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Neutron Diffraction Studies of NaH and NaD

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Neutron diffraction patterns for NaH and NaD are given from which it is established that the crystal structure is analogous to that of NaCl with the hydrogen centers replacing chlorine. It is shown that both sodium and deuterium scatter neutrons with a positive scattering amplitude whereas hydrogen scattering is characterized by a negative scattering amplitude. The coherent scattering cross sections for hydrogen and deuterium are determined as 2.0 ± 0.3 and 4.1 ± 1.2 barns, respectively. Using this value of the coherent scattering cross section for hydrogen and Melkonian's value of 20 barns for the total scattering cross section by a free proton, the scattering amplitudes characteristic of the two proton spin states have been evaluated, and these are in good agreement with the latest data on the scattering of neutrons by *o*- and *p*-hydrogen. The range of nuclear forces present in the neutron-proton triplet interaction is evaluated as $1.6\pm0.2\cdot10^{-13}$ cm.

INTRODUCTION

THE preceding paper[1] has described in some detail the general problem of neutron diffraction as related to the nuclear properties and the structural array of atoms in crystalline materials. The present paper is concerned with studies which have been made on hydrogen and deuterium containing crystals by use of the techniques described in the previous paper, which for convenience will be referred to as I.

The diffraction of neutrons by hydrogen and deuterium containing crystals is of interest for two reasons; (1) this technique offers a promising method of obtaining information on the location of hydrogen positions in crystalline and molecular structures whereas similar analyses by the diffraction of x-rays or electrons can only rarely give such information, and (2) the scattering of neutrons by protons or deuterons is of importance from a theoretical physics point of view since these simplest of nuclear reactions can be treated theoretically for comparison with experiment. Information pertinent to both of these items has been obtained.

EXPERIMENTAL RESULTS

Perhaps the simplest of hydrogen-containing crystals from the structural point of view are the alkali hydrides. X-ray diffraction studies have shown that the metallic atoms in LiH, NaH, KH, CsH, etc. are arrayed in a face-centered cubic structure. However, it is only in the case of LiH, where the x-ray structure factors of the two atoms are sufficiently the same, that the hydrogen positions have been located.[2] For this case the hydrogen centers are also found to be at face-centered cubic positions and the structure is identical to that occurring in NaCl with hydrogen replacing chlorine. By analogy to LiH the other simple hydrides are suspected also to crystallize in the NaCl structure.

NaH was selected for the present study because of (1) its commercial availability, (2) it could be prepared in the laboratory thereby permitting the preparation of the deuteride, and (3) the absorption cross section is low in contrast to the relatively high absorption cross section of LiH samples. In the laboratory preparation of the hydride (or deuteride) the product was formed by the direct reaction of molten sodium with hydrogen catalyzed by a small amount of stearic acid. The hydrogen was obtained by electrolysis of water after which it was cleansed of (1) residual oxygen by passage over copper at 300°C and (2) residual water vapor by passage through a liquid nitrogen trap. The reaction was then performed by bubbling the hydrogen gas through molten sodium contained in a stainless steel tube and maintained at a temperature of 380°C.

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[1] E. O. Wollan and C. G. Shull, Phys. Rev. **73**, 830 (1948).

[2] E. Zintl and A. Harder, Zeits. f. physik. Chemie **B14**, 265–284 (1931).

Since the reaction rate is rather low, recirculation of the unreacted gas was found desirable and was accomplished by means of a thermal pump.

Three batches of the material were used for examination: (1) commercially prepared NaH,[3] (2) laboratory-prepared NaH, and (3) laboratory-prepared NaD. X-ray diffraction analyses[4] were obtained on these preparations and showed the presence of minor impurities, mostly metallic sodium, in (1) and (2) whereas a considerable impurity of sodium and sodium hydroxide or deuteroxide was indicated in preparation (3). Since some of the diffraction lines for sodium and sodium hydroxide fall at or near to the positions of the principal NaD lines, a certain ambiguity in the relative intensities of the latter lines is introduced through the presence of the impurities. The effect of this upon the quantitative interpretation of the NaD pattern will be discussed in a later section.

