabarro (University of the Witwatersrand), and Mrs. Frank and F. C. Frank (University of Bristol).

quantitatively and the theories were highly qualitative. Now it appears that, with the sorting out of the role of imperfections in crystal growth, rapid progress is being made toward a more quantitative description and understanding of impurity effects. Price, Vermilyea, and Webb have analyzed kinetically the problem of concurrent impurity adsorption and crystal growth. On the basis of this they have been able to account semiquantitatively for the role of impurities in the growth of electrolytic whiskers. The treatment of impurity adsorption and crystal growth as competitive rate processes at the surface appears to have the potentiality, as Cabrera and Vermilyea explained, of illuminating other impurity phenomena as well. Although it was emphasized that there is still great mystery surrounding impurity effects there is good reason to hope that we are on the threshold of rapid advances in this field.

It appears that the exchanges of views between the polymer and other crystal-growth scientists at the conference were very useful. 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 pointed 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. Because of their molecular complexity, however, polymers rarely grow as isolated single crystals but rather as spherulites 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. Hence 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 I have not attempted to do justice to all the contributions individually. However, all together they made for a lively and stimulating conference.

The papers and discussions presented at the conference have been edited by R. H. Doremus, B. W. Roberts, and the writer. They have been assembled into a book entitled "Growth and Perfection of Crystals", published by John Wiley & Sons, Inc. In order to facilitate rapid publication the printing was done by the photo-offset process.