These developments are beginning to influence the attack on many complex industrial problems connected with extrusion and the like, just as earlier work on linear viscoëlasticity has had a pronounced influence on the resolution of many problems concerned with the processing of complex materials. Formulations now available are limited in at least two ways. First, they assume that only the first gradient of deformation need be considered, thus ruling out any influence of gradients of rotation, an a-priori assumption that has never been adequately checked. Second, all theories developed to the point permitting experimental evaluation assume incompressibility. The justification for this assumption, speaking somewhat loosely in linear terms, is that for systems usually employed in the study of nonlinear phenomena the shear moduli are very much less than the bulk moduli. This justification is recognized as a shortcoming of all such theories, but experiments suggesting how a better description could be included are only being initiated now.

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TWENTY YEARS OF PHYSICS

SOLID STATE

By JOHN M. ZIMAN

THE LAST TWO DECADES may well have been the era of solid-state physics. Certainly it has growed and growed; absolutely, of course, like all science and all physics, but also relatively to other fields. I guess it now occupies almost 40% of the family bed, instead of about 15% at the end of World War II. With its leading American and British exponents at the head of the National Academy of Sciences and in the Cavendish Chair, even the disciples of Rutherford are being forced to acknowledge its existence!

Excuse the impudence of trying to sum up such a vast amount of human activity. Intellectual history is notoriously difficult and always false. "No names: no pack drill" is a safe principle—and not inappropriate to a discipline that is not yet entirely dominated by the "star" system. Solid-state physics is too diversified, in subject matter, technique and scientific motivation, to be ruled by too few big names or to be corrupted by the lure of too many Nobel prizes. Let me write, instead, about trends and fashions, movements and achievements even though these only exist in the minds of tens of thousands of research workers and in the words and symbols of a hundred thousand papers.

A golden heritage

Surprisingly our era was not a period of rampant ideological revolution. Most of the basic concepts of the modern theory were already invented by 1945. The foundations of lattice dynamics (that is, *phonons*), of *electronic band structure*, of electron dynamics in crystals (for example, *holes* in filled valence bands) and of *spin waves* had been well laid in the 1930's as an immediate consequence of the discovery of quantum mechanics. It was already established practice to use *group theory* wherever possible; *many-body* effects associated with the electron–electron coulomb interaction were recognized; the *Ising model* for order–disorder phenomena was familiar; the analysis of imperfect crystallinity in terms of relatively well defined and stable entities called *dislocations* was already well understood by those who could understand that sort of thing.

Has our generation invented new concepts to match the power of these? I can think of only two really big and revolutionary ideas that have been both invented and come to fruition in our time. The first would be the *quasiparticle* concept. The "true" particles of any solid—atomic nuclei and electrons—are always interacting so forcibly that one would think that they must always merge their individuality with the crowd. Sometimes this process is so, as in lattice waves and plasma oscillations; but the solid often behaves as if it were merely an assembly of nearly independent entities with dynamical and electrical properties akin to those of ordinary particles. Something like this was divined by the pioneers, who treated metals very successfully as if full of free electrons. Many-body theory, leaning heavily on the methods of quantum field theory, has shown how to derive, justify and make quantitative this fruitful fudge.

The notion of a *pseudopotential* is not so deep but has also proved extraordinarily useful. The problem was to decouple the electrons from the fields of the ions of the crystal lattice; out of the strong must come weakness. The discovery that the algebra used in calculating electronic band structure could be rearranged to give results that did not depend very much

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SCREW DISLOCATION AND GROWTH SPIRAL in transparent silicon carbide. As crystal grows, the atoms form a spiral of constant step height, six molecules high.

on the detailed arrangement of the ions furnished us with a whole new kit of tools for calculating the electrical and dynamical properties of metals and semiconductors without excessive labor. This concept is actually not standing up very well to rigorous mathematical analysis, but that is not a sufficient reason for abandoning it when it works well.