Physically, sodium hydride is a grey or white powder with a solid density of 1.37 g/cm^3. It is extremely active towards water or water vapor and, consequently, must be handled in a controlled atmosphere and kept in sealed containers. The sample holder was similar to that described in I with thin aluminum windows for air-tight construction. Samples of different thicknesses ranging from about 0.5 g/cm^2 to 0.8 g/cm^2 were used in evaluating the intensity of the diffraction pattern.

Typical diffraction patterns for NaH and NaD covering the inner diffraction peaks are shown in Fig. 1. A pronounced (111) peak and a very weak or absent (200) peak is to be noted for NaH in contrast to the reversed intensities of these peaks for NaD. If sodium were the only element contributing to the pattern (as is the case in x-ray diffraction analysis) one would expect a (111) peak about twice as strong as the (200) peak. Since neither the NaH nor NaD pattern shows this ratio of peak intensities, it is immediately concluded that both hydrogen and deuterium are contributing to the coherent scattering. Moreover, the reversal of intensities in the two patterns suggests that the hydrogen and deuterium centers are scattering in opposite phase with respect to each other. These data do not, however, permit a conclusion as to the relative phase of scattering of hydrogen (or deuterium) with respect to sodium because of the uncertainty in the crystal structure of sodium hydride. Before this can be accomplished it is necessary to establish without ambiguity the correct structure.

TABLE I. Experimental intensities and values calculated for possible structures of NaH.

Diffraction peak	Experimental intensity	Calculated for ZnS structure	Calculated for NaCl structure
(111)	37	$f_{\mathrm{Na}}^2+f_{\mathrm{H}}^2$	$(f_{\mathrm{Na}}-f_{\mathrm{H}})^2$
(200)	<2	$(f_{\mathrm{Na}}-f_{\mathrm{H}})^2$	$(f_{\mathrm{Na}}+f_{\mathrm{H}})^2$
(220)	0	$(f_{\mathrm{Na}}+f_{\mathrm{H}})^2$	$(f_{\mathrm{Na}}+f_{\mathrm{H}})^2$
(311)	25	$f_{\mathrm{Na}}^2+f_{\mathrm{H}}^2$	$(f_{\mathrm{Na}}-f_{\mathrm{H}})^2$
(222)	0	$(f_{\mathrm{Na}}-f_{\mathrm{H}})^2$	$(f_{\mathrm{Na}}+f_{\mathrm{H}})^2$
(400)	<5	$(f_{\mathrm{Na}}+f_{\mathrm{H}})^2$	$(f_{\mathrm{Na}}+f_{\mathrm{H}})^2$
(331)	15	$f_{\mathrm{Na}}^2+f_{\mathrm{H}}^2$	$(f_{\mathrm{Na}}-f_{\mathrm{H}})^2$
(420)	0	$(f_{\mathrm{Na}}+f_{\mathrm{H}})^2$	$(f_{\mathrm{Na}}+f_{\mathrm{H}})^2$

Among the several structures of face-centered cubic type which are known to exist, there are

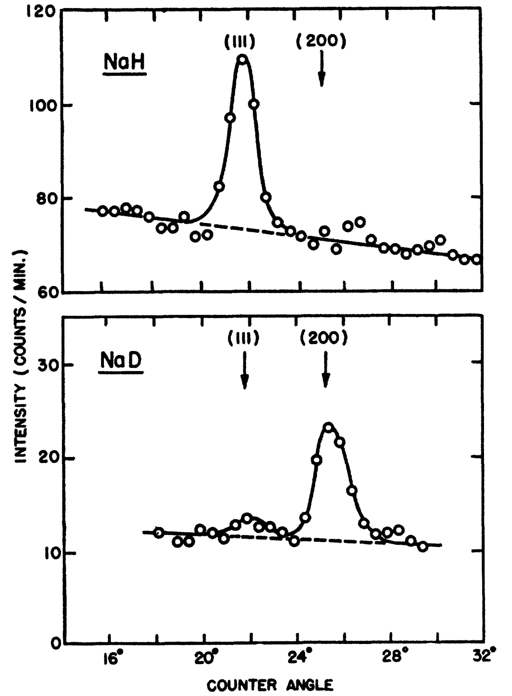

FIG. 1. Powder diffraction patterns over the (111) and (200) peaks of NaH and NaD. The diffuse scattering for NaH is seen to be much larger than that for NaD.

