APR 29 1966

The Application of Direct Methods to Neutron Crystallography
and Vice Versa*

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MASTER

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IN NUCLEAR SCIENCE ABSTRACTS

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Introduction

I would like to present in this paper the results of some rather brief considerations that I have given to the problems of applying direct methods to neutron crystallographic data. There are, as you will see, some additional complications that one must take into account; on the other hand there are compensations available in that there are a few new things that can be done. This discussion has some importance because the time has come when neutron sources are intense enough and automatic data collection so easy that many structures will be determined by neutron diffraction without prior knowledge of the structure obtained from x-rays.

I intend, though, to devote the major portion of my talk to the vice versa. I refer to the discovery that inelastic neutron scattering leads to an exciting new approach to structure determination. Observation of the coherent one-phonon scattering leads to a partial solution of the phase problem and also to a technique which can be used to enhance the scattering from selected portions of crystal structures.

Direct Methods

You may first ask, "Why is there any difference between applications of direct methods to neutron crystallography and to x-ray crystallography?"

* Research performed under the auspices of the U. S. Atomic Energy Commission.

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At first glance, there should not be, for the definition of the structure factor is the same in both cases. The differences of course lie in the fact that the atomic scattering factors are different for the two methods. These differences are both quantitative and qualitative.

First, as you know, the nucleus acts as a point scatterer for neutrons; there is therefore no angle dependence of the scattering factor. This is a rather trivial difference in the application of direct methods, except insofar as the extension of the data to higher scattering angles leads to more data, which is always helpful in any of the direct methods. One can also perhaps obtain more reliable normalized structure factors, since one has to correct only for the temperature factor and not for the angle dependence of the atomic scattering factor itself.

The important quantitative difference is that, whereas the scattering factor for x-rays is proportional to the atomic number, the neutron scattering factors for most elements are of the same order of magnitude. (See Table 1) This means that many problems in neutron diffraction are "equal-atom" problems, much more so than in the x-ray case, for the neutron scattering factors for most of the heavy elements are in the range typical for the elements occurring in organic compounds. This can be both an advantage and a disadvantage. One result is that the "heavy-atom method" is of limited utility in neutron diffraction. This is one of the reasons why an x-ray study has often preceded a neutron study of a complex problem. This has not been universally the case however; a number of complex structures have recently been solved by the group at Oak Ridge without previous knowledge as to the x-ray structure. As the use of direct methods becomes more widespread, I think we will see more

and more complex structures being solved by neutron diffraction without a previous x-ray study.

Now, since almost every problem becomes an approximate equal-atom problem for neutrons, some of the phase determining methods that depend on the assumption of equal atoms are more applicable to neutron problems than to many x-ray problems. This fact may in part make up for the fact that one no longer has the heavy-atom technique to play with.

So far as what we have said so far, direct methods can be applied in exactly the same way in the two techniques. The fly in the ointment is the qualitative difference occasioned by the fact that the scattering amplitudes of some elements have opposite signs to those of the majority. With most elements, there is a phase change of π in the scattering process as there is with x-rays; this is conventionally taken to be associated with a scattering amplitude which is positive. Several nuclei however scatter neutrons with a phase change of 0, and these must be assigned a negative scattering amplitude. The nucleus with this property most often encountered is that of H^1 , ordinary hydrogen. And, for better or for worse, there is hydrogen in almost every interesting crystal structure. Despite its negativity, the hydrogen scattering amplitude is moderately large, and thus neutron diffraction has found great favor for the location of hydrogen atoms.

But what does this negative scattering amplitude mean in terms of direct methods? First of all, it means that the scattering density is sometimes positive, sometimes negative, not always positive as in x-ray diffraction. This in turn implies that the Patterson function as well has negative regions. Let us examine in detail the effect that these facts have on the various direct methods.

The Sayre relationship and the Karle-Hauptman

$$\sum_2$$

formula, to

which it is related, as well as a number of other sign-determining relationships, depend for their validity on the assumption that the scattering density and thus the Patterson density is everywhere positive. This is of course true for x-ray diffraction. It is not true for neutron diffraction. In the scattering density function, peaks corresponding to hydrogen will be negative; in the Patterson, H-H peaks will be positive, but H-OTHER peaks will be negative. It is of course possible that relations similar to those mentioned above might be developed to allow for negative atoms; undoubtedly these relations will have less power in some sense.