Of course there has been continual technical development of the older ideas. Mathematical fictions hidden in obscure theoretical papers have become the physical realities of everyday conversation in experimental laboratories; we juggle with *phonons* and *carriers*, *magnons* and *excitons*, *dislocations*, *jogs* and *stacking faults*, and devise techniques to isolate, purify and visibly observe them. Perhaps we have already manufactured other theoretical concepts that will similarly become part of our physical "intuition." It is difficult to know whether simple ideas such as *flux quantization* in superfluids or intellectual subtleties such as the notion of *broken symmetry* will come out of their homesteads into wider circulation. Nor can we be sure that the highbrow apparatus of *Green's functions* and diagrammatic series, which has provided analytical justification for more naive points of view, is destined to replace our old friend the Schrödinger equation as the natural language of the subject. Such trends are often self generating. To quote Marcel Proust: "It was Beethoven's Quartets themselves . . . that devoted half a century to forming, fashioning and enlarging a public for Beethoven's Quartets, marking in this way, like every great work of art, an advance if not in artistic merit at least in intellectual society, largely composed today of what was not to be found when the work first appeared, that is to say of persons capable of enjoying it."

Our era has certainly demonstrated that there is plenty of scope within solid-state theory for those who enjoy constructing elaborate formalisms; some who feast heavily at this table do not always repay their hosts by genuine contributions to practical knowledge. My impression is that, until recently, solid-state theoreticians were such rare birds that they were forced to converse with their experimental colleagues. By gathering in larger flocks, they begin to address their papers only to one another, and thus become as alienated from the matter of their science as schools of pure mathematics or Babylonic cuneiform.

On the other hand, mere arithmetic, however rapidly performed, has not solved many problems. The genius of the subject is judicious approximation. There are still surprisingly few situations in which the details of geometry, forces, fields and wave functions are sufficiently accurately known for a lengthy computation to pay off with good numbers. With Brute Force goes, as the proverb has it, Ignorance. . .

Not Greece, but Rome

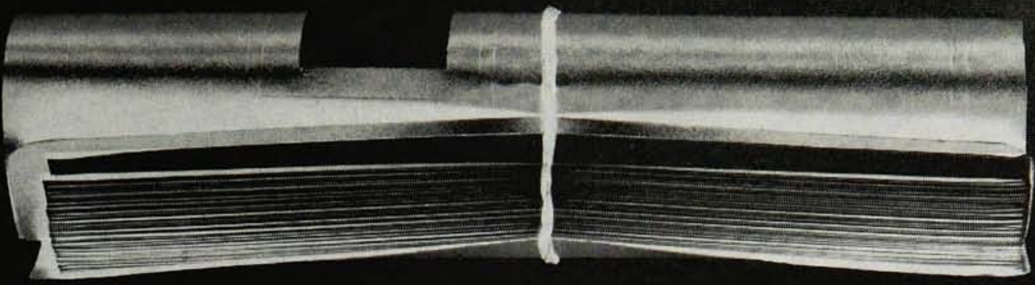
This epoch was, if not intellectually revolutionary, certainly a period of enormous technical progress. A number of entirely new experimental and observational methods have grown to maturity since the war and have vastly enlarged our knowledge of the solid state.

For example, production of bulk liquid helium has transformed *low-temperature physics* from a specialized technique, practiced in only a few laboratories and concerned mainly with the exploration of the "properties of matter" under extreme conditions, into an ordinary piece of laboratory apparatus used to study phenomena under the simplified circumstances where thermal vibrations are stilled.

Similar freedom from extraneous interference is achieved with very *pure* and *perfect crystals*. New techniques for crystal growth, such as *zone refining* and "pulling" from the melt, were needed originally in the fabrication of germanium and silicon semiconducting devices, but they have profoundly altered the solid-state physicist's attitude to the objects of his regard; for they allow the observation of phenomena that would otherwise be completely obscured by the scattering of electrons or phonons from static impurities and imperfections.

As in all branches of science, *electron microscopy* has revolutionized the study of crystal imperfections. Until the mid 1950's, dislocations were almost unobservable hypothetical entities invented by armchair theorists to explain the complex phenomena of plasticity; seeing them being produced, running about, jogging each other, piling up, getting pinned, etc., has transformed this empirical branch of physical metallurgy into a "first-principles" discipline.

The development of *microwave* radar during the war also had immense consequences for solid-state physics. A strong magnetic field in a resonant cavity is an ideal milieu for tickling up the spins and orbital motions of electrons and nuclei in solids, with measurable consequences of such complexity as to demand whole tomes of explanation. At first this technique was applied mainly to relatively isolated nuclei or atoms, in crystals di-



