CRYSTALLOGRAPHY

By James A. Ibers

The annual meeting of the American Crystallographic Association (ACA) was held July 24-31, 1964, on the beautiful campus of Montana State College at Bozeman, Montana. Approximately 400 crystallographers, over thirty percent of the membership of the ACA, took an active part in the meeting. Of the 170 papers of 15-minutes duration, about 50 were presented in single sessions, and the rest were distributed between two simultaneous sessions.

It would be impossible for one individual to understand all of the papers, at least in sufficient detail to analyze them in an article such as this, even if it had been possible to hear them all; nor is it likely that the reader would appreciate such an analysis. Rather, I shall attempt to present for the nonexpert in crystallography a view of the current trends in crystallographic research as reflected by the meeting. With a few exceptions I shall not discuss individual work in any detail, nor will I even cite a significant fraction of the papers presented. For those who wish more details on this and earlier ACA meetings, programs and abstracts are available from Polycrystal Book Service, PO Box 620, Brooklyn 1, New York.

Perhaps ninety percent of the papers presented at this ACA meeting were related to techniques —experimental, theoretical, or calculational—involved in the determination of crystal structures from diffraction data or to the results of such determinations. The remaining papers were on a variety of topics such as imperfections, crystal growth, phase transitions, and x-ray physics. Because of this distribution, this report will concentrate on the determination of crystal structures, and other topics will be mentioned only briefly.

In order to make such a discussion meaningful, it is well to summarize the steps involved in the determination of a crystal structure. The object of a crystal-structure determination, as reflected in the efforts of the majority of active participants at the ACA meeting, is to determine the positions of all of the atoms in the unit cell, or translational building block, of a presumed completely ordered three-dimensional structure. In some cases, additional quantities of physical interest, for example the amplitudes of thermal motion, may also be derived from the experiment. The processes involved in such crystal-structure determinations may be divided conveniently into (1) collection of the data, (2) solution of the phase relations among the scattered rays (phase problem)—determination of a correct trial structure, and (3) refinement of this structure.

The data consist of intensities $I(hkl)$, where h, k, and l (the Miller indices) represent a vector triplet which conveniently identifies the beam diffracted from a single crystal. In a typical determination, there may be one to two thousand such $I(hkl)$. The intensity is related to the structure factor $F(hkl)$ by the relation,

$$I(hkl) = K\,F(hkl)\,F^*(hkl), \qquad (1)$$

where K is a known, relative factor, and where F^* is the complex conjugate of F. The structure factor itself is related to the scattering by the j atoms in the unit cell by the relation,

$$F(hkl) = \Sigma_j f_j T_j \exp[2\pi i(hx_j + ky_j + lz_j)], \qquad (2)$$

where f_j are the individual atomic scattering fac-

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tors, T_j are the individual modifications of the scattering as a result of thermal motion, and x_j,y_j,z_j are the fractional positions of atom j along the three crystallographic axes. In a typical determination, j may be between 10 and 60. The scattering density $\rho(xyz)$ is derivable from the relation,

$$\rho(xyz) = V^{-1} \sum_{-\infty}^{\infty}{}_{h,k,l} F(hkl) \exp[-2\pi i(hx + ky + lz)], \quad (3)$$

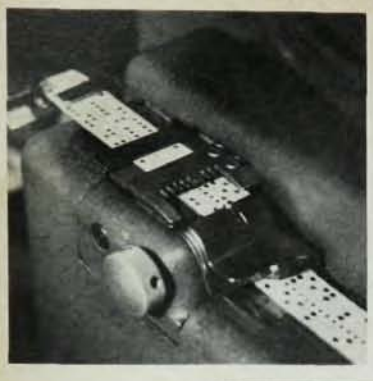
where V is the volume of the unit cell.