As a way around this difficulty, Karle⁽¹⁾ has proposed an ingenious approach. For a given structure composed of atoms at positions $\underline{r}_1$ with scattering factors $\underline{a}_1$, Karle defines the squared structure as the structure which has atoms at positions $\underline{r}_1$ with scattering factors $\underline{a}_1^2$. Such a structure will have positive scattering density everywhere. If the observed structure amplitudes were available for such a structure, the direct methods in their usual form could be applied, and the squared structure might possibly be obtained. One would then use chemical sense and peak heights to decide which of the atoms had negative scattering factors. Unfortunately, the structure amplitudes for the squared structure are not available. The experimental measurements are obviously for the unsquared structure. Karle has again invoked probability relations to obtain from the structure amplitudes for the real structure estimated

(1) J. Karle, Acta Crystallographica, in press.

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structure amplitudes for the squared structure. These are then used in the usual phase-determining formula to arrive at phases for the squared structure and finally the structure itself. This method has not been adequately tested, but it will perhaps be valuable.

The situations regarding direct interpretation of the Patterson function for hydrogen-containing structures as opposed to other direct methods would seem at the present time to be more favorable. Nevertheless, some changes must of necessity be made in the usual procedures. Suppose one wishes to look at the first order consistency function defined in terms of symmetry operators S_i and weights w_i

$$M(r) = \text{Min} \{ P(r), w_1 P(S_1 r), \dots \}. \quad (1)$$

This is the function which attempts to determine possible atomic positions by examining possible positions of vectors between atoms related by the symmetry operations of the space group. Since we are dealing here with self-peaks in the Patterson function, these are all positive, and the situation with respect to H...H peaks is exactly the same as that for other self peaks. If the Patterson consists of resolved peaks, no more need be said. In a complex structure, however, there is no reason to believe that single peaks will be resolved in the Patterson; one has the possibility then that a negative H-OTHER peak will be superimposed on a positive self peak of either the H-H or the OTHER-OTHER variety. If one is then forming the consistency function as a minimum function, he may get into trouble; the minimum may be zero or negative, and there may be self-peaks which are not revealed in the consistency minimum function. Thus, it seems that in cases where overlap is anticipated one would be better off using either

the sum (average) function or a modification of the product function--perhaps an absolute product function--in forming the consistency function for this type of problem. As Buerger has pointed out, however, the sum and product functions are probably not as good as the minimum function from other points-of-view.

Having found a few vectors, one can go on to higher order consistency functions; here one can ask questions regarding the positive and negative regions--again taking due account of the possibility of overlap. Thus perhaps in the later stages of image-seeking, the negativity of some regions becomes an advantage. Obviously, when one goes all the way to the point of the scattering density map, the negative regions can be immediately identified as hydrogen atoms, the remaining regions as other atoms.

Going back to the Patterson function itself, the negative regions will correspond only to H-OTHER vectors; if there is much overlap, these regions may not be as negative as they should be. In any case, these negative regions will represent images of the structure as seen from the hydrogen atoms. This effect can be accentuated and much overlap eliminated if one has data for a compound and for the same compound in which some of the hydrogen has been replaced by deuterium, which has a different and positive scattering amplitude. Let us denote by R_{ij} a peak due to an interaction between atoms i and j . H will denote hydrogen, D will denote deuterium, and O will represent all other atoms. n_i is the number of atoms of type i . The Patterson function for the hydrogen compound may be written

$$P(H) = \sum_{H=1}^{n_H} f_H^2 R_{HH} + \sum_{H=1}^{n_H} \sum_{O=1}^{n_O} f_H f_O R_{HO} + \sum_{O=1}^N f_O^2 R_{OO} \quad (2)$$

and for a deuterated compound

$$P(D) = \sum_{D=1}^{n_D} f_D^2 R_{DD} + \sum_{D=1}^{n_D} \sum_{O=1}^{n_O} f_D f_O R_{DO} + \sum_{O=1}^{n_O} f_O^2 R_{OO} \quad (3)$$

The difference Patterson may be written

$$P(D) - P(H) = \Delta P = \sum_{D=1}^{n_D} (f_D^2 - f_H^2) R_{DD} + \sum_{O=1}^{n_O} (f_D - f_H) f_O R_{DO} \quad (4)$$

(The notation implies that H atoms which are not replaced by deuterium are included in OTHER rather than in H.)

$$\Delta P = 0.20 \sum_D R_{DD} + f_O \sum_{D,O} R_{DO} \quad (5)$$

If there is only one replaceable hydrogen, the difference Patterson gives directly a single image of the structure, as seen from the replaceable hydrogen atom. (Such an application has been made by C. Johnson in a paper to be reported later in this meeting). I would like to illustrate this approach by using as an example the structure of tetracyanocyclobutane which is to be reported by Greenberg and Post later in this meeting. The crystals are monoclinic, and there are two hydrogen atoms in the asymmetric unit. We have done no neutron diffraction work on this compound; the figures are based on calculated neutron structure factors from the coordinates given by Greenberg and Post. We will illustrate only the [010] projection.

