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"NEUTRON DIFFRACTION ANALYSIS OF NaH AND NaD"

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NEUTRON DIFFRACTION ANALYSIS OF NaH AND NaD

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The preceding paper described in some detail the neutron diffraction spectrometer shown in the first slide. This instrument was (Slide I) used to determine the diffracted intensities from sodium hydride and sodium deuteride, in order to obtain further inform- ation about the scattering cross-sections of hydrogen and deuterium.

The interest in these two nuclei is two-fold. First, from a theoretical point of view the proton and deuteron are sufficiently simple to have permitted rather detailed calcu- lation of their properties, which is not possible for heavier nuclei. Second, crystal struc- ture analysis by means of X-rays rarely gives information as to the positions of hydrogen atoms in the unit cell because of the very small scattering factor of hydrogen. However, neutrons are strongly scattered by hydrogen, as will be discussed later, and consequently hydrogen positions can be located by neutron diffraction analysis. Furthermore, deuterium, which is chemically identical to hydrogen, has a very different scattering factor for neutrons This offers the possibility of selective substitution of deuterium for hydrogen in certain crystals permitting the identification of specific hydrogen positions, where there may be many hydrogen atoms in a unit cell.

Sodium hydride and deuteride were made by the direct reaction between sodium and hydrogen, catalyzed by a small amount of stearic acid. The generator used for the prep- aration of the two materials is shown in the second slide. In this figure "A" is the electro- lytic cell, charged with light or heavy water for producing hydrogen or deuterium. The gas from the electrolytic cell passes over copper at 300°C in chamber "B" to promote re- action between hydrogen and any oxygen that might be present in the gas. After passing through the drying cell "C" the gas is lead into the thermal pump "D". This pump circu- lates the hydrogen through the reaction chamber "E". All of the circulated hydrogen passes through a liquid nitrogen freezing trap for further drying. The reaction chamber consists of a Pyrex envelope containing a stainless steel crucible which carries the sodium. The hydrogen is introduced through a stainless steel tube which extends to the bottom of the crucible so that the gas bubbles through the molten sodium. A rotatable steel stirring rod runs through the tube and is sealed with a piece of pressure tubing in such a way that the material in the crucible can be agitated without letting air into the system. Since a re- latively high temperature is required for the reaction, a heater in the form of a cylindrical electric oven surrounds the reaction chamber.

At the start of a preparation run the system is evacuated to a low pressure, to remove all oxygen and water vapor. Enough hydrogen is then generated to bring the pressure in the system to slightly more than one atmosphere. The temperature of reaction chamber is next raised to 380°C and the circulating pump started. The reaction chamber was usually charged with 10 to 15 gms of sodium and the reaction allowed to proceed until 30 to 50% of the sodium had been converted to the hydride. The rate of reaction varied between 1 gm/hr and 0.3 gms/hr.

Physically sodium hydride is a grey or white powder with a density of 0.92 gms/cm^3. It is extremely active towards water or water vapor and consequently must be handled in a dry box and kept in sealed containers. The sample holder which was a rectangular metal frame, with 2 mil aluminum windows on each side to transmit the neutron beam, had also to be constructed so that it was air tight.

Earlier X-ray measurements of NaH showed it to have a cubic unit cell with $a_0 =$ 4.87 A^0. The Na atoms are in face-centered cubic positions, but the hydrogen atoms cannot be assigned definite location by X-ray analysis so that the crystal may have either an NaCl or ZnS structure. The crystal has however been described as having an NaCl structure because of its similarity to LiH whose structure is known.

The neutron diffraction intensities obtained with NaH and NaD are shown in the next slide (Slide III). It will be seen that for NaH diffracted peaks occur at angles corresponding to the (111) (311) and (331) planes, while the measured intensity does not rise above the background at the (200) (220) or (400) position. With NaD on the other hand fairly strong peaks of intensity are found in the (200) (220) and (222) positions, and a weak one in the (111) position.