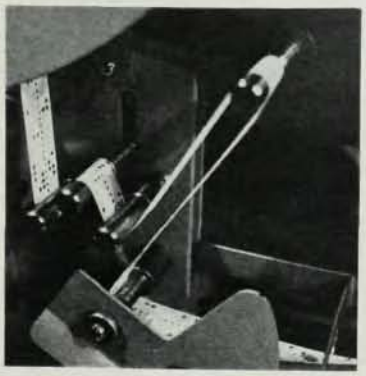
The famous "phase problem" in crystallography arises because in the usual experiment—eq. (1)—the magnitudes of the complex structure factors are obtained, but not the phases. Yet in order to obtain the scattering density, and hence the positions of the atoms, the phases as well as the magnitudes of the structure factors are necessary —eq. (3).

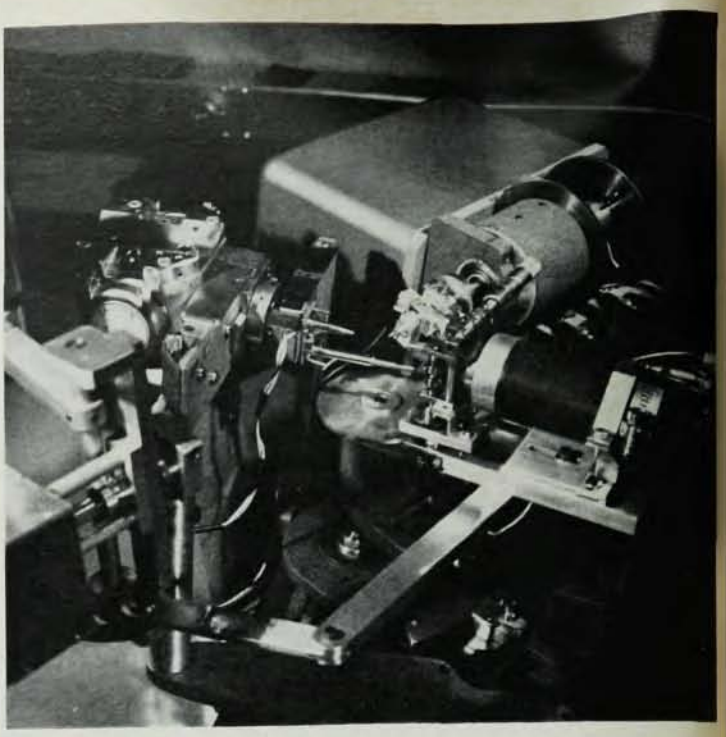
Once the phase problem is solved, then the positions of the atoms may be refined by successive structure-factor calculations—eq. (2)—and Fourier summations—eq. (3)—or by a nonlinear least-squares procedure in which one minimizes, for example, $\Sigma\ w(|F_{obs}| - |F_{calc}|)^2$, with weights w taken in a manner appropriate to the experiment. Such a least-squares refinement procedure presupposes that a suitable calculational model is known.

It is perhaps useful to indicate how the attention of crystallographers to these three steps in the solution of a structure has changed in the past decade. In 1954, the time involved in the arduous task of collecting the three-dimensional data—step (1)—needed for the solution of a complex problem was generally short in comparison with the time needed to solve the phase problem —step (2). This time involved in step (2) of course depended (and still depends) upon the complexity of the problem, and on the ingenuity, luck, and perseverance of the investigator, but it was true in many cases that step (2) was the rate-determining step in the entire process. This in part was because little attention was paid to detailed refinements —step (3); in 1954, three-dimensional least-squares refinements of complex structures were out of the question computationally, and even Fourier refinements were rare, for on computing systems advanced for those days (e.g., IBM punched-card tabulators, sorters, and primitive electronic computers), a three-dimensional Fourier summation might require forty man-hours (or more probably graduate-student hours). In fact, in 1954 it was usual for the crystallographer to examine the unit cells of a number of related substances and to pick the problem that was crystallographically most favorable (and perhaps soluble from two-dimensional data), even though this problem might not be the one of greatest chemical or physical interest. Ten years later the situation has changed markedly, mainly because of the availability of high-speed computers. It is still true that there are classes of problems where step (2) is rate-determining, but these problems are far more complex than those attempted in 1954. Yet there is an extensive class of problems in which today the solution of the phase problem is straightforward and rapid. The crystallographer is thus often working on the problem of greatest chemical or physical interest, and is able to obtain a solution in times commensurate with the attention-spans of chemists and physicists. Relatively complete refinement of structures is now the rule, since it is a reasonably fast and effortless procedure. Thus it turns out that in many crystallographic problems the rate-determining step is data collection. For this reason, there has been a dramatic increase in interest in ways of making data collection less tedious, more rapid, and more accurate, and this interest was most evident at the ACA meeting.