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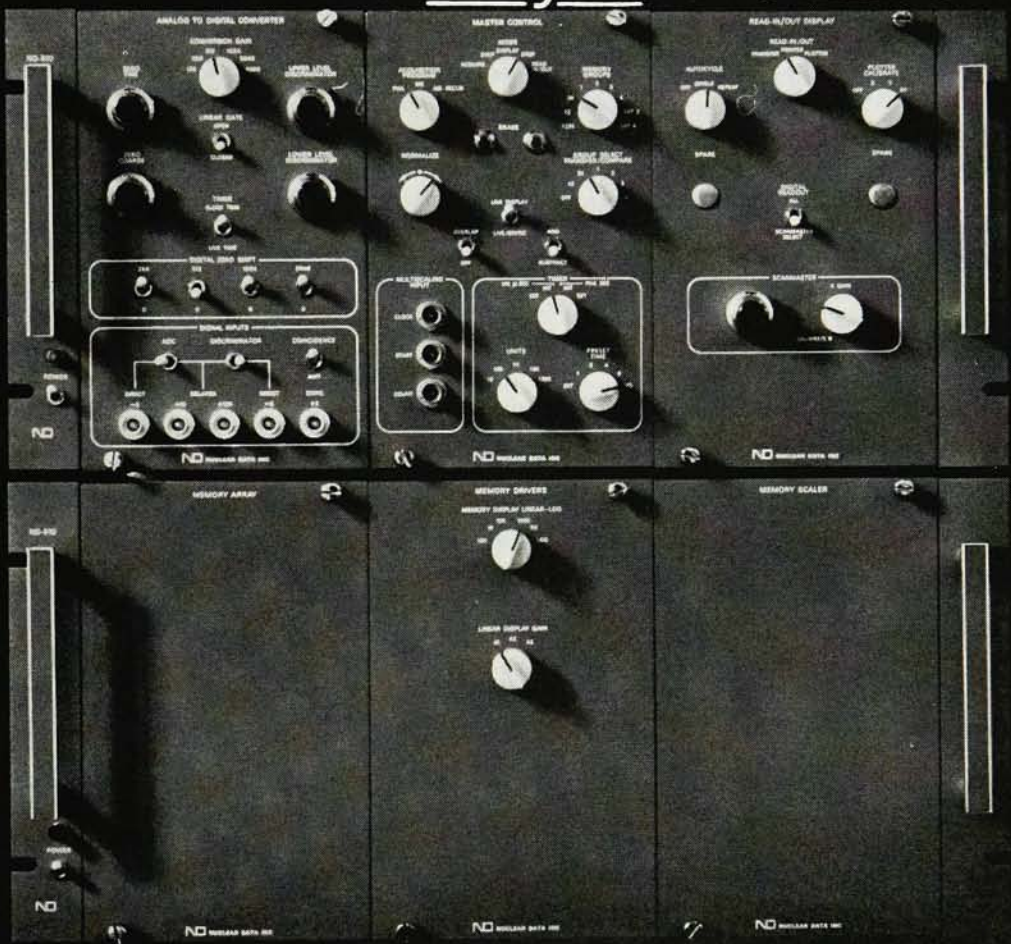

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1330 E. GOLF ROAD, PALATINE, ILLINOIS 60067 PHONE 312/529-4600 NUCLEAR DATA INC., GMBH, FRANKFURT, GERMANY luted with much water of crystallization, but we have now learnt to resonate with the elementary quasiparticle excitations of the solid as a whole, such as electrons, "holes" and "magnons."

Finally I would mention *inelastic neutron diffraction* as a technique that is slowly rewriting our knowledge of the dynamical motion of atoms in solids. Given a high flux of thermal neutrons, careful instrumentation and plenty of time, one can unscramble the lattice spectrum mode by mode and also look at complicated magnetic structures and spin waves. The dream of 50 years ago, that one could discover the forces between atoms by analyzing lattice vibrations, is now realizable in practice.

Improvements in conventional laboratory techniques have also opened up new fields: Consider, for example, the precision and sensitivity now available in infrared spectroscopy, calorimetry or x-ray diffraction. They also make orthodox solid-state physics vastly more expensive. Except with neutron diffraction, we are not yet Big Science on the Gevavolt–Megaton–Gevabuck scale, but it requires a touch of inspiration to get publishable results without apparatus in the $10 000 range. Unfortunately two modern phenomena that can be observed cheaply—positron annihilation and the Mössbauer effect—have turned out to be difficult to use quantitatively in the study of the solid state itself. Yet the field of phenomena to be explored and charted is endless: Freeze a beakerful of water; can you understand everything you see?