The effective scattering factors F^2_{hkl} for the various combinations of P_{hkl} can be calculated from the measured intensities by means of the relation

$$\frac{P_{hkl}}{P_0} = \lambda^3 l M^2 \frac{h \rho' e^{-\mu h \sec \theta}}{4 \pi r} \frac{h \rho' e^{-\mu h \sec \theta}}{\rho \sin^2 2\theta} j \cdot F^2_{hkl}$$

where:

P_{hkl} and P_0 are the peak and incident beam intensities
λ the neutron wavelength
l and h the width and thickness of the specimens
M the number of molecules per cubic centimeter
ρ' and ρ the powder and crystal density
μ the absorption (linear) coefficient
j the multiplicity factor for the planes in question
and θ the angle between the plane and beam.

As with X-rays the scattering factor F_{hkl} is made up of the scattering contribution for each of the two atoms involved in amounts which depend upon arrangement of the atoms in the unit cell.

The values of F_{hkl} in terms of the scattering factors f_{Na} and f_H for the two possible structures in comparison with those obtained from the measurement are shown in the next slide. (Slide IV) It will be observed that the measured F values for NaH satisfy the intensities for the NaCl structure if it is assumed that the scattering phase of hydrogen is opposite from that of sodium. The ZnS structure cannot be satisfied by any combination of f_{Na} and f_H since the absence of the (200) (220) and (222) reflections require that $f_{Na} = f_H$ but when this condition is fulfilled there should be a reflexion in the (400) position.

For NaD the measurements are satisfied by the NaCl structure if it is assumed that f_{Na} and f_D have the same sign and that their ratio differs but slightly from unity.

An analysis of the error of measurement of the observations shows that the ratio $P^2_{(200)} / P^2_{(111)}$ is less than 5%. This permits setting an upper and lower limit to the ratio f_H/f_{Na} of - 1.8 and - 0.5 , inasmuch as the scattering cross-sections are proportional to the square of the f-values. Therefore the ratio of the cross-sections lies between the limits of about

$$0.2 < \sigma_H / \sigma_{Na} < 4$$

and the phase of the wave representing the neutrons coherently scattered by hydrogen, unambigously differs by 180° from that representing sodium scattering.

Measurements on other materials indicate the coherent cross-section of sodium to be 0.7 barns. Assuming this cross-section to be correct the cross-section for hydrogen is between 0.2 and 3.0 barns.

The reversal of phase observed for hydrogen arises from the spin dependence of the interaction between the neutron and proton. The binding energy of the deuteron indicates that it is normally in a triplet S-state with a ground energy level of $\sum = 2.17$ Mev. However, there is also a virtual singlet S-state with energy of $\sum' = 0.068$ Mev, as can, for example, be demonstrated by the difference in scattering cross-section of para and ortho hydrogen.

On this basis the total scattering cross-section of protons for neutrons is:

$$\sigma_s = \frac{4 \pi h^2}{M} \left[\frac{3}{4} \frac{1}{\sum + \frac{1}{2}E_0} + \frac{1}{4} \frac{1}{\sum + \frac{1}{2}E_0} \right]$$

where M is the mass of the protons and E_0 the energy of the incident neutron. For thermal neutrons E_0 can be neglected in comparison with $\sum$ and $\sum'$. Furthermore, if the proton is bound the reduced mass increases the effective cross-section by a factor of 4. Hence the total scattering cross-section becomes:

$$\sigma_s = \frac{16 \pi h^2}{M} \left[\frac{3}{4} \frac{1}{\sum} + \frac{1}{4} \frac{1}{\sum} \right]$$

$$= 84 \text{ barns}$$

For the coherent scattering involved in neutron diffraction the effective cross-section σ_c however is very much less. This is a consequence of the fact that the spin directions of the protons in the hydride crystal are randomly oriented and the resultant coherent scattering is the algebraic sum of that from the singlet S and triplet S proton-neutron combination. Therefore the coherent scattering is

