Some Aspects of Neutron Single Crystal Analysis

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THIS PAPER PRESENTS a few observations on single-crystal analysis, based upon experience with the method at the Brookhaven National Laboratory reactor during part of the summer of 1952, and a comparison of neutron and x-ray scattering.

FOURIER METHODS IN NEUTRON ANALYSIS

One previous writer (*1, 2*) has held that Fourier methods cannot be used for crystal analysis from neutron-scattering data because of the nature of the nuclear form factors. Thewlis (*3*) has suggested that the application of a strong artificial temperature correction could overcome this difficulty. Other convergence factors could also be used (*4, 5*), however, to provide better approximations to the correct density distributions. But it should be noted that nonconvergence is a problem only for simple structures in which most atoms are in special positions. In such cases Fourier methods are likely to be unnecessary anyway. As indicated by Wilson and co-workers (*6*), the Fourier coefficients for random structures comprised of point atoms, none of which possesses excessively large scattering power, fall off with increasing scattering angle in a manner depending upon the crystal symmetry. When the effects of thermal oscillations are superposed on this convergence, it can be expected that little additional convergence factor will be required for complex structures.

This conclusion has been borne out very well in the case of the ($h, k, 0$) projection of KH_2PO_4, single-crystal neutron-scattering data for which was recently collected by B. C. Frazer and the writer at the Brookhaven National Laboratory reactor. The structure, and particularly the (0, 0, 1) projection, is actually not a favorable one from the point of view of the Wilson statistics. Phosphorus and potassium atoms are in special positions on the four-fold axes and are superposed in the (0, 0, 1) projection. Nevertheless, the observed structure factors fall off sufficiently fast with increasing $\frac{\sin\theta}{\lambda}$ to permit computations of excellent Patterson and Fourier maps. The Patterson map showed well-defined negative peaks representing the vectors between negatively scattering hydrogen and positively scattering P, K, and O nuclei, and well-defined positive peaks for the other interatomic vectors. Approximate hydrogen positions could be assigned, then, directly from the Patterson map. The Fourier map for the nuclear density distribution shows the P, K, and O nuclei, and the protons appear in double minima between the O—H...O bonded oxygens, with apparently half a proton, on the average, occupying each of the doubled positions. Patterson and nuclear density maps were also computed using calculated coefficients, assuming a single H-minimum between O—H...O oxygens, and with temperature-corrected scattering factors for the P, K, and O atoms as deduced from the x-ray analysis of KH_2PO_4 (*7*) and a temperature correction for the H-atoms as found by Levy and Peterson in NH_4Cl (*8*). These were in good agreement with the maps utilizing observed data, except for the appearance in the nuclear density maps of the doubled (disordered) hydrogen positions.

The statistical convergence of neutron-scattering factors in more or less random structures, coupled with the effects of natural thermal oscillation or artificial convergence factors, will evidently permit the rather general use of Fourier methods in neutron crystallography. A much more optimistic view of the power of the neutron technique is thus permissible than has been presented heretofore.

EXAMPLES OF NEGLIGIBLE INFLUENCE OF EXTINCTION

It has also been held that the effects of extinction may seriously limit the size of crystals that can be used in single crystal analyses (*9, 10*). In the case of the KH_2PO_4 study reported above, a cylindrically ground *c*-axis crystal about 3 mm in diameter and 1 cm long was utilized. The crystal was dipped several times into liquid nitrogen, in order to carry it back and forth through the ferroelectric transition point from tetragonal to orthorhombic symmetry. Extinction effects were found to be negligible. It is questionable whether the low-temperature treatment was necessary, but it was employed because of the limited time available, which would not have sufficed to permit repetition of the measurements. The smallness of the influence of extinction has been reported previously by Levy and Peterson in the case of NH_4Cl single crystals (*8*).

