AMERICAN CRYSTALLOGRAPHIC ASSOCIATION MEETS IN MOTEL

By Kerro Knox

A report on the most recent winter meeting of the ACA. The author is associate professor of chemistry at the Case Institute of Technology.

The American Crystallographic Association made an experiment in departing from the form of previous meetings for its winter meeting, February 24-26, 1965. The meeting was held, not on a university campus, but at a commercial motel in Suffern, New York, where the isolation provided little distraction from business. A small meeting was planned, but nearly 200 crystallographers eventually showed up. The first day was devoted to six invited papers in a symposium organized by S. C. Abrahams on accuracy in x-ray intensity measurement. This subject has become of vital interest and some controversy among diffractionists with the growing sophistication of their experimental and computational techniques. This was followed by four sessions comprising 43 contributed papers, most of which illustrated directly the theme of the symposium.

Crystallographers may be chemists, physicists, metallurgists, geologists, or biologists. Some are interested in structures and their relationship to the physical and chemical properties of substances. A few are interested primarily in the phenomenon of x-ray diffraction per se, and B. W. Batterman, the first speaker in the symposium, is one of these. He called attention to the power of intensity measurements in powder diffraction work. Whereas single crystal methods give reliable information about the atom "positions" (the centroids of the electronic distributions), the determination of absolute intensities with powders is necessary to give information about the electronic distribution within the atom. In particular, such measurements can indicate how this distribution is perturbed relative to the free atom because of solid-state effects. Such detailed information cannot reliably be obtained from single crystals.

When a secondary standard has been established, no one need do absolute measurements, except once "for the good of his soul". Batterman pointed out the virtues of carbonyl iron as the standard powder and called for volunteers to make independent measurements on it or some other standard. A similar project, with a single crystal, would also be extremely valuable.

W. C. Hamilton discussed the statistical treatment of diffraction data, explaining how to recognize good data and how to estimate systematic errors by analysis of variances. The crystallographer knows that not all of his errors of measurement are random, and so, before the accuracy of his structural refinement can be assessed, suitable statistical analysis must be employed. Hamilton set out criteria for getting good values for structural parameters (precise measurements, sensitive measurements, and many measurements) before exploding the myth of the low R-factor.

The "reliability factor" is $R = \Sigma \big| \, |F_{meas}| - |F_{calc}| \, \big| \div \Sigma \, |F_{meas}|$ where the F's are structure factors. The myth that has pervaded much diffraction work is that if R is low, e.g., <0.05, both the measured data and the model from which the matching values were calculated are highly accurate.

W. H. Zachariasen then treated the nonrandom effects of secondary extinction and multiple diffraction, which, like the poor, are always with us, and which in extreme cases tend to equalize the intensities of all the diffracted beams from a crystal. Various approximate formulas can be used

T. C. Furnas, Jr., of Picker X-Ray Corporation, with his plexiglass model illustrating x-ray diffraction geometry. The axial rod in the sphere represents the diffraction vector. The ball centered on the rod represents the specimen. The edges of the two discs represent the range of diffraction angles relative to the specimen for two successive orders of reflections. The sphere rests on a cup that allows it to be placed in any desired orientation. The cup can be rotated about an axis shared by two curved rods on which are movable pointers representing the x-ray source and the x-ray detector.

to correct for extinction, but the general solution, including polarization effects, is too messy to be solved. To minimize extinction, one should work with long wavelength x rays.

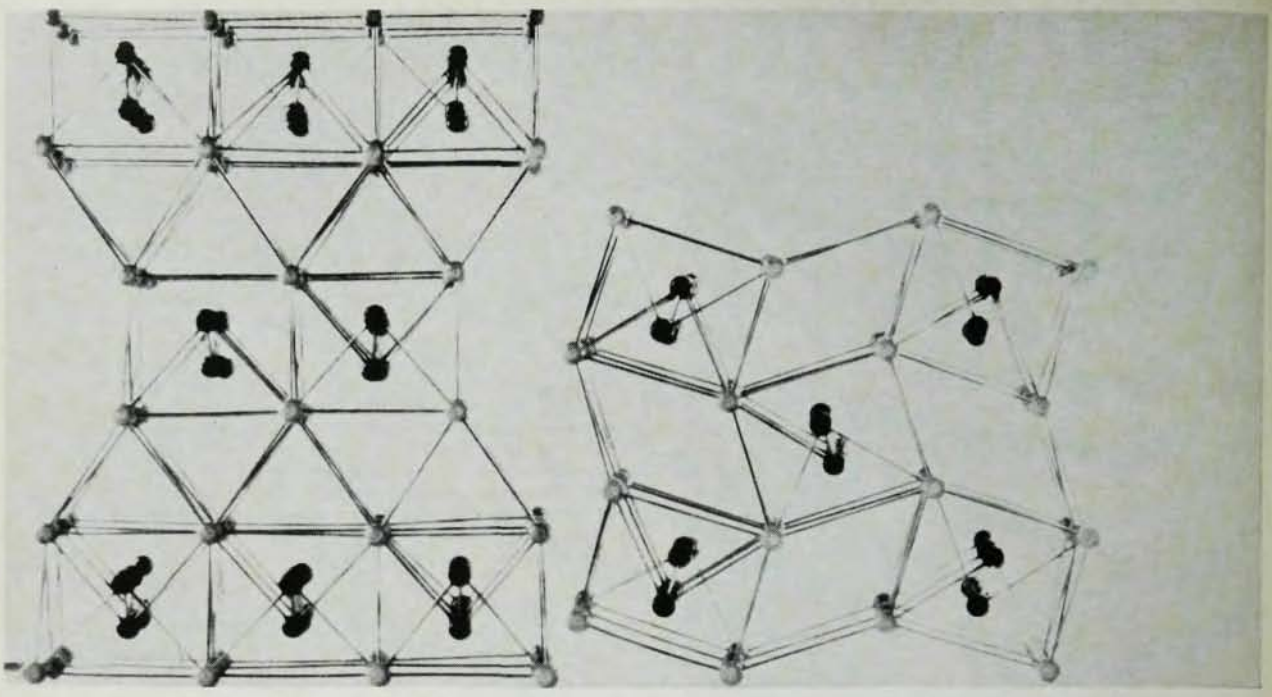
The afternoon session, with papers by R. A. Young, T. C. Furnas, and J. Ladell, dealt with the experimental techniques of collecting data. Young summarized the factors affecting background and how to control them. He recommended the use of various techniques, such as monochromators vs balanced filters, and measurements at different temperatures to improve precision and, it is to be hoped, accuracy.