$$\sigma_c = \frac{16\,\pi\,h^2}{M}\left[\frac{1}{4}\left(\frac{1}{\Sigma}\right)^{\frac{1}{2}} - \frac{3}{4}\left(\frac{1}{\Sigma}\right)^{\frac{1}{2}}\right]^2$$

$$= 4.2 \text{ barns}$$

It should be pointed out that this is the maximum value the coherent cross-section can have. Thermal motion of the crystal atoms, loss of coherency when there is an energy change in the interaction between neutron and protons and similar effects decrease the coherent cross-section by a considerable factor.

It can be shown that the background scattering is the difference between the coherent cross-section and the total scattering cross-section. If the proton behaves as though it is rigidly bound in the lattice this difference is about 80 barns and gives isotropic scattering. On the other hand, if the protons responsible for the incoherent background behave primarily as though they were free the cross-section would be only 20 barns and the scattering would vary with angle.

The measurements of sodium deuteride show that the ratio

$$\frac{F^2_{(111)}}{F^2_{(200)}} = 0.285$$

consequently

$$f_{D}/f_{Na} = \frac{F_{(200)} \pm F_{(111)}}{F_{(200)} \pm F_{(111)}} = 0.55 \text{ or } 1.80$$

From the measurement of NaD above the order of the signs in the fraction on the right is ambigous. Therefore the cross section of deuterium must be either $\sigma_D = 3.1\ \sigma_{Na}$ or $0.3\ \sigma_{Na}$. Furthermore a comparison between the measured values of $F_{(200)}$ NaD and $F_{(111)}$ NaH show that the cross section for hydrogen must be either

$$\sigma_H = 3.4\ \sigma_{Na} \text{ or } 0.39\ \sigma_{Na}$$

By comparing the absolute diffracted intensity from NaH with the scattering from Diamond cross sections can be assigned to these elements. This comparison shows that the effective coherent cross section in the (111) direction should be 5.8 barns. On this basis two possible sets of cross sections may be designated, namely

	A	B
f_{Na}	0.71	2.2
f_H	2.60	.91
f_D	2.40	.85

Diffraction measurements on other sodium containing crystals have yielded the value σ_{No} = 0.7 barns. This makes it probable that the assigned coherent cross sections for hydrogen and deuterium should be 2.6 and 2.4 barns respectively.

The diffuse background superimposed on the diffracted peaks was also measured for the hydride and deuteride. The measured intensity of the background is related to the diffuse scattering factor S by the following expression:

$$\frac{P_d}{P_o} = e^{-\mu h \sec} \quad \sin \quad \frac{h\rho}{\rho} \quad \frac{1 \, \Delta \, \theta}{r} \quad S^2$$

(Slide)