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PHASE DETERMINATION FROM NEUTRON DATA

It is well known that the chief difficulty in x-ray structure analysis is the absence of direct information on the phases of the scattered x-rays. Methods based upon nonnegativity and "atomicity" of the electron distribution permit the deduction of some phase information (*11, 12*), and "marked atom" methods (heavy atoms, with or without isomorphous replacement) have been particularly advantageous (*13*).

In their first paper on algebraic relations, Harker and Kasper (*14*) pointed out that their phase-determining conditions were strengthened if the observed crystal structure factors were divided by the value for the same scattering angle of the atomic structure factor, taking an "average" type of atom in the structure and correcting the "average-atom" factor for temperature oscillation. The effect of this modification of the observed structure-factor amplitudes is to simulate Fourier coefficients for a point-atom structure without thermal vibrations; and such point-atom coefficients afford the strongest phase-determining conditions. It is unfortunately true that, in the majority of structures involving different kinds of atoms, the structure-factors for these atoms are not sufficiently similar in form to permit choice of an "average" atom that will lead to accurate coefficients for the point-atom structure; and thus there is introduced into the already complex phase-determination algebra the further complication of inexact data.

It is interesting to note that neutron-scattering factors are just those corresponding to thermally oscillating point atoms; hence the only correction needed to reduce the Fourier coefficients to those for a distribution of fixed point-scatterers is to correct for the temperature effects. This can generally be done with much greater accuracy than is possible in the correction for atomic structure factors, and it must be done in both cases (for either nuclear scatterers or electron cloud distributions). Therefore, neutron-scattering data are more amenable to algebraic phase-determining methods than are x-ray data.

MARKED ATOM METHODS

The effects on structure analysis of variation of neutron-scattering power for the various nuclei in the periodic table have been discussed elsewhere. A few such effects should be particularly noted here. In one sense the "heavy-atom" method of x-ray analysis is possible to a much more limited extent with neutrons, since the variation of scattering cross sections is random throughout the periodic table, and the coherent scattering cross sections do not vary much from one element to another. Striking use of the isomorphous replacement method is possible with replacement of hydrogen by deuterium. The coherent scattering cross section here changes from -0.38 for H to $+0.65$ for D. The incoherent scattering of H may be troublesome in some cases, although to a much lesser extent with single crystals than in powder diffraction—as Levy and Peterson (*8*) and others have pointed out. The small influence of H-atoms upon x-ray scattering is, of course, an advantage in many-atom organic structures, where location of nonhydrogen atoms is already difficult and the structures would probably be impossible to determine if many hydrogen parameters would also have to be established before structure factors could be calculated. In structures where hydrogen positions are important, the obvious procedure is to determine non-H atom coordinates with x-rays, and then locate H (or D) atoms with neutrons.

Isomorphous replacement depends, of course, upon both chemical and packing-size similarities in the replaceable atoms. If enriched isotopes were readily available, isotopic replacement would be very advantageous in the cases (including H) shown in Table 1. Data for this table and for the discussion below are from C. Shull and E. O. Wollan, of the Oak Ridge National Laboratory (*15*).

Whereas replacement of halogens is very useful in the x-ray isomorphous methods, Cl is the only outstandingly heavy scatterer among them for neutrons. S (0.31) and Se (0.89) are good pairs for neutron studies. Na or K (0.35), Rb (0.55), Cs (0.49), and Tl (0.75) are not as advantageously different as in the x-ray case; but replacement of NH_4 by K, Rb, or Tl should provide interesting and perhaps useful effects. Ca, Sr, and Ba are not sufficiently different to be useful in the neutron case. Ti (-0.38) and Zr ($+0.62$) make an extremely good pair for the isomorphous replacement method.

TABLE 1

ISOTOPES FOR USE IN ISOMORPHOUS REPLACEMENT METHOD

Isotope	Scattering factor $\times 10^{-12}$ cm	Isotope	Scattering factor $\times 10^{-12}$ cm
^{1}H	-0.38	^{57}Fe	0.23
^{2}H = D	$+0.65$	Fe*	0.96
^{6}Li	0.7	^{58}Ni	1.44
^{7}Li	-0.25	^{60}Ni	0.30
Li*	-0.18	^{62}Ni	0.87
Ca*	0.49	Ni*	1.03
^{44}Ca	0.18	^{107}Ag	0.83
^{54}Fe	0.42	^{109}Ag	0.43
^{56}Fe	1.01	Ag*	0.61

* In natural abundance ratio.