Although in the early days the Braggs and others used ionization chambers for the collection of x-ray intensities, these methods were gradually abandoned in favor of photographic film techniques. Up until a few years ago the great majority of structure determinations were based on photographically recorded intensities, usually visually estimated. This process is a slow one: the typical time involved in the collection and estimation of a data set of two thousand intensities is perhaps six to eight weeks. Collection of intensity data from protein crystals is far more challenging and time-consuming, both because the number of data to be collected is far greater and because the crystals are unstable and rapid collection is thus desirable. For these reasons, Harker and his coworkers, particularly Furnas, then at Brooklyn Poly, were among those instrumental in developing scintillation-counter methods for collecting three-dimensional x-ray data. Diffractometers with single-crystal orienters, based on the so-called Eulerian geometry developed by Harker and Furnas, as well as on the more conventional Weissenberg geometry, have become available commercially in the last few years and have engendered widespread interest in counter techniques. Data collection by counter techniques, as practiced by most workers, is still an arduous task, since the setting of a number of orientation angles is involved. Program or computer control of such set-







ting operations is an obvious extension. Especially for neutron diffraction studies, such programmed control of diffractometers has been the rule for some time, with units operating at Oak Ridge, Brookhaven, Argonne, and Harwell. Although these units were not commercial ones, a number of firms are just beginning to market program-controlled x-ray diffractometers. Nevertheless, a programmed unit will do only what it was designed to do, whereas a computer can be programmed to perform new tasks or operations as they seem necessary. At the 1964 ACA meeting there were several reports on operating or projected computer-controlled diffractometers. Cole and Okaya (IBM) described the operation of their diffractometer, which is run on-line by an IBM 1620. Even with elaborate checks on background, crystal orientation, peak shape, etc., they are able to collect automatically about 2400 reflections a month. Thus, assuming the phase problem is not a serious one for their structures, they are able to make a complete and accurate structure determination each month. This is, of course, a somewhat expensive system, and it is still not clear whether the advantages of computer control over program control are sufficient to warrant the added expense. On the other hand, Hamilton (Brookhaven) described a projected system for the control of nine diffractometers on a time-shared basis from the same on-line computer. The expense involved is not vastly different from that required for the construction of nine individual program units, and yet the advantages of computer control will be realized.

Thus far, we have emphasized the fact that counter methods, particularly when semiautomatic or completely automatic, enable more rapid data collection than is possible photographically. What is equally important is that they should also enable more accurate data to be collected. The general level of accuracy of intensities obtained photographically is perhaps 15 to 20 percent. Such a level has proved sufficient for the solution of conformational or stereochemical problems, but not necessarily for the determination of meaningful descriptions of thermal motion or bonding. Thus the crystallographer is vitally interested in more accurate data collection, and the problems of doing this with counter techniques have been tackled by a number of workers. One of the major problems is how to handle background radiation; the eye is a marvelous discriminating device and is capable of fairly accurate intensity estimation over regions of widely varying background. A counter, of course, counts signal and background simultaneously and methods must be developed to minimize the errors introduced by background. There is still no general agreement on such methods. Abrahams (Bell) has consistently emphasized that there are many subtle problems that must be solved before we can be assured that our intensity measurements are as accurate as they seem precise. A