Furnas emphasized that in diffraction processes we are dealing with nonpoint geometry rather than the point geometry usually assumed and hoped that other people would do experiments which would test the differences. He demonstrated a versatile plexiglass model representing x-ray diffraction geometry to illustrate the exact equivalence in point geometry of two common diffraction techniques usually considered to be different. For the usual "chemical-structure" determination, he recommended the use of a monochromator, since the advantages it gives by improving the signal-to-noise ratio outweigh the disadvantages. One of these is that not all of the crystal is irradiated by all of the spectral range of the incident beam.

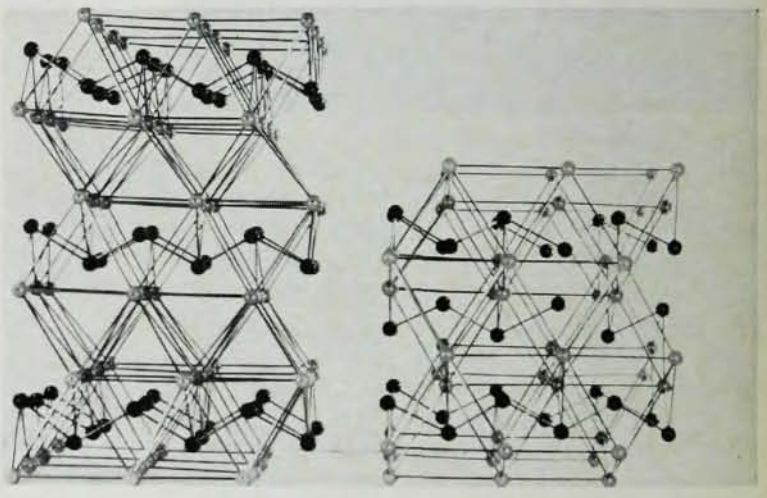
Ladell presented the case for crystal monochromators and equi-inclination geometry. He pointed out that, as counters become more widely used to measure the intensities of x-ray beams, more information on how to use them must be made available.

The symposium was on the whole a valuable airing of the many factors which have to be studied before the accuracy of x-ray intensity measurement can begin to match its precision. The ample time left for discussion contributed greatly to the success of the invited papers. The symposium talks and discussions were tape-recorded for possible subsequent publication.

The contributed papers generally described the results of increasingly refined techniques of collecting data and of treating them. The papers of L. H. Jensen and R. F. Stewart can be cited as examples. The former showed experimentally in *n*-nonanoic acid that the thermal parameters for hydrogen usually turn out to be lower than those for the atoms to which it is bonded. This result in x-ray diffraction is the opposite to that found in neutron diffraction. It was ascribed to the usual spherical approximation for a free hydrogen atom used to calculate the form factor ("scattering factor"). Stewart calculated the form factor for a hydrogen atom in a hydrogen molecule and showed how it could lead to the determination of more reasonable interatomic distances. Accurate extension of this work to carbon-hydrogen bonds will be difficult, owing to the lack of suitable wave functions for the C-H bond. A number of



Shown above is a model of the CrB structure (left) and FeB structure (right), which was discussed in a paper by Erwin Parthé of the University of Pennsylvania. The photo gives a view along the direction of the black B-B chains parallel to c_{CrB} and b_{FeB} axes. The B atoms in CrB and FeB are located in the centers of trigonal prisms. These are stacked one behind the other to form prism rows. CrB and FeB differ only in the way the prism rows are arranged in space. The photograph at right shows a side view of the same model along the a_{CrB} and a_{FeB} axes. One sees the white, trigonal prisms centered with black B atoms. The prisms are stacked in such a way as to allow the formation of B-B zig-zag chains.



papers reported work using the fruitful technique of investigating the relations among two or more closely related substances.

An example of the large amount of information that can be gotten from a highly refined crystal structure is provided by the work of S. C. Abrahams on the piezoelectric, ferromagnetic gallium-iron oxide. The combination of x-ray-diffraction data and single-crystal magnetic-anisotropy data showed that the direction of the magnetic-spin alignment was the c axis, without recourse to neutron diffraction. The data were accurate enough to give physically meaningful thermal parameters from which a model for the mechanism of the piezoelectricity was derived.

Finally, there was the report of W. R. Busing on the progress at Oak Ridge in setting up a four-circle automatic diffractometer controlled by a small computer. Many of the functions of the conventional electronic circuitry will be taken over by the computer itself, which will count the pulses from the detector as well as set the angles for the crystal and the counter. The system will be in operation very shortly.

X-ray crystallography has now reached an exciting stage where much of the tedium of making thousands of measurements has been eliminated by automation and that of elaborate computations by fast digital computers. The crystallographer is presented with the interesting problem of how to use his instruments properly and how to improve them to get the best possible data with which to describe the properties of crystals related to their internal electronic distribution.