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[3] Available from the Electrochemicals Department, E. I. duPont deNemours and Company, Niagara Falls, New York.

[4] We are indebted to Mr. A. C. Eckert of the Carbide and Carbon Chemical Corporation who supplied some of the analyses for us.

only two (B-1 type, NaCl and B-3 type, ZnS) which are possible structures for NaH. Other structures are ruled out because of unit cell size. Fortunately it is possible to determine rather easily the correctness of either the NaCl or the ZnS structure on the basis of the relative intensities of some of the outer diffraction peaks. Figure 2 shows additional diffraction data for some of the higher index peaks of NaH. Peaks at the (311) and (331) locations are to be observed while the (220), (400), and (420) are either too weak for measurement or are absent.

A comparison of the measured intensities with those calculated for the two possible structures is given in Table I. The squares of the crystal structure factors (approximately proportional to the diffraction peak intensities) are given here in terms of the individual nuclear scattering amplitudes. Either the ZnS structure with a common sign for f_{Na} and f_{H} or the NaCl structure with opposite signs for the amplitudes would satisfy the experimental data for the (111) and (200) peaks but the relative intensities of the (220), (311), (420), and (331) eliminate the ZnS structure from consideration. For instance, the (220) reflection of the ZnS structure should exhibit a strength close to that of the (111) and (311) reflections, and this is in contradiction to the experimental data. Similar considerations with respect to the (420) and (331) peaks lead to the same conclusion. *Thus it is established that sodium hydride possesses the same type of structure as* NaCl *and that sodium and hydrogen are scattering neutrons with opposite phase. It also follows that sodium and deuterium are scattering neutrons with common phase.*

EVALUATION OF THE COHERENT SCATTERING CROSS SECTIONS FOR HYDROGEN AND DEUTERIUM

The intensities of the diffraction peaks, illustrated in Figs. 1 and 2, can be used to evaluate coherent scattering cross sections just as has been performed in I. Equation (15) of I has been used along with the diamond calibration data in evaluating the crystal structure factor F_{hkl} for several of the diffraction peaks, and this permits a determination of the individual nuclear scattering amplitudes.

For the case of NaH, values of F_{111} and F_{200} will, in principle, determine values of f_{Na} and f_{H} since two independent expressions in terms of the nuclear scattering amplitudes are available. In practice, however, it is found that the resultant values of f_{Na} and f_{H} are quite sensitive to the value of F_{200}, which is in turn dependent upon the intensity of the unmeasurably weak (200) peak in the NaH pattern. Such a procedure yields a hydrogen cross section with a considerable probable error because of the uncertainty in the measurement of the (200) peak intensity. For this reason an alternative procedure has been used which combines values of F_{hkl} for NaH with previously obtained data on the nuclear scattering amplitude for sodium.

A further difficulty in the analysis of the hydrogen scattering data arises because of the lack of information on the magnitude of the thermal oscillations in the NaH crystal, and hence of the uncertainty in the temperature corrections to be applied to the data. No direct experimental data on the characteristic temperature of NaH are available but a comparison of

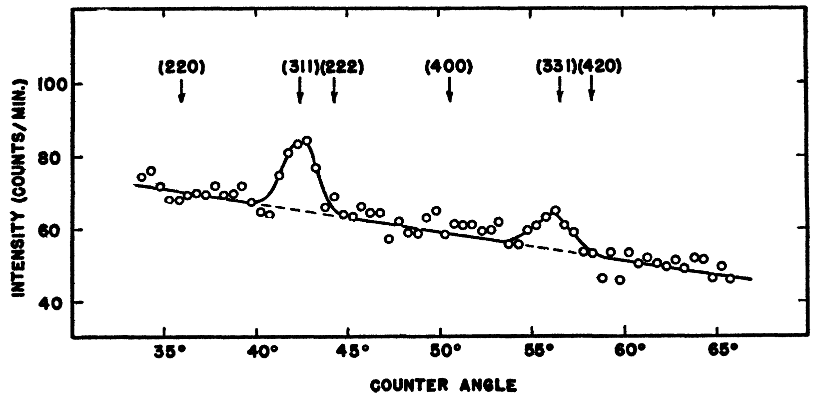

FIG. 2. Powder diffraction pattern for NaH showing some of the higher indexed peaks.