Programmed x-ray diffraction apparatus for automatic determination of crystal structure receives punched-tape instructions, carries out measurements, and records data on output tape.

this ACA meeting he was joined by others on this point. There are many questions whose answers are not generally agreed upon: What is the best geometry for data collection? Should one minimize the background problem by monochromatization of the incident radiation, or through some sort of filter system? What is the best x-ray source for intensity measurements? What source stability is needed? How can one put intensity measurements on an absolute scale? How can one be sure the optics in the experiment are proper? These and other questions remain, although many of those with experience in the collection of data by counter methods (Abrahams and Burbank of Bell Laboratories, Alexander of Mellon, Furnas of Picker, Harker of Roswell Park, Ladell of Philips, Templeton of California, Young of Georgia Tech, to name just a few) contributed papers on various aspects of the subject and also contributed to what can perhaps best be described as an exciting and at times unruly discussion.

Answers to some of these questions may come from the Single-Crystal Project, organized by Abrahams, who is chairman of the Apparatus and Standards Committee of the ACA. Selected single crystals will be distributed to various workers who will measure the intensities of particular reflections in the manner they prefer. The results of these various experiments will be subjected to careful analysis. A similar project a few years ago, which dealt with the precise measurement of lattice constants, revealed that individual estimates of accuracy are extremely optimistic!

It is currently possible to measure intensities with counter techniques much more rapidly and with little or no sacrifice of accuracy over photographic techniques. Despite the current uncertainties concerning the preferred techniques for the collection of accurate intensities, there is every reason to believe that in the near future x-ray intensities will be measured much more accurately than has been possible. This should lead to the derivation from diffraction data of reliable physical information of great interest on such phenomena as thermal motion and bonding.

The counter methods of intensity collection mentioned here are serial in nature. MacIntyre of the University of Colorado described the concept of a parallel machine in which the detector is a wire-wound spark chamber with about 15 000 counting elements. These elements could readily be connected to a computer memory. The system might ultimately be capable of collecting the complete diffraction pattern of any crystal in a few hours! Whether or not such a device can be developed in a practical way remains to be seen, but obviously effort in this direction is to be encouraged.

Step (2) in the process of structure determination, namely the solution of the phase problem, continues to occupy the efforts of a number of crystallographers. This is natural, for the phase

problem is central in modern crystallography. Moreover, there are still many "equal-atom" structures of great physical or chemical interest that present severe challenges to the investigator using current methods of finding trial structures.

There are two approaches to the solution of the phase problem that have remained in favor. The first is based on the tremendously important discovery of Patterson in the 1930's that the Fourier summation of eq. (3), with the experimentally known quantities $F^2(hkl)$ replacing $F(hkl)$ leads not to a map of scattering density, but to a map of all interatomic vectors. The second approach involves the use of so-called direct methods developed principally by Karle and Hauptman of the US Naval Research Laboratory.

The Patterson function has been the most useful and generally applicable approach to the solution of the phase problem, and over the years a number of ingenious methods of unraveling the Patterson function have been proposed. Many of these methods involve multiple superpositions of parts of the map, or "image-seeking" with known vectors. Such processes are ideally suited to machine computation. Whereas the great increase in the power of x-ray methods of structure determination in the past few years has come simply from our ability to compute a three-dimensional Patterson function, it is reasonable to expect that as machine methods of unraveling the Patterson function are developed, this power will increase many fold. Numerous workers, including Jacobson now of Iowa State, Kraut of La Jolla, and Hamilton of Brookhaven, have described practical methods for computer interpretation of Patterson functions. At the 1964 ACA meeting, Jacobson gave a particularly interesting illustration of how one can take advantage of the logical structure of the computer to make very rapid bit-by-bit comparisons (or superpositions).