Scattering with negative phase occurs for H, ^{7}Li, and Li in natural abundance ratio, Ti, Mn, and ^{62}Ni. As in the case of the KH_2PO_4 Patterson map, vectors between positive and negative scattering centers will appear in the Pattersons as negative peaks; all other interactions produce positive peaks. The aid that this provides in identification of the atoms responsible for the peaks is obvious.

It must be borne in mind that the algebraic relations in x-ray analysis which depend upon nonnegativity of the distribution of scattering material will *not* apply without modification when negative scattering centers are present in the neutron case. *Boundedness* of the function can, however, be utilized (*16*); and when the position of negative scatterers is known, but the distribution of other nuclei is not yet established, a set of Fourier coefficients for the negative scatterers alone can be computed, and these can be subtracted from the corresponding coefficients for the complete crystal. Relations arising from nonnegativity can then be applied.

CONCLUSIONS

Neutron diffraction has been regarded by some workers as a supplement to x-ray methods, to be used chiefly for structure refinement or location of light x-ray scatterers among heavy scatterers. There are cases, however, where neutron methods should provide more direct approaches to an unknown structure from the outset. Although it has been stated that Fourier methods will not be possible with neutron data, it is demonstrated both experimentally and theoretically that this is not true in cases where such methods will really be advantageous—i.e., for structures where the atoms are for the most part not in special positions.

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Hugo Iltis: 1882–1952

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HUGO ILTIS, professor of biology at Mary Washington College of the University of Virginia, died at Fredericksburg, Virginia, on June 22, 1952. In the United States he was best known as the biographer of Mendel and the organizer of the Mendel Museum. In his native city of Brünn, Czechoslovakia, where he was born in 1882, he was known also as the professor of biology of the Deutsche Gymnasium (1905–38), *Privatdocent* of botany and genetics in the Deutsche Technische-Hochschule, and the founder and director of the Masaryk People's University (1921–38). To the German National Socialists and racists generally he was known as the declared enemy of the pseudo science on which Hitler's state was founded. His great energy and intensity of purpose enabled him to carry on simultaneously his activities as scientist, biographer, educator, organizer, and writer for the public. In fact, it was the mutual interdependence among these aspects of his life and character, a kind of synergistic interaction, which enabled a man who was not robust, and who was often in frail health, to accomplish so much in the two decades between the founding of the Czechoslovak state by Masaryk and its destruction by Hitler.

It was in this period that he published his *Gregor Johann Mendel: Leben, Werk und Wirkung* (Berlin: J. Springer [1924]; English ed., London: Allen & Unwin; New York: Norton [1932].) The first half of this work was a careful, appreciative account of Mendel's life based on the few original documents available, some of which Iltis himself rescued from oblivion at the Altbrünner Königinkloster. This is still the definitive biography of Mendel. The second half, an account of the development of Mendelism after the rediscovery of the principles in 1900, was of less permanent value and was not included in the English translation.

In the same year (1924) Iltis published his account of the founding of, and his program for, the Volkshochschule, an evening school for adult education that was unique for its time and place. He edited, from 1927 to 1938, the quarterly journal of this school, which bore the same title as Iltis' own bookplate, *Licht ins Volk.* One of the 1931 issues was a *Festschrift* celebrating the opening by this people's university of its own house, an effort for which Iltis had provided the moving spirit and raised most of the funds. The democratic purposes of this venture in popular education were explicit in its curriculum and activities; they were the outward manifestations of Iltis' own deeply felt political beliefs, as expressed in two pamphlets published in 1926: *Kampf um den Darwinismus* and *Naturwissenschaft und Sozialismus.* The second of these began: "The building-up of scientific knowledge is the essential foundation for the