the characteristic temperatures of other alkali compounds suggests the value of 650°K as is shown in Fig. 3. Since the masses of the sodium and hydrogen centers are so different it is not feasible*** to apply a temperature correction factor based upon a single characteristic temperature. Fortunately it has been found possible to obtain a unique value of the hydrogen scattering amplitude from values of F_{111} and F_{311} without having a detailed knowledge of the hydrogen thermal oscillations.

In the NaH diffraction pattern there are three peaks of measurable intensity, namely, (111), (311), and (331). The first two are of comparable intensity and can be measured with an accuracy better than ten percent while the third peak is quite weak and cannot be determined with any significant accuracy. The crystal structure factors for these two peaks can be written as

$$\begin{aligned} F_{111} &= \exp[-\alpha \sin^2\theta_{111}]f_{\mathrm{Na}} \\ &\quad -\exp[-\beta \sin^2\theta_{111}]f_{\mathrm{H}} \\ F_{311} &= \exp[-\alpha \sin^2\theta_{311}]f_{\mathrm{Na}} \\ &\quad -\exp[-\beta \sin^2\theta_{311}]f_{\mathrm{H}}. \end{aligned} \tag{1}$$

In these equations, the algebraic sign of f_{Na} is considered to be positive in keeping with the convention discussed in I, while that of f_{H} is to be considered negative since hydrogen is scattering out of phase with respect to sodium. The exponential coefficients are temperature correction factors necessary to correct for thermal motion of the scattering centers and these are not necessarily the same for the two scattering atoms. Values of the crystal structure factors have been obtained experimentally, giving

$$F_{111} = 0.69_5 \cdot 10^{-12},$$

and (2)

$$F_{311} = 0.59_1 \cdot 10^{-12} \text{ cm}.$$

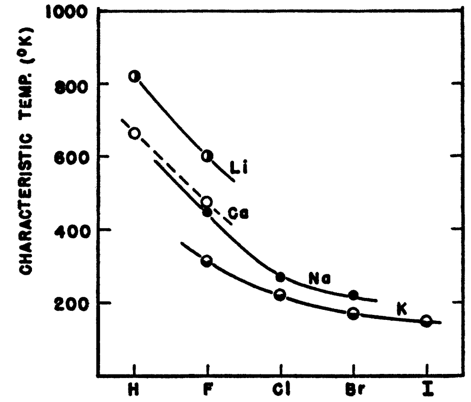

Fig. 3. Values of the Debye characteristic temperature for various alkali metal compounds.

When use is made of the previously obtained (see I) value for f_{Na} of $0.345 \cdot 10^{-12}$ cm, one has available two equations containing the three unknowns α, β, and f_{H}. Under these conditions a unique solution is, of course, not possible but nevertheless considerable information on the value of f_{H} can be obtained. Table II lists several sets of consistent solutions to Eq. (1) covering a wide range of possible values for the sodium temperature correction factor in the (111) peak. It is seen that the resultant values of f_{H} are very insensitive to the temperature correction factors as long as these are consistent with the data indicated in Eq. (1) and in the range indicated on Table II. Some information on the latter point is obtained from a study of the (111) peak intensity at liquid nitrogen temperature as compared to room temperature. Measurements of the effect of specimen temperature upon the (111) intensity indicate that

$$\frac{F_{111}(78°K)}{F_{111}(300°K)} = 1.00 \pm 0.02 \tag{3}$$

and this implies that the sodium temperature correction factor in Table II lies between 0.96 and 1.00. Thus it is established that the coherent

Table II. Various sets of consistent solutions to Eq. (1).