Figures 1 and 2 show the scattering density for the hydrogen and deuterium compounds. A comparison of these two shows that it might be easier to interpret the hydrogen map than the deuterium map for a structure of unknown chemistry. Figures 3 and 4 show the two Patterson functions; again there are predominant features of the hydrogen Patterson which might make its interpretation easier than the relatively featureless deuterium Patterson; note the pronounced modulation in one direction showing that the hydrogen atoms lie approximately in layers. Finally Figure 5 shows the difference Patterson. Note the increased resolution as compared with the Patterson functions. Although it is still difficult to pick out a single molecular image, there is a striking resemblance between certain features of this map and the scattering density maps. The most notable resemblance is in the strong line of density extending from the upper right to the lower left of the projection. Furthermore, regions suggestive of the four membered ring and the CN groups are apparent. In three dimensions, the structure could probably have been easily obtained from the difference Patterson.

To summarize this section of my contribution I may perhaps make the following conclusions:

- 1) Direct interpretation of the Patterson may be facilitated by the presence of the negative regions corresponding to hydrogen atoms. The very fact of the negativity provides a qualitative difference which should be useful in the Patterson interpretation. It seems likely that functions other than the minimum function will be most useful for such structures.

- 2) The squared structure approach of Karle should be given a good test. Further investigation seems to be needed to see whether the really direct methods cannot make use of the negativity of the hydrogen peaks rather than artificially get rid of them; it seems like Karle's approach is throwing away information.
- 3) Direct methods in neutron crystallography should be of increasing importance as more and more structures are determined using neutrons alone. This will be particularly true of problems where neutron diffraction is essential for determination of light atom positions.

I would like to conclude this portion by making a few remarks concerning the experimental techniques of neutron diffraction. First, a deuterated crystal is by no means necessary for the study of a compound containing hydrogen; many people still seem to have this impression. I would just as soon work with a hydrogen crystal. Second, we still need crystals somewhat larger than those required for x-ray diffraction. Something like a minimum of 0.02 mm^3 in the beam is essential.

Table 1. Neutron scattering amplitudes for a few nuclei.

Units are 10^{-12} cm.

C	0.66
H	-0.38
D	0.65
N	0.94
O	0.58
Cl	0.98
P	0.53
Fe	0.96
I	0.52
Pt	0.95

A Solution of the Sign Problem and a New Approach to
Crystal Structure Determination²

The major part of my talk will be devoted to what I consider to be the most interesting thing I have come upon in many months. I have recently become intrigued with the possibility of obtaining structural information from the inelastic scattering of thermal neutrons. Now, inelastic scattering has received much attention from solid state physicists in recent years because of the possibility of determining accurately for the first time dispersion curves for solids. These people have naturally attacked simple crystals in their first steps in this direction. The possibilities of applying neutron inelastic scattering to the general problem of vibrational modes in molecular solids has been vigorously pursued by Rush in the studies he has made of hydrogen bonded solids. This is a field that promises much for the future, not only for incoherent scatterers such as hydrogen, but for other molecular crystals as well. Single crystal coherent inelastic scattering seems to offer much greater promise for the study of vibrational modes in solids than does polarized infrared work.

Much of the work in the literature has the flavor of the following statement, "The inelastic scattering can most easily be interpreted in cases where the crystal structure is known, for the position of the atoms in the crystal does influence the coherent scattering. We will work on crystals with known simple structures in order to get out the information of interest to us, namely the dispersion curves." (The dispersion curves are of interest because of the information they can give concerning force constants in solids.)