For a crystal of firmly bound atoms the value of S should be independent of angle θ. This had been found to be true for such materials as CaO, NaCl, etc. However, for NaH the value of S is a pronounced function of angle. The S value for NaD also varies with angle but to a lesser extent than the hydride.
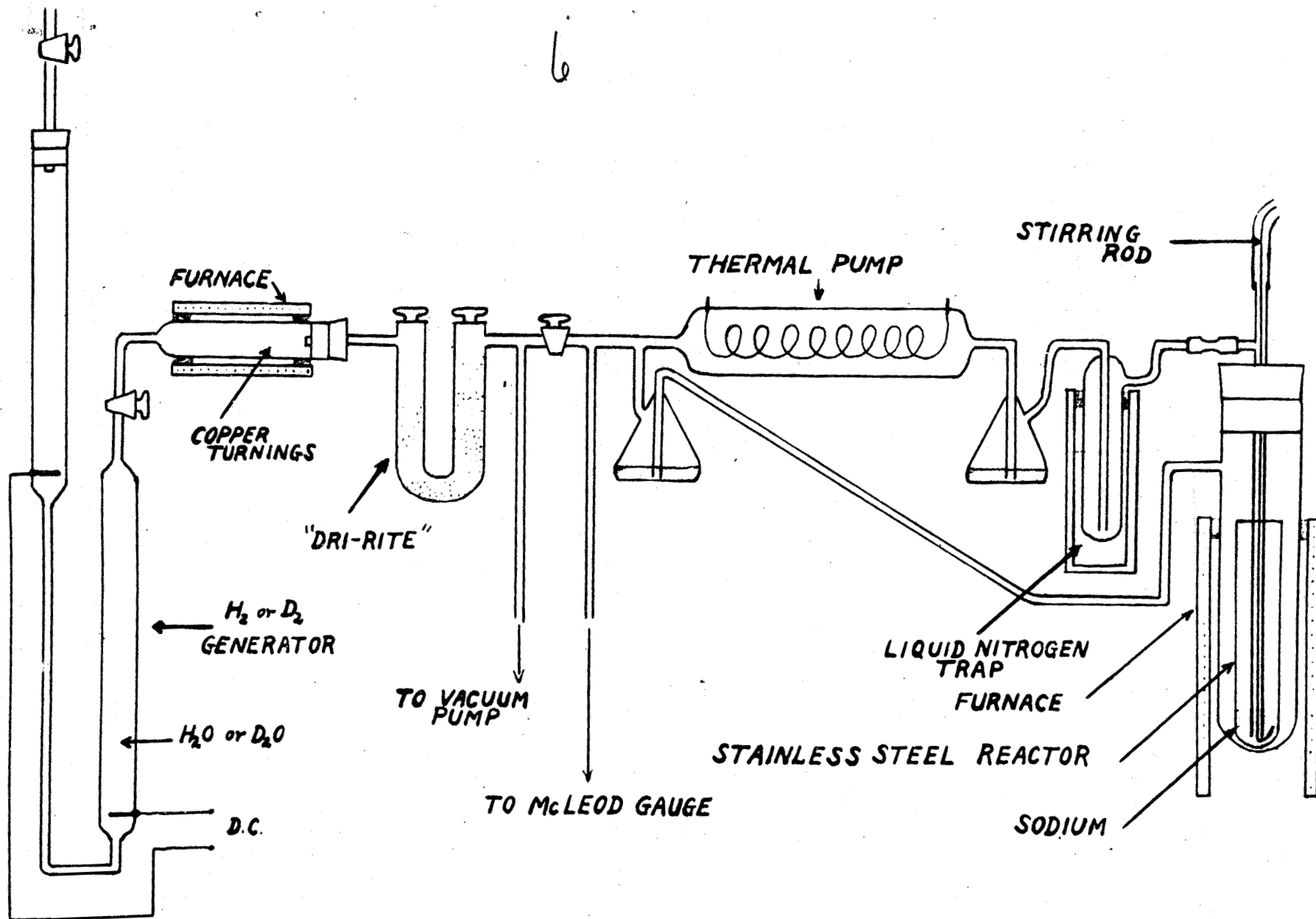
Intergrating the scattering over a sphere the total scattering cross-section is found, for NaH, to be about 24 barns. This is to be compared with the 84 barn cross-section expected from bound hydrogen, and 20 barns for free-protons. The contribution due to the sodium is at most 3.5 barns.