Equally impressive at this meeting was the work of Nordman of Michigan and Stout of Washington on the unraveling of the Patterson function (by use of a computer) when a part of the molecular configuration is known or can be guessed at. Nordman has developed powerful methods of rotating and translating the known vector set in order to find the best fit to the Patterson function. Thence the other vectors can be determined. In the particular illustration given by Nordman, the relative orientation of only 8 atoms out of 22 were known, and yet the trial structure was found readily.

The direct method of phase determination makes use of probability theory to give probable relations between phases of different structure factors. At the meeting, Hauptman discussed the incorporation of a priori knowledge about the structure to make these direct methods more powerful. Karle discussed the use of such direct methods in the solution of complex noncentrosymmetric crystal structures. It has been clear for some time that these direct methods are useful and powerful, and their use should become more widespread as the computer programs developed by Karle and Hauptman are distributed to others. Whether or not such methods in principle provide information that is not derivable from the Patterson function remains a point of some discussion.

Step (3), the refinement of crystal structures, continues to enjoy a considerable amount of interest. Reasonably complete refinement is routine these days, owing in large measure to the availability of suitable computers. For reasons that are both practical and mathematically sound, the least-squares approach to refinement has gained favor over the successive structure-factor—Fourier approach. Yet the computational problems often tax this generation of computers. If one assigns a single isotropic thermal parameter to each atom, then there are four parameters, three positional and one thermal, to be determined for each atom. In the least-squares procedure, if one stores the upper right triangle of the normal-equations' matrix, then $\frac{1}{2}N(N+1)$ elements are required, where N is the number of variables. In a machine with a memory of 32 000 words, a practical limit is reached at about $N = 200$, if one wishes to keep the rest of the program in core. Thus refinement of a 50-atom problem often taxes the memory capacity of the machine, and for larger problems special computational or mathematical tricks are needed. One of these tricks is to make use of known features of the structure or the thermal motion to reduce the number of parameters. Ibers of Brookhaven discussed the use of rigid-body refinements, in which certain features of the structure (e.g., phenyl rings) are constrained to their well-known geometry. The reasons for this, in addition to reducing the number of variables with consequent decrease in computing time, are that convergence can be achieved from a less-accurate trial structure, and, perhaps most important, the elucidation of an unknown aspect of the structure may suffer less from correlation with errors of assumption than it would from correlation with experimental errors of measurement for the alternative full determination. The most sophisticated description of the thermal motion of atoms in use by crystallographers is still naive and

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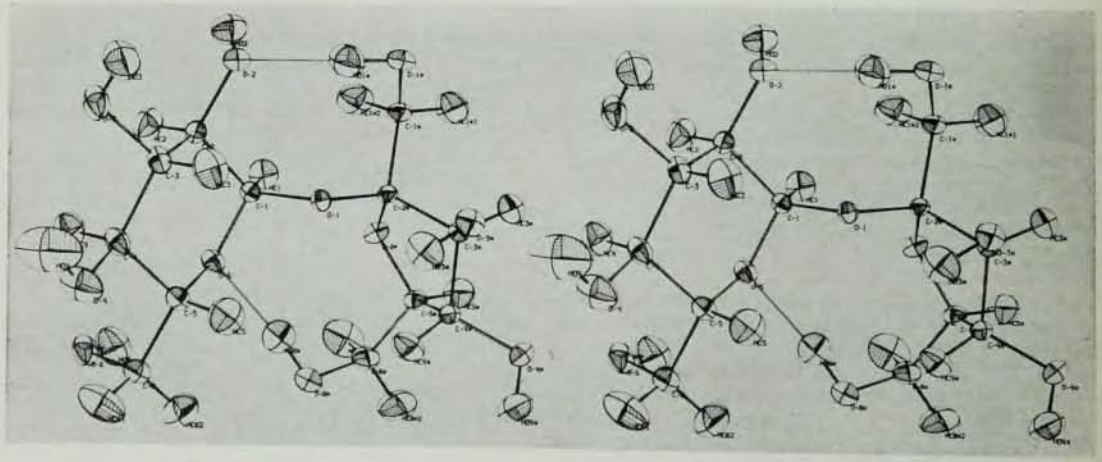
assumes that each atom can be described by a vibrational ellipsoid. (Such an assumption neglects, for example, possible anharmonicities in the vibrations.) In some cases, after such vibrational ellipsoids have been derived from the data, it has been possible to carry out an analysis to convert the individual ellipsoidal descriptions into a description in terms of rigid-body motions of the entire molecule. Pawley of Harvard described the alternate process of imposing, during the refinement, those relations between thermal parameters that result from the assumption of rigid-body motion. In this way again fewer parameters are needed and one has taken advantage of known physical information.