² A mathematically more detailed account of this material will be published elsewhere

Now from the point-of-view of the chemical crystallographer, this is all wrong. For example, in the usual crystal structure determination, we take exactly the opposite tack. We are interested in the structure and carry out our anisotropic thermal refinements not so much to learn something about anisotropic thermal motion, but because this must be considered in order to get out the best chemical structure. Obviously both approaches are important. Now, the chemical physicists have learned to extract much valuable information from the anisotropic thermal parameters determined by crystallographers. Why should not we also try to extract the structural information that is in the inelastic scattering? There is just as much there (and perhaps more in a sense) than there is in the coherent Bragg scattering.

In inelastic scattering, the scattered neutron has a different energy than the incident neutron because it has either excited or deexcited vibrational energy levels in the crystal. A particular normal mode in the crystal can, for example, be excited from its ground state to its first excited state. The neutron which induces this transition will lose an equivalent amount of energy. By measuring the neutron energy changes, one can carry out vibrational spectroscopy on the solid state system. This has been the major emphasis in neutron inelastic scattering work. I am confining this discussion to neutron scattering, since the energies of thermal neutrons are comparable in magnitude to the separations of vibrational energy levels in solids. Hence, the changes are large compared to the incident energy and are easily measured. This is not the case with x-rays. Thermal neutrons have energies which are in the neighborhood of 0.1 e.v. or 800 cm^{-1} . Typical x-rays used in structure work have energies of the order of a few thousand electron volts.

A monochromatic neutron beam incident on a crystal may be characterized by a wave vector $\underline{k}_0$ in the propagation direction. The magnitude k_0 of $\underline{k}_0$ is related to the wave length λ_0 and the energy E_0 of the neutron by

$$k_0 = 2\pi/\lambda_0 \quad (6)$$

and

$$E_0 = h^2 k_0^2 / 8\pi^2 m. \quad (8)$$

In equation (2), h is Planck's constant, and m is the neutron mass. The scattered neutron may be described similarly by k_s , λ_s , and E_s . The change in the neutron energy is

$$E_s - E_0 = \Delta E = (h^2/8\pi^2 m)(k_s^2 - k_0^2). \quad (8)$$

The scattering vector is defined by

$$\underline{\kappa} = \underline{k}_s - \underline{k}_0. \quad (9)$$

If a crystal consists of atoms at positions $\underline{r}_i$, each of which has an atomic scattering factor a_i , a Debye-Waller temperature factor T_i and a mass M_i , the usual geometric structure factor for elastic Bragg scattering is

$$F(\underline{\kappa}) = \sum_{all} a_i T_i \exp(i \underline{\kappa} \cdot \underline{r}_i) \quad (10)$$

We may similarly define a normal-mode structure factor by

$$H(\underline{\kappa}) = \sum_{all} a_i T_i M_i^{-1/2} (\underline{\kappa} \cdot \underline{e}_i) \exp(i \underline{\kappa} \cdot \underline{r}_i) \quad (11)$$

$C_{\underline{i}}$ is the normal mode coefficient vector which relates the atomic displacement vector $\Delta \underline{r}_{\underline{i}}$ to the normal mode coordinate q by

$$\Delta \underline{r}_{\underline{i}} = C_{\underline{i}} q. \quad (12)$$

The intensity of the inelastic scattering from a particular normal mode is proportional to $|H|^2$, just as the intensity of Bragg scattering is proportional to $|F|^2$.

There are two very important implications inherent in the definition of H and in the conditions under which it can be observed.

Taking the latter point first, $H(\underline{K})$ is observable at all points in reciprocal space, not just at the reciprocal lattice points. The transform of the scattering density can be measured everywhere, not just sampled at a finite number of lattice points! Aside from the fact that this means that more information is available, it means that in a centrosymmetric crystal one has available a means of sign determination. By varying the parameters of the experiment in such a way that the scattered intensity is measured out along a row in reciprocal space, every time the sign of H changes, there will be a node in the intensity. By mapping out these nodes, one can determine the boundaries between positive H and negative H and hence arrive at a complete determination of signs for the centrosymmetric crystal. (See Figure 6) One can proceed immediately to a Fourier inversion of H to obtain a scattering density map.