Both the amount of the scattering, and the variation with angle can be explained, by the assumption that the diffuse scattering comes primarily from hydrogen, and that this hydrogen behaves as though it were very loosely bound in the lattice.
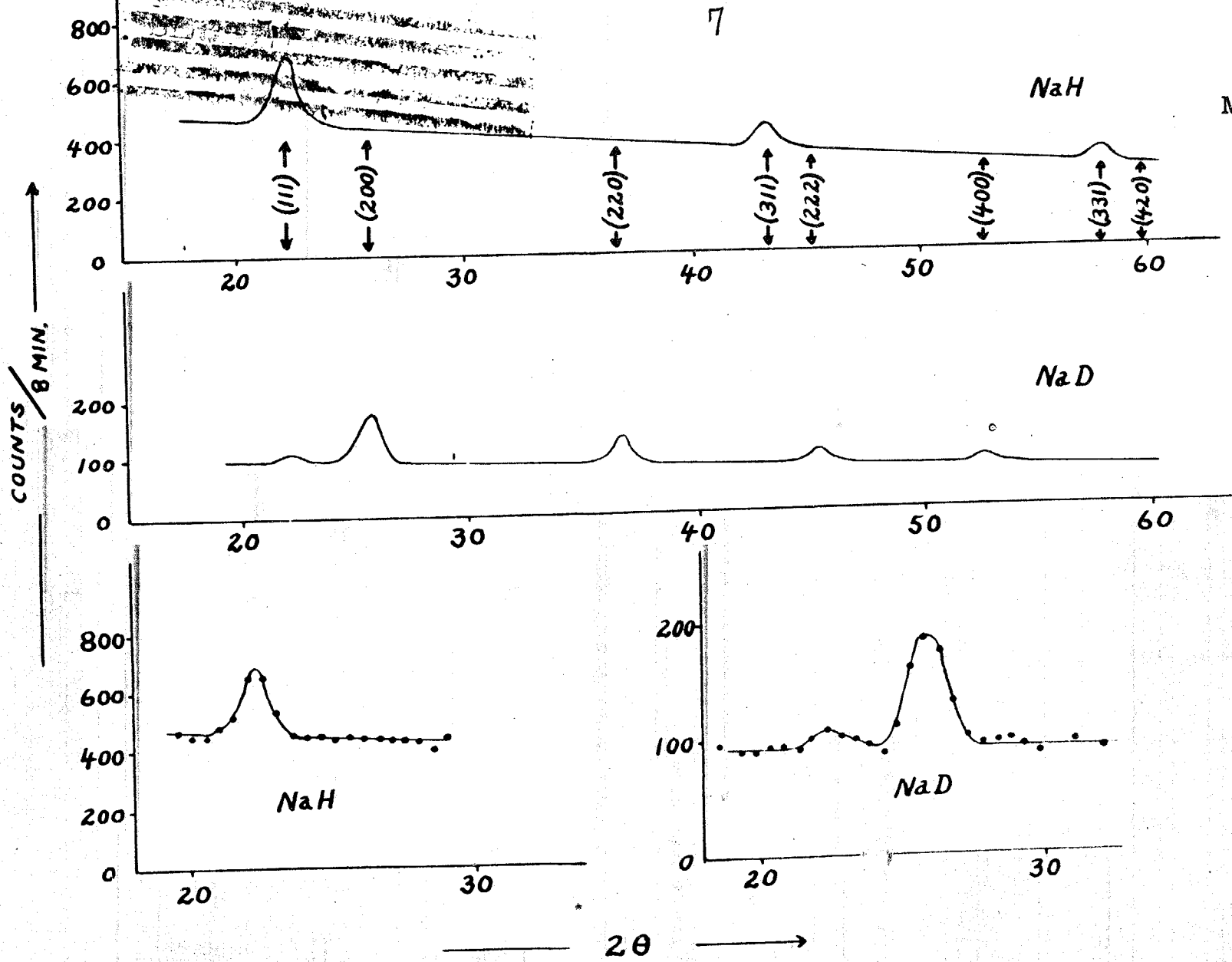
The diffuse scattering for the NaD molecule is much smaller being only about 6 barns. Furthermore, as has already been pointed out, its variation with angle is less. This is again