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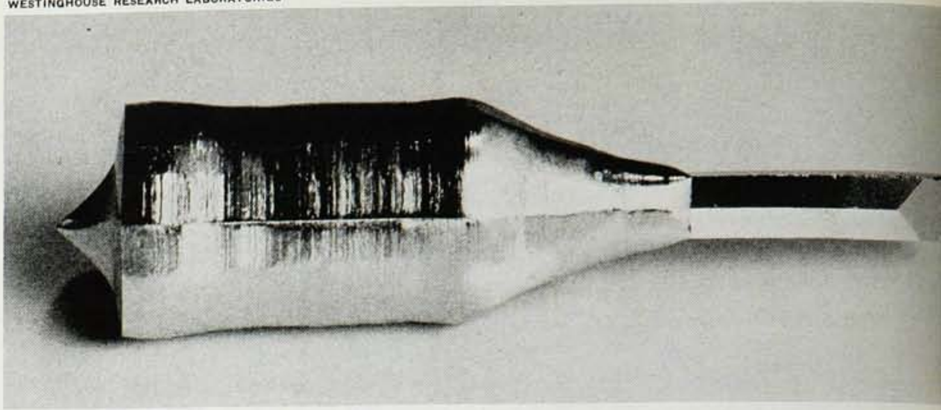

GERMANIUM BICRYSTALLINE INGOT, showing edge of {221} boundary.

Everest conquered

With our new experimental and theoretical techniques, what have we learnt? The most important discovery of the epoch was undoubtedly the explanation of *superconductivity*. For half a century this mysterious state has been a subject of intensive research. By the end of the 1930's many of the macroscopic properties, such as the expulsion of magnetic flux, the variation of critical temperature with magnetic field, the nature of the intermediate state, etc., were quite well known. After the war, improvements of cryogenic technique and microwave spectroscopy elucidated some further subtle properties but did not provide a basic theory. An important step was the recognition of the electron–phonon interaction as the fundamental mechanism, but the last 1000 feet could only be climbed with oxygen: Field theoretical methods facilitated construction of new quantum states of the many-body system of interacting electrons and phonons, and the demonstration that these corresponded to a stable condensed state (the "superfluid") with quasiparticle excitations of finite energy above it.

Following the success of this brilliant theory, superconductivity has been, for the past decade, the favorite son of our subject. Many new phenomena such as flux quantization, coherent tunnelling and Type II superconductivity have been discovered, and the periodic table has been explored thoroughly for new superconductors. The theory has been so developed that I sometimes think we know more about the superconducting state of many materials than we do about the so-called "normal" state. By a reasonable convention, the study of *superfluidity in liquid helium* at very low temperatures is considered part of solid-state physics, and this too has now been explained qualitatively, although the quantitative calculation of observable parameters in these systems is by no means easy.

An entirely unexpected discovery was that of superconducting materials that can retain their vanishing electrical resistivity in magnetic fields of 100 kilooersteds or more. Use of these materials in powerful magnets for bubble chambers, magnetohydrodynamic rigs, thermonuclear reactors and other expensive toys is only at its beginnings. All who have had faith in serendipity and in the potential applicability of all science, however pure, have been heartened by this success, and the hunt is on for a material that remains superconducting at room temperature (for instance). Good hunting to them, say I, provided they do not call "Tally ho!" prematurely; for wild geese have been augured in that quarter.

Making better mousetraps

Superconductivity was mysterious and only observable under extreme conditions; *semiconductivity* was well understood in principle, and quite common, so it was not nearly so closely studied! Until the famous researches that earned a Nobel prize and elucidated the role of minority carriers, the properties of p–n junctions, transistor action and other interesting effects, semiconductors were not given the attention they deserved. That heroic episode occurred at the beginning of our epoch and has been one of the main causes for the enormous expansion, in money and men, of our discipline.

There is no need, in this magazine, to emphasize the astonishing virtuosity of the practitioners of the new art of solid-state electronics; they can shrink a camel-sized computer until it can pass through the eye of, well, a darning needle; with a tiny crystal of semiconductor, ferrite, ferroelectric or superconductor they can measure, create and control heat, light, sound and electricity; their devices are perfectly robust, infinitely flexible in use and capable of endless refinement. This is the era of solid-state physics; we do not know when it will end.