You will note that the major difference between the structure factor expressions F and H is the inclusion of the term $(\underline{K} \cdot C_{\underline{i}})$ in H . If atom $\underline{i}$ has a large amplitude of motion in the direction of the scattering vector for the particular normal mode being examined, this atom will

contribute heavily to the scattering. This fact leads to the suggestion that this term may be manipulated to simplify the structure solution. By choice of a suitable normal mode for examination, $|C_1|$ may be made large for certain groups of atoms and small for others. The effective atomic scattering amplitude $h_i(\underline{\kappa}) = a_i T_i(\underline{\kappa}) (\underline{\kappa} \cdot \underline{C}_1)$ can thus be varied. By judicious application of this principle, any problem can be made into a heavy-atom problem. For example, one may select a mode that is primarily associated with the stretching frequency of a C-O bond. If this frequency is well resolved from others, the effective atomic scattering factor h will be large for the carbon and oxygen atoms involved in such bonds but will be small for others. Thus these C and O atoms become heavy atoms for the structure and their location may be easily obtained. Thus the method might well be used when it is the orientation of particular groups within the crystal which is desired as opposed to a complete structure determination. On the other hand, the structure might be built up completely in a piecemeal fashion, first determining the positions of one group of atoms and then another. The concept also lends itself quite naturally to the difference Patterson idea. One essentially has enormous flexibility in making isomorphous replacements--without doing any chemistry!

In order to make this story complete, we should examine in some detail the experimental factors involved; in particular we should discuss possible difficulties with what at first sight looks like a very powerful method.

First, what kind of intensity can be expected for this scattering? It is of course low. Any diffractionist will tell you that there is more intensity per unit solid angle at the reciprocal lattice points than there

is in between. I have estimated that in typical situations, the ratio of the average Bragg scattering cross-section to the average one-phonon cross-section is about 100:1. There are obviously cases where the ratio is either much higher or much lower than this. In this connection it should be pointed out that neutron fluxes available today surpass the best that was available a few years ago by a factor of 100, so that from the point-of-view of intensity it should be just as easy to measure the one-phonon scattering as it was to measure data for a structure determination by conventional means a few years ago. It should also be remarked that great success has attended the efforts of those who have been active in measuring dispersion curves by this technique. Nevertheless, large crystals will be required for sometime to come. A volume of several mm^3 in the beam would appear to be essential.

Another point regarding the intensity is this: The intensity of the scattering is proportional to the population of the initial state in the scattering process. For most vibrational levels, the ground state is the predominantly populated state at normal or below-normal temperatures. Thus, the greatest scattered intensity should be obtained in a process in which the neutron gives energy to the system and excites it up one notch in some mode of vibration. The other process, in which the neutron gains energy from the crystal, is relatively less favorable because of the much lower populations in the excited states which are to be deexcited by the scattering. The technique in which a very low energy (cold) neutron gains energy from the lattice has been widely used for the study of very low-frequency modes in a number of crystals. If the neutron is to lose energy, it obviously has to have enough initial energy to excite the

the mode in question. The largest flux available in research reactors is for neutrons with a wavelength of about 1 Å. This corresponds to a frequency of 665 cm^{-1} . Thus only vibrational levels with a separation of less than 665 cm^{-1} could be excited. Many of the modes of interest will have higher frequencies, and it would be necessary to go to higher energy incident neutrons to scatter from these more interesting modes. Because of the Maxwell distribution of energies, there will be fewer of these higher energy neutrons.

Another disadvantage of leaving the scattered neutron with very little energy is that the radius of the sphere of reflection for inelastic scattering is determined by the energy and hence wavelength of the scattered neutron. Thus, a process in which most of the incident neutron energy were lost could be studied in only a limited region of reciprocal space.

Suppose that there is plenty of intensity to study the normal mode of interest in a particular region of reciprocal space. The question arises as to how much background intensity there is, that is, how hard it will be to separate the one-phonon coherent scattering for the transition of interest from scattering due to multiphonon processes and incoherent scattering of all kinds. In many cases, the multiphonon scattering will be sufficiently low to cause no trouble. The question of incoherent scattering is something else again. Since H^1 has a very high spin incoherent scattering amplitude, it seems unlikely that the proposed technique can be successfully applied to crystals containing hydrogen at the present time. This eliminates most organic compounds, unless one resorts to almost complete deuteration before the structure work is undertaken.