in agreement with the assumption that the scattering is chiefly from a deuterium atom which behaves as though it were loosely bound. The total scattering cross-section of deuterium is about 6 barns, and because of its greater mass, its scattering has a much smaller angular dependence.
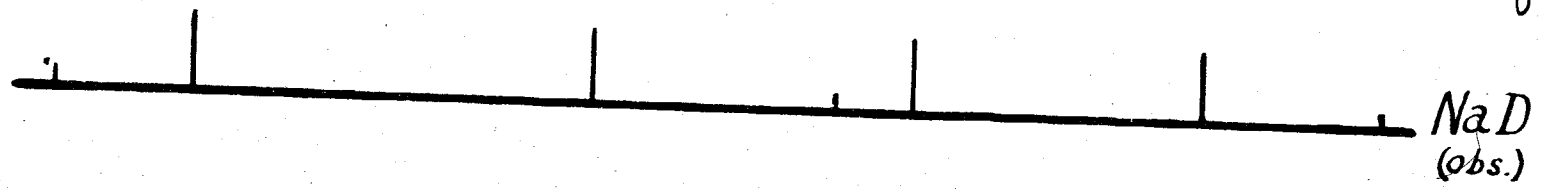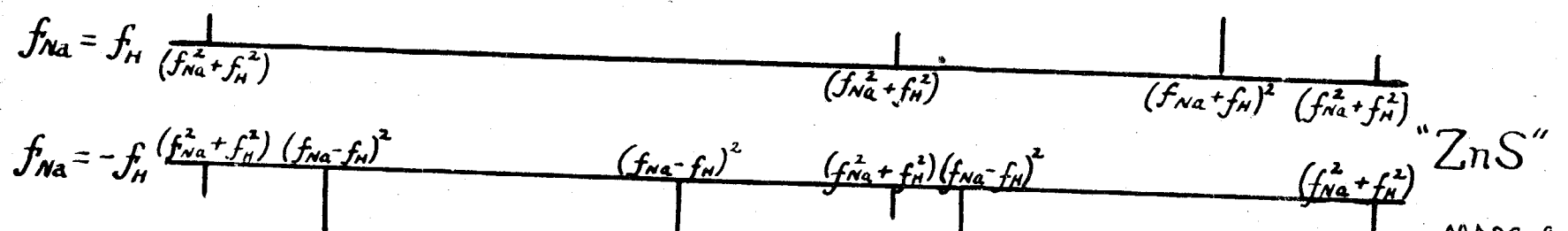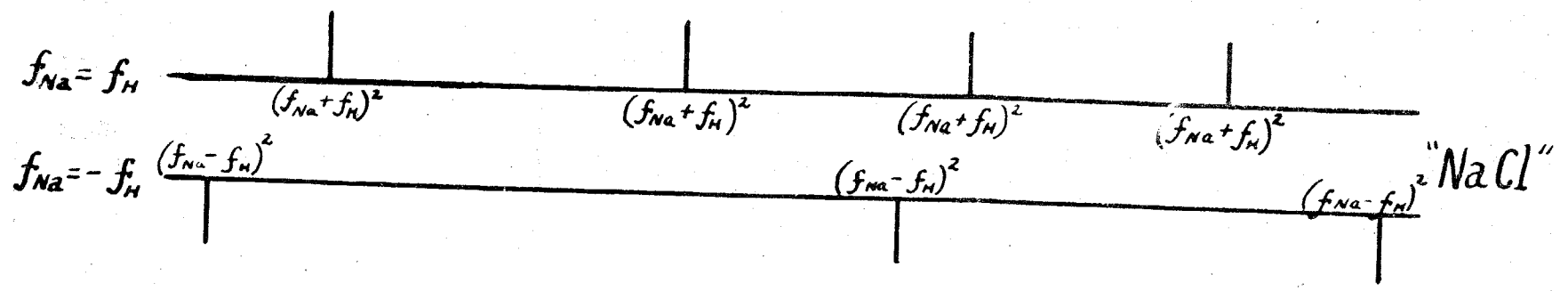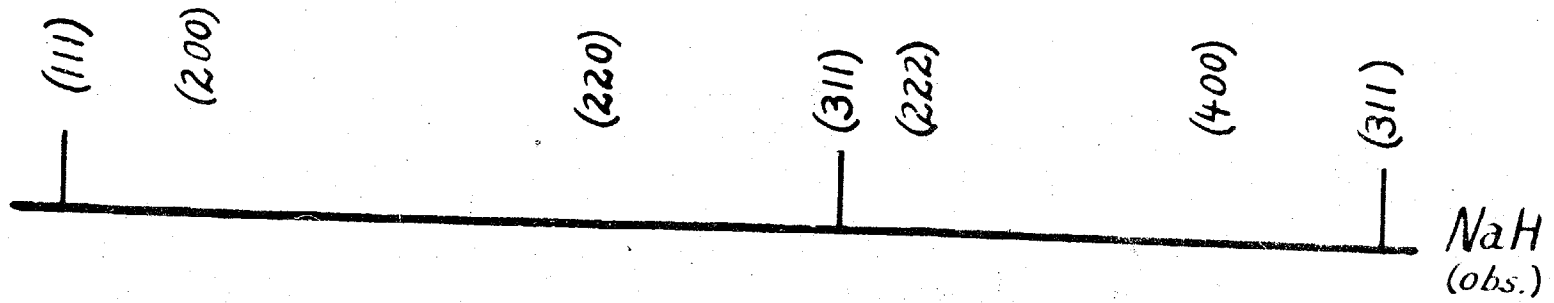
To summarize:

(1) The crystal structure of NaH and NaD was unambigously established as being the NaCl type rather than ZnS.

(2) The coherent scattering cross-section of hydrogen was found to be between 2.0 and 3.0 barns, giving a scattering wave 180° out of phase with that of sodium.

(3) The coherent scattering cross-section for deuterium was found to be between 2 and 3 barns, and to be in phase with the scattering of sodium.

(4) The background intensity and angular dependence indicated that the hydrogen and deuterium atoms behaved as though they were almost free atoms.

FURNACE

THERMAL PUMP

STIRRING ROD

COPPER TURNINGS

"DRI-RITE"

H_2 or D_2 GENERATOR

H_2O or D_2O

D.C.

TO VACUUM PUMP

TO McLEOD GAUGE

LIQUID NITROGEN TRAP

FURNACE

STAINLESS STEEL REACTOR

SODIUM

APPARATUS FOR PRODUCING NaH AND NaD.

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$$\frac{P_{hkl}}{P_o} \;=\; \frac{\lambda^3 M1}{4\pi r}\; \frac{h\rho'}{J^3}\; \frac{e^{-\mu h \sec\theta}}{\sin^2 2\theta}\; j\, F_{hkl}^{\,2}\,.$$

(111) (200) (220) (311) (222) (400) (311)

NaH (obs.)

$f_{Na} = f_H$ $(f_{Na}+f_H)^2$ $(f_{Na}+f_H)^2$ $(f_{Na}+f_H)^2$ $(f_{Na}+f_H)^2$

$f_{Na} = -f_H$ $(f_{Na}-f_H)^2$ $(f_{Na}-f_H)^2$ $(f_{Na}-f_H)^2$ "NaCl"

$f_{Na} = f_H$ $(f_{Na}^2+f_H^2)$ $(f_{Na}^2+f_H^2)$ $(f_{Na}+f_H)^2$ $(f_{Na}^2+f_H^2)$

$f_{Na} = -f_H$ $(f_{Na}^2+f_H^2)(f_{Na}-f_H)^2$ $(f_{Na}-f_H)^2$ $(f_{Na}^2+f_H^2)(f_{Na}-f_H)^2$ $(f_{Na}^2+f_H^2)$ "ZnS"

NaD (obs.)

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DIFFUSE SCATTERING/MOLECULE