Moreover the advancement of the practical art has gone along with serious study of the fundamental physics of the phenomena involved. To construct that ideal medium in which carriers, phonons, magnons, photons and other entities interact in desirable ways, we need to know a great deal about the electronic band structure, lattice spectrum, mobility, dislocation density, impurity levels, trapping centers, etc., of the material. There is no doubt at all that the sustained effort to acquire this knowledge, required for practical use, has uncovered many new physical phenomena, clarified many hazy ideas, motivated the development of many new experimental techniques, and set a standard of scientific precision that was previously lacking in this field. Even if many of the phenomena exploited in semiconductor devices are somewhat contrived and do not tell us very much about the microtheory of the solid state, the fact that expensive factory production can depend on correct measurements of basic parameters gives us some assurance that these will be observed with care. One must surely rejoice to see one's academic pursuits so closely linked to the real world of things to make and things to do.

Making maps

Low-temperature microwave spectroscopy, perfect crystals and pseudopotentials were the recipe for another major development—the exploration of the *Fermi surfaces* of metals. As I have remarked, the idea of representing the electronic properties of a metal by the shape of the constant-energy surface enclosing the occupied states in momentum space dates back to about 1930, but attempts to calculate these surfaces from first principles were dismally unsuccessful. The trouble was that these calculations could not be checked backwards for errors and omissions because the observable properties deduced from them were only simple scalar or tensor quantities like electrical conductivity or Hall constant. I can think of only one prewar set of observations—the magnetoresistance of some metal single crystals at helium temperatures—that contains enough "bits" of information to tell us directly about the Fermi surface.

But in the late 1950's a number of different phenomena were suddenly shown to depend very sensitively on various geometrical parameters of the Fermi surface, and hence could be transformed into new techniques of observation. Thus the *anomalous skin effect* "measures" an average curvature, the *de Haas–van Alphen effect* an area of cross section, the *magneto-acoustic effect* a caliper diameter, etc., of this purely hypothetical mathematical construction. It became possible, by a series of careful experiments, to build up the whole diagram on which all other electrical properties of the metal should depend.

The very first complete Fermi surface was, in fact, so surprisingly different from our expectations that some of the best theorists had to think very hard about what it signified, and had to recall some of those fundamental properties of electron states in crystals that everyone was supposed to know but had almost forgotten. The concept of a multiply connected Fermi surface was not new, but our imagination had not grasped its potentialities.

The data came pouring in and would have saturated the input channels if the pseudopotential concept had not turned up, and it was discovered that most metals had nearly free-electron Fermi surfaces after all. Nowadays the mapping of a Fermi surface is a relatively routine operation, and suitable candidate metals are getting rarer; this is a pity since various techniques by which the whole research could be conducted far more efficiently are continually invented. However, almost all these techniques only measure at the Fermi level in pure, perfect crystals, at low temperatures. There is enormous scope for further in-depth exploration of the electronic band structure in alloys, amorphous solids, etc., with optical, x-ray and photoemission methods.

Meanwhile perhaps we have learnt to be cautious about going off on a spree of computation without sufficient moorings of experimental information. In this branch of solid-state physics we may believe with justice that we understand all the phenomena "in principle," and yet a large technical step must be taken before one can confidently proceed to quantitative predictions.

Bush whacking

The study of *crystal imperfections* is still in a much more primitive stage of development. The dislocation concept explained the weakness of real crystals, and at the beginning of our two decades it was also shown to be the key to the mechanism of crystal growth. But without the means to observe dislocations in action, it was possible only to guess at the events within the crystal when the material was plastically deformed, hung, drawn and quartered, broken on the rack, work hardened, or allowed to creep away. How were dislocations produced and multiplied; how fast could they move; how do they interact with one another and with impurities, vacancies, interstitial atoms, grain boundaries and other types of imperfection? Some excellent hypotheses were put forward—but also some overconfident interpretations based on purely conjectural configurations and interactions.

The direct observation of dislocations by electron microscopy and other means has brought this speculative phase to an end. On the other hand, it has demonstrated the enormous complexity of the phenomena as they really are. Trying to explain a stress–strain curve by a back-of-envelope calculation may be too naive; merely to *describe* all the creepy-crawly creatures to be seen in an electron micrograph of a thin film of stainless steel is beyond our analytical powers. In this field, as in the cognate study of *radiation damage*, we may expect only step-by-step progress, without spectacular single discoveries (although the focusing collision phenomenon is very pretty) but patiently building up a body of reliable knowledge based on sound evidence.

Fortunately there are enormous financial interests behind such studies; goodness knows how many million dollars it is worth to know what really happens to graphite in a power reactor—and metals can get fatigued at alarming rates in expensive aircraft. We may even be on the verge of another technological revolution. The next two decades may well be the epoch of "Materials Science," where the deliberate design of fibrous mixes, alloys and ceramics may transform mechanical and civil engineering on the same scale as solid-state physics has transformed electrical and electronic engineering.