As intensity data are measured more accurately and as refinements are carried out more completely, there arises the need for more reliable input data in the calculational model. Among such data discussed at the 1964 ACA meeting were the handling of anomalous dispersion (Ibers and Hamilton) and improved atomic scattering factors from self-consistent field calculations (Cromer, Los Alamos).

There is, of course, a fourth and most important step in structure determinations and that is the preparation of the manuscript. In fact, as Cole and Okaya emphasized this can be the rate-determining step! One of the problems the crystallographer faces, not always squarely, is the presentation of his three-dimensional structures in two-dimensional form in a manner that can be understood both by his colleagues and by interested chemists and physicists. C. K. Johnson of Oak Ridge described and demonstrated the success he has had in computer-drawn stereoscopic pairs of perspective projections (as in the example shown below). When such pairs are viewed through inexpensive hand stereoscopes a strikingly effective three-dimensional perspective view of the structure is achieved. It may be that by publishing such stereoscopic pairs in the journals, at the expense of a slight increase in space, far clearer views of complex structures will be obtained.

To give some idea of the current interests of crystallographers, there were described in the abstracts 7 intermetallic structures, 25 organic structures, 27 inorganic structures, 22 biological structures, 21 organometallics and coordination compounds, and 5 mineral structures. There is little object in attempting to describe in any detail these various structure determinations, but let me single out a few for some discussion.

Samson of Caltech described the structure of β (MgAl), which should be written, in terms of cell content, Mg_{448} Al_{720}. This very complex structure was solved largely by intuitive means and



Stereoscopic pair of perspective projections showing the molecular structure of sucrose and the vibrational ellipsoids of the nuclei [G. M. Brown and H. A. Levy, Science, 141, 921 (1963)]. The figure was drawn entirely by an automatic plotter. Stereo viewing of the figure is facilitated with an inexpensive hand stereoscope, but it can sometimes be realized without optical accessories.

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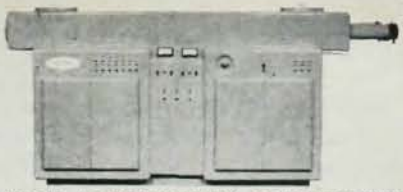

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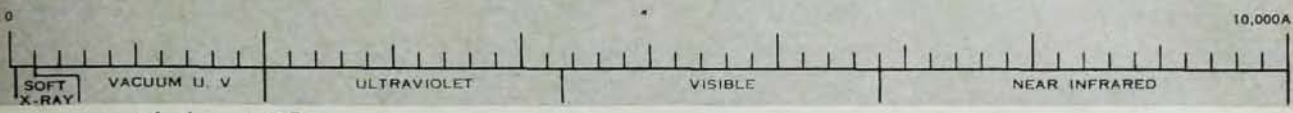

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by model building. Direct solution of such a structure from the Patterson function is probably impossible.

Zalkin, Forrester, and Templeton (Lawrence Radiation Laboratory and University of California) described the structure of an iron-containing cyclic hexapeptide produced by a certain fungus. The molecule is $C_{41}H_{58}N_9O_{20}Fe{\cdot}4H_2O$, and is therefore of unusually great complexity for such a complete structure determination.