One also wonders how easy it will be to resolve the normal mode of interest from other neighboring frequencies. Infrared spectroscopy on solids would seem to indicate that such resolution can be obtained in a number of cases. One must remember that as one measures $\underline{H}$ out along a row in reciprocal space, one is traveling along a dispersion surface for the vibrational mode in question. The dispersion curve gives information on the way the frequency changes with $\underline{\kappa}$, for analagous to the fact that elastic coherent scattering takes place only at the reciprocal lattice points is the fact that here the scattering vector $\underline{\kappa}$ must be related to a reciprocal lattice vector $\underline{h}$ and the phonon wave vector $\underline{f}$ by

$$\underline{\kappa} = \underline{f} + 2\pi\hbar$$

One expects that in molecular crystals the dispersion surfaces will be relatively flat for the so-called optical modes. Nevertheless, these curves have not been measured for complex crystals, so that one cannot be sure that the experiments will be as clean as the foregoing theoretical analysis has suggested.

Aside from these possible experimental difficulties, there is the question of the shape of the modified atomic scattering factor $\underline{h}$. This is not generally known, for the normal mode coefficient vectors $\underline{C}_i$ are rarely known. It does not even seem likely that they can be described in terms of simple models with only a few parameters to be refined. Thus, normal mode structure factor calculations and least squares refinements would seem to be too difficult now to undertake for any complex crystals. On the other hand, we still expect that a Fourier inversion of $\underline{H}$ will yield a map with peaks at the atomic positions. The shapes of these peaks will in general not be ellipsoidal, but their shapes may tell us many

interesting things about the dynamics of the crystal. Thus, if it is the static structure rather than the dynamics which are of interest, it seems that the proposed technique will be of most use in the early stages of the investigation when the phase problem remains to be solved and some atoms found. The refinement could be completed with data based on more conventional procedures.

There is obviously a great deal of experimental work that remains to be done here, and we hope to be getting on with it shortly. One of the first steps would be the measurement of the dispersion curves for the optical modes in some rather complex molecular crystals. These will be interesting results in any case, but it is my feeling that the prognosis is good for this technique to become an important tool in structure determination.

Thank you very much.

Following Hamilton's talk

Kartha: ??? (Would you care to comment further on the relationship of the E values to the squared structure?)

Hamilton: Dr. Karle is responsible for this approach, and he might like to answer that.

Karle:.....

Templeton: To what extent are these normal modes centric or non-centric. Do you know anything about the relative probabilities of exciting them? In speaking of signs, it is necessary to have a centrosymmetric normal mode, and even in a centric crystal you will have modes that are not centric.

Hamilton: You have a good point there. Actually, I believe that with regard to any centrosymmetrically related pair of atoms, a normal mode will be either symmetric or antisymmetric. In either case, the normal mode structure factor will be real. Your second question regarding the probabilities of excitation brings up an interesting point. One of the nice things about neutron inelastic scattering is that there are no selection rules in the sense that they exist in infrared spectroscopy. There are to be sure selection rules that are determined by symmetry. What they all involve is that it is necessary to have a large component of C_1 in the direction of the reciprocal space vector being measured.

Next question is Karle, I think: I would like to make a spur-of-the-moment suggestion, and being a spur-of-the-moment suggestion it is probably wrong. In connection with this curve you were talking

about, it would of course be very nice to know where to draw the line through in order to pick off the nodes as you go from a positive to a negative region. The thought occurs to me that the cross-section represents an intensity. If one takes the Fourier

transform, this may have the meaning of the probability distribution that is associated with this mode of vibration.

Now I don't know if this is true, but there is a real possibility that that is what the transform means. In that case, one can do what one does in electron diffraction, namely, insist that you get a positive structure and level this particular curve at such a point that the transform corresponds to positive probabilities.

Now I don't know if this could be helpful or not.

Hamilton: Yes, that's an interesting suggestion. It is true that the transform of $H(\)$ measured out along a single direction of is the one-dimensional Patterson function for the normal mode in that direction. The criterion of positivity in the Patterson function is as you have so often pointed out the basis of many of the direct methods. In the present context, it might indeed prove quite useful in drawing the background lines. (This comment was not made at the symposium, but has been added in the manuscript stage.)

Question following Buerger's talk.

Hamilton: I was interested in the last point brought up by Professor Buerger, namely the question of interpolation in image-seeking procedures. I would like to hear some comment from you and others who have had extensive experience in image-seeking methods as to how closely the grid points ought to be spaced for effective use of these procedures.

Following Okaya's talk:

Hamilton: The problem of visual display is a very important one in crystal structure analysis. Obviously, we are dealing with three-dimensional objects, and we have all been aware for a very long time that one of the end results of the structure determination ought to be some nice pictures of the structure. And, as we all have seen, computers are doing a good job of this now. The other point you brought out, though, is especially important, namely that rapid automated drawings can be of great help in the solution of the structure. How much more useful it is to have a three-dimensional display of an E-map than it is to riffle through thirty sections at one time!