$\exp[-\alpha \sin^2\theta_{111}]$	$\exp[-\beta \sin^2\theta_{111}]$	f_H
0.990	0.890	$0.398 \cdot 10^{-12}$ cm
0.980	0.902	0.396
0.960	0.922	0.395
0.940	0.941	0.395
0.920	0.958	0.395
0.900	0.972	0.396

*** We are indebted to Professor O. Halpern for pointing this out to us in a private communication. In an earlier report [Phys. Rev. **73**, 262 (1948)] an erroneous temperature correction factor based upon the conventional Debye-Waller expression with the above characteristic temperature was used, and this led to a value for the coherent scattering cross section for hydrogen which differs somewhat from the present value. The procedure described here requires no advance knowledge of the characteristic temperature or of the thermal oscillations but rather these are determined, in effect, from the consistency of the intensity data.

scattering amplitude for hydrogen is given by

$$f_{\mathrm{H}} = -0.39_6 \pm 0.02 \cdot 10^{-12}\ \mathrm{cm} \tag{4}$$

with the suggested error obtained from the uncertainties in the experimental values of F_{111} and F_{311}. This amplitude corresponds to a coherent scattering cross section for hydrogen of

$$\sigma_{\mathrm{H}}{}^{\mathrm{coh}} = 2.0 \pm 0.3\ \text{barns}. \tag{5}$$

Such a scattering cross section for hydrogen is seen to be much smaller than the total scattering cross section for bound protons, namely, 80 barns. The reason for this difference lies in the pronounced spin dependence of scattering in hydrogen, as will be discussed in a later section.

The experimental data for NaD have been treated in the same fashion as those for NaH. The crystal structure factor F_{200} can be written

$$F_{200} = 0.978 f_{\mathrm{Na}} + 0.934 f_{\mathrm{D}}, \tag{6}$$

where the temperature correction factors have been obtained from information suggested by the above analysis of the hydrogen data. When use is made of the earlier value of f_{Na} and the experimental data on the intensity of NaD (200) peak it is obvious that the scattering amplitude for deuterium can be obtained. However, because of the considerable impurity in the NaD preparation and the uncertainty in the quantitative composition of the NaD sample, there is a fairly large possible error in the value of F_{200}. This turns out to be $0.87 \cdot 10^{-12}$ cm with an estimated error of possibly $0.07 \cdot 10^{-12}$ cm. Substitution into Eq. (6) leads to

$$f_{\mathrm{D}} = +0.57 \pm 0.08 \cdot 10\ \mathrm{cm}, \tag{7}$$

and hence,

$$\sigma_{\mathrm{D}}{}^{\mathrm{coh}} = 4.1 \pm 1.2\ \text{barns}. \tag{8}$$

Thus deuterium shows a coherent scattering cross section about twice that of hydrogen.

SCATTERING BY THE SPIN STATES OF HYDROGEN AND DEUTERIUM

The coherent scattering amplitudes for hydrogen and deuterium can be used in conjunction with the total scattering amplitudes of the free nuclei to evaluate the scattering amplitudes characteristic of the two spin states of scattering for each of these nuclei. It can be shown that the coherent scattering amplitude for hydrogen f_{H} can be expressed as

$$f_{\mathrm{H}} = 2(\tfrac{3}{4}a_1 + \tfrac{1}{4}a_0), \tag{9}$$

where a_1 and a_0 are the triplet and singlet scattering amplitudes of a free proton for which the spins of the proton and the incident neutron are, respectively, parallel and antiparallel. The fractional multipliers of a_1 and a_0 are the spin weighting factors characteristic of the two states, and the common factor 2 is the reduced mass factor (see I). Also from Eq. (13) of I, the total scattering cross section of the free proton σ_f can be expressed as

$$\sigma_f = 4\pi(\tfrac{3}{4}a_1{}^2 + \tfrac{1}{4}a_0{}^2). \tag{10}$$

Using the coherent hydrogen scattering amplitude of $-0.396 \cdot 10^{-12}$ cm and a free proton scattering cross section[6] of 20 barns results in

$$\begin{aligned} a_1 &= +0.520 \cdot 10^{-12}\ \mathrm{cm}, \\ a_0 &= -2.35 \cdot 10^{-12}\ \mathrm{cm}. \end{aligned} \tag{11}$$

The value of the singlet scattering amplitude a_0 is determined almost completely by the free proton scattering cross section. On the other hand, the triplet scattering amplitude a_1 is sensitive about equally to errors in both the coherent scattering cross section and the free proton cross section.