Unfinished business

I have discussed a few of the major achievements of solid-state physics:

I could have mentioned many other topics such as *magnetism*, the properties of *ionic crystals*, the study of *surfaces* and *thin films*, the prediction and detection of *plasma modes*, the theory of *order–disorder phenomena* and so on that have developed almost beyond recognition in the past 20 years. But complacency is our vice; so let us notice that some problems have remained manifestly obdurate.

For example, the basic theory of *ferromagnetism* in metals has not significantly advanced since the war. Yes, I know that a lot of hard work has been done, many new hypotheses hypothecated, and all sorts of formalisms formulated, but we still seek a procedure for describing the d electrons in iron, both as free, to share in the band structure, and as localized, with strongly interacting spins.

Again the attempt to calculate the *cohesive energy* of metals has scarcely been carried beyond the first column of the periodic table. It is not just a question of using the right gimmick for the exchange and correlation energy of a free-electron gas; the chemistry of ions themselves plays a role here that we scarcely comprehend. As for thermodynamic properties of *alloy phases*, these are altogether beyond the reach of current theory. Man has known for several millenia how to mix copper and tin to make bronze—but why, why, does this work so well?

Melting, now, and the ordinary *liquid state*—these are not understood in any quantitative manner. We do not have an adequate language to describe the "structure" of amorphous materials such as glasses and ceramics; we talk glibly of "local order," or else we construct a hierarchy of *N*-particle correlation functions and hope for the best. Even pure mathematicians might find "statistical geometry" rather fun.

But much simpler properties of almost perfect crystals have never been calculated quantitatively from first principles: the thermal conductivity of sodium chloride, the electrical conductivity and thermoelectric power of copper, the superconducting transition temperature of lead, the melting point of mercury, the diffusion coefficient for vacancies in sodium. One may find recipes for calculation of most of these properties in books published before the war, but we still await a cook who can handle all the ingredients. Perhaps it is better to travel hopefully than to arrive! □

TWENTY YEARS OF PHYSICS

STRUCTURAL CRYSTALLOGRAPHY

By JAMES A. IBERS

THE INFLUENCE of structural crystallography on physics, chemistry and biology is now far greater than it was 20 years ago. By the late 1930's crystallographic studies had laid the groundwork for interpretations of many phenomena of the solid state by providing detailed information on the metric aspects of simple molecular and crystal structures. But 20 years ago the chemist, let alone the biologist, would not come to the crystallographer for the determination of a complex structure. Structures, some of them complex, were being solved then, but the process was slow, uncertain and arduous. Structures were simply not being solved within the attention span of physicists, chemists and biologists, and there is no reason to suspect that that span was longer in those days than now. For the history of x-ray diffraction and personal reminiscence see P.P. Ewald, *Fifty Years of X-Ray Diffraction*, Utrecht 1962.

The table attempts to summarize some of the developments in structure solving over the past two decades. It is apparent that more complex structures are now being solved more rapidly and more accurately than in 1948. Without question, the fast digital computer has been the major factor in improving the effectiveness of structural crystallography in the last 20 years.

Application of computers

The necessary computations are highly repetitive and time consuming. The three-dimensional Patterson function, still the mainstay in the solution of the phase problem, is essentially a three-dimensional Fourier summation of a few thousand terms, in which the function is evaluated at 60 000–100 000 points (PHYSICS TODAY, January 1965, page 28). That this calculation required 40 hours of constant attention to card sorters, tabulators and collators in 1948 and that it can now be performed on new-generation computers, such as the CDC 6600, in less than five minutes is a dramatic example of the influence of the computer on structural crystallography. The time-consuming computations of crystallography, such as the least-squares refinement, are central-processor bound, which is another way of saying that the crystallographer can expand to tie up almost any machine, and that he eagerly looks forward to the next generation of computers.

Another application of computers to crystallography is the presentation, in two dimensions, of results about the three-dimensional structure. This problem has been elegantly solved by Carroll K. Johnson and others who have produced computer programs that enable one to draw stereoscopic views of crystal or molecular structures directly on the plotter attached to a fast computer.

When structures could finally be refined properly, it became apparent that the scattering model was not sufficiently good. Among the various aspects of the model that have been improved in the past 20 years are better atomic scattering factors (dependent