Mrs. Donnay:

Okaya:

Furnas:

Okaya:

Furnas:

Meyer:

Okaya:

Hamilton: I think that is certainly true. We are going to see an excellent example later on in the form of a three-dimensional color movie which has been produced by Drs. Quintin Johnson, Guy McMillan and Gordon Smith at Livermore, using Carroll Johnson's very fine plotting program as a basis.

Fleischer's talk follows.....

Following Fleischer's contribution

Hamilton: In response to this talk, I would like to remark that it is becoming apparent that a number of excellent computer programs exist for carrying out the symbolic addition procedure as well as for using some of the other direct methods that we have discussed today. Yet not many of these programs appear to have wide distribution. I would like to encourage all those who have such programs to try to get them widely distributed, even if the programs and writeups are somewhat incomplete. If they are at the stage where other people with a little hard work can make use of them, it would be very nice to get them around. In this connection, I might mention that the ACA will be establishing a computer program library in the near future, and we would certainly like to get programs using direct methods into the library at the earliest possible date.

O. Johnson's paper follows

Film:

Following film:

(The film was followed by enthusiastic applause and comments.)

Hamilton (Summary of day's proceedings)

I think that this has certainly been a successful day. We have all learned a lot about the present state of the art in the application of direct methods and automatic interpretation of the Patterson function. It is obvious that we owe a great debt to the pioneers in this field: to Professor Patterson for having started the whole thing, to Professor Buerger who had the persistence to work in this area when the methods were extremely tedious and who has given us a fine introduction to today's session, and to Hauptman and the Karles who have kept true to the faith for 10 these many years. Now that computers are available to do the tedious work that many of these methods involve, the fruits of all this early work are appearing in abundance.

I have made a summary of the methods which have been used for the solution of structures reported at this meeting. First of all, let us consider the heavy atom technique. By the heavy atom technique, I mean an interpretation of the Patterson function which is more or less trivial followed by a series of difference syntheses. There were 27 structures reported here which used this technique simply because the crystal of interest happened to contain a heavy atom; these include a number of transition metal complexes and other metal structures. There was one structure reported where the heavy atom had been introduced to aid in the determination of the more interesting parts of the structure. Two structures were solved by isomorphous replacement.

Of the direct methods, symbolic addition and other use of the $\sum_2$ relationship resulted in the solution of 10 structures! Only one structure was reported as being solved by superposition in the abstracts

of the rest of the meeting, but we have heard from Professors Raman, Nordman, and Jacobson and Dr. Corfield about other powerful applications of this method. There were eight other structures in which the method of solution was not listed and where at first sight the problem appeared too complex to solve by a trivial interpretation of the Patterson. Perhaps superpositions in some guise or other were used in some of these; most of them probably did involve checking the Patterson for consistency.

Finally one structure was reported to have been solved in the "usual manner".

I think that these statistics show that we have come a long way in the last year or two, and that many structures once thought to be almost impossible to determine in a finite length of time might soon yield to a few hours of routine calculation on a fast digital computer. In most cases, it is still obvious that chemical sense can decrease the amount of necessary computer time by a factor of 10 or 100, and it is for this reason that one cannot overemphasize the importance of graphical display as one of the most important features of the man-computer interaction which has been discussed by Dr. Okaya. Some of us continue to hope that it is the interest in the chemical or physical structure rather than the exhibition of clever techniques which is the real motivation for each structure determination.

I would like also to repeat what I said earlier about the need for wide distribution of computer programs using these methods. For those writing programs, I would suggest that they be written in an algorithmic language so that the program listing can serve as an instruction manual in the method. Furthermore, it is often worthwhile to sacrifice speed for the sake of generality.

I will close by again thanking the speakers for a most interesting day and will express the hope that the publication of the proceedings of this symposium will get into print some of the details and lore which have been passed by word-of-mouth among workers in the field. The increased activity and interest in this field portends great things for all of crystallography.

Harker: I remember at Cambridge in 1960 a lecture by Sir Lawrence Bragg in which he mentioned that there were direct methods by which crystal structures could be determined, but that they came on the scene a little bit late because the heavy atom and isomorphous replacement methods worked more efficiently than anything. That was only six years ago. Things are changing fast.