These values for the scattering amplitudes of the two spin states are in good agreement with those obtained by Sutton, Hall, and others[7] from the scattering by *o*- and *p*-hydrogen, namely,

$$\begin{aligned} a_1 &= +0.522 \cdot 10^{-12}, \\ a_0 &= -2.34 \cdot 10^{-12}. \end{aligned} \tag{12}$$

It is also possible to evaluate the range of the neutron-proton force acting in the triplet interaction from the values of the scattering amplitudes. Hamermesh and Schwinger[8] have discussed this relationship and using their calculations and the amplitudes of Eq. (11), the triplet range is evaluated as

$$r_0 = 1.6 \pm 0.2 \cdot 10^{-13}\ \mathrm{cm}. \tag{13}$$

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[6] E. Melkonian, Bull. Am. Phys. Soc. **23**, No. 2, AU7 (1948).

[7] R. B. Sutton, T. Hall, E. E. Anderson, H. S. Bridges, J. W. DeWire, L. S. Lavatelli, E. A. Long, T. Snyder, and R. W. Williams, Phys. Rev. **72**, 1147 (1947).

[8] M. Hamermesh and J. Schwinger, Phys. Rev. **71**, 678–680 (1947).

This is seen to be appreciably smaller than that generally attributed to the proton-proton singlet interaction (namely, $2.8 \cdot 10^{-13}$ cm), and presumably this indicates a real difference between these interactions. The present value is likewise in good agreement with the value $1.5 \cdot 10^{-13}$ cm indicated in the *ortho-para*-hydrogen experiments.[7]

For the case of neutron scattering by deuterium, the coherent scattering cross section of 4.1 barns can be used to establish the presence or absence of spin dependent forces just as has been done for hydrogen above and for sodium in I. Using 3.1 barns as the scattering cross section for free deuterium[9] one calculates the cross section for bound deuterium to be 7.0 barns. This is somewhat larger than the coherent scattering cross section of 4.1 barns. If this difference is real, then the scattering amplitudes characteristic of the two spin states must differ and there must be spin dependent forces present in the neutron-deuteron reaction. However, the present lack of precision in the evaluation of the coherent scattering cross section for deuterium does not permit significant conclusions concerning the magnitude of the spin dependent effects. Additional diffraction data taken on deuterium containing materials whose purity is better established than for the present NaD preparation must be obtained before conclusions can be assured.

DIFFUSE SCATTERING BY NaH

It will be noticed in Figs. 1 and 2 that the diffraction peaks for NaH are superimposed on a high background of diffuse scattering. This is not surprising since the total scattering cross section for hydrogen is unusually high (ranging from 20 to 80 barns depending upon the neutron energy and the conditions of binding) and the large fraction of spin incoherence for hydrogen has caused most of the scattering to appear as a diffuse component. The large spin incoherence is a consequence of the presence of opposite signs in the scattering amplitudes of the two spin states as discussed in the preceding section. Measurements of the transmission cross section (total scattering and capture cross section) have been made on a number of NaH samples and these indicate a total scattering cross section per NaH molecule of 32 barns. This value is, of course, representative for our particular neutron energy of 0.0724 ev only and would be different for other energies. Since the total Bragg scattering cross section for all of the peaks in the diffraction pattern amounts to only 1 or 2 barns, there must be 31 barns of scattering in the diffuse part of the pattern. A direct measurement of the integrated diffuse scattering would provide an interesting comparison with this value, but unfortunately the presence of multiple scattering in the specimen increases the diffuse scattering intensity sufficiently to make the integrated value considerably larger than the transmission value.

The large diffuse scattering obtained with hydrogenous compounds increases the difficulty of obtaining the Bragg scattering features from which structural analyses are derived. This complication does not arise with deuterated compounds however, so that it would appear more feasible to perform crystallographic studies with such compounds. Evidence in favor of this conclusion has already been obtained in the study of the structures of ice and water. In any event, the coherent scattering cross sections for both hydrogen and deuterium are conveniently near the values characteristic of most elements, and hence crystallographic analysis of hydrogen atom positions should be readily possible.

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[9] W. W. Havens and L. J. Rainwater, Report No. CP-2293, Manhattan District Plutonium Project.