There is great interest among chemical physicists in the symmetry of very strong O-H-O hydrogen bonds. Because of the tendency of the H atom to lie, at least statistically, on a symmetry center, it has generally been impossible, even with neutrons, to decide whether such a bond is truly symmetric (single-minimum potential function) or is statistically disordered (double-minimum potential function with minima of the same depth). Ellison and Levy of Oak Ridge at this ACA meeting discussed a neutron-diffraction determination of the structure of potassium hydrogen chloromaleate. They find the O-H-O bond length to be 2.403 Å and the hydrogen to be centered. The significant feature of this determination is that there are no symmetry restrictions on the hydrogen position. Hence this determination probably represents the best authenticated case for a symmetric hydrogen bond.

Finally, Kraut and Harker summarized their current efforts to solve the structures of the proteins, chymotrypsinogen and ribonuclease. To solve the phase problem for a protein structure one needs a variety of heavy-metal derivatives that are isomorphous or nearly isomorphous with the parent protein. Then one can determine the phases from the differences in scattering of the various isomorphs and eventually obtain a Fourier map of scattering density out to a certain resolution which is a function of the number of data and the degree of isomorphism. In the cases of hemoglobin and especially of myoglobin it was possible to obtain important information about the molecular structures, even from maps of limited resolution. One of the reasons for this is that hemoglobin and myoglobin contain a high proportion of alpha helices, and the structure of the alpha helix, as proposed by Pauling and Corey, was available at the time the maps of hemoglobin and myoglobin were being studied. Kraut now has a map at 4 Å resolution on chymotrypsinogen and it is essentially uninterpretable in terms of a chemically or biologically meaningful structure; the reason for this appears to be that the protein does not contain a high proportion of any entity, such as an alpha helix, whose structure has been guessed at. Similarly, Harker's maps on ribonuclease do not yield to a clear interpretation. Somewhat more discouraging is the fact that it may not in all cases be possible to get maps of higher resolution, because of the inherent limitations on the degree of isomorphism of the various derivatives. Kraut describes partial success in developing computer programs for model building and fitting of known amino-acid geometries in known sequence into the map. What seems to be clear at this time is that the initial success on myoglobin and hemoglobin resulted in large measure from fortunate circumstances, and we are not going to see in the near future a large number of other protein structures.

Among those papers not directly connected with structure determinations, a few in particular are worth mentioning. Papers by Warren of MIT and Guentert of Raytheon showed conclusively that the anomalous surface reflection of x-rays reported by Yoneda—Phys. Rev. **131**, 2010 (1963)—can be interpreted as small-angle scattering on irregularities or dirt on the surface, followed by total external reflection of part of the scattering. It is possible that out of this will be developed a useful new tool for studying the nature of surfaces. Wang and Buehler of the Naval Ordnance Laboratory described the extraordinary properties of the alloy TiNi. If a wire or sheet of this material is deformed at temperatures below the transition, it will regain its original shape when heated to temperatures above the transition. If deformed above the transition, it holds its shape when cooled below. Then, if straightened out, it will redeform on heating above the transition again.

Now that Eastern and Midwestern crystallographers have been introduced to the concept of mountains, ACA meetings in the West have become very popular. (The 1964 meeting was held jointly with the meeting of the Mineralogical Society of America, and in their sessions forty papers were presented in two days and the rest of the time was devoted to field trips. It is glorious country around Bozeman, and many of the ACA members, while sitting through the five days of sessions, wistfully thought of the fortunate mineralogists and their field trips. Yet when the one-inch hail stones were falling one afternoon, there was a certain comfort in being in session.) This particular meeting at Bozeman was a memorable one, not only for the grandeur of the countryside and the campus, but also for the magnificent way in which the local arrangements were handled by Charles N. Caughlan and his committee.