

## Neutron Diffraction Study of the Structure of Ice\*

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The crystal structure of ice in which the location of the hydrogen atoms cannot be determined by x-ray means, has been studied by the neutron diffraction technique. The intensities in the neutron diffraction pattern from a powdered sample of heavy ( $D_2O$ ) ice, maintained at  $-90^\circ C$ , were measured and compared with the intensities which would result if ice possessed any one of four proposed structures. The oxygen atom positions have already been determined from x-ray measurements and the proposed structures are considered here with respect to the location of the hydrogen (or deuterium) atoms. The structures considered are (a) the Barnes model, in which the hydrogen atoms are midway between oxygen

atoms, (b) the Bernal and Fowler model which maintains a molecular grouping of two hydrogen atoms close (0.96Å) to each oxygen atom with a definite repeating orientation, (c) a model consisting of hydrogen molecules rotating about the oxygen atoms as centers, and (d) the Pauling model, suggested on the grounds of a residual entropy at low temperatures, in which hydrogen molecules possess some randomness of orientation under the restriction that one and only one hydrogen atom lies on each of the lines joining one oxygen atom to its neighbor. Structures (a), (b), and (c) are definitely ruled out by the neutron measurements while the Pauling structure agrees well with the measurement.

THE crystal structure of ice has been the subject of considerable study over a period of many years. X-ray diffraction studies<sup>1-3</sup> have led to a definite determination of the oxygen atom positions in the ice crystal lattice but the positions of the hydrogen atoms in the crystal cannot be determined by this means. Information on this point can be obtained from considerations of the physical and chemical properties of water and ice but this information is in some respects less definite than that obtained by x-ray studies where such studies are possible.

With the development of neutron diffraction techniques, we are now in a position to make a direct structure examination of hydrogen containing crystals. The coherent cross section for the scattering of neutrons by hydrogen and deuterium is quite comparable to that for oxygen and hence interference effects for neutrons scattered by these nuclei can be observed.

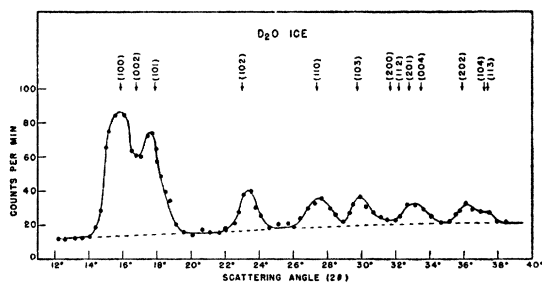


FIG. 1. Neutron diffraction powder pattern of heavy ice ( $D_2O$ ) taken at  $-90^\circ C$  with neutrons of wave-length 1.06Å.

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\*\* On leave (1946-1947) from B. F. Goodrich Company, Akron, Ohio.

<sup>1</sup> David M. Dennison, *Phys. Rev.* **17**, 20 (1921).

<sup>2</sup> W. H. Barnes, *Proc. Roy. Soc.* **A125**, 670 (1929).

<sup>3</sup> W. H. Bragg, *Proc. Phys. Soc. (London)* **34**, 98 (1922).

### MEASUREMENTS

The neutron diffraction measurements have been made with heavy ( $D_2O$ ) ice.  $D_2O$  was used because the coherent neutron scattering cross section for deuterium ( $\sim 5$  barns), is larger than for hydrogen ( $\sim 2$  barns), and also the diffuse scattering for deuterium is much smaller than for hydrogen.

The measurements were made with the powdered crystal technique with monochromatic neutrons from the ORNL pile as previously described<sup>4</sup> for other powdered crystal measurements. In this case the powdered ice was held in a special cold cell maintained at  $-90^\circ C$  by a dry ice-acetone cooling mixture. The  $D_2O$  was frozen, powdered in a mortar and loaded into the cooling cell, the work being done in a dry box so as not to contaminate the  $D_2O$  with ordinary water.

The average results of a number of diffraction measurements with separately prepared powdered samples is shown in Fig. 1. The intensities in this pattern were obtained in terms of absolute cross sections by comparing the pattern for a known amount of ice with the pattern given by a known amount of diamond which is used as a standard since the carbon coherent cross section is accurately known. It will be noticed from the figure that some of the diffraction lines are not resolved. It is not possible with the presently available intensities to resolve the closely spaced lines in a crystal with hexagonal symmetry such as ice. This lack of resolution in the measurements can in some cases limit the significance of the data for structure determinations, but in the present case sufficient information is obtainable from the pattern so that a definite choice can be made between a number of proposed structures for ice. The absolute integrated intensities for the measured peaks are shown in the last

<sup>4</sup> E. O. Wollan and C. G. Shull, *Phys. Rev.* **73**, 822 (1948).

column of Table I, together with other information to be described below.

### PROPOSED STRUCTURES

Ice possesses hexagonal symmetry and the oxygen atoms are known from x-ray diffraction measurements to be located in a tetrahedral array, any one oxygen atom being located at the center with four other oxygen atoms occupying the corners of the tetrahedron. The distance between oxygen neighbors has been determined from the x-ray measurements to be 2.76Å.

Several proposals have been made over a period of years with regard to the location of the hydrogen atoms in the ice structure. In 1929 Barnes<sup>2</sup> proposed a structure for ice in which the hydrogen atoms lie at the midpoints of lines joining neighboring oxygen atoms. The unit cell in this case contains 4 H<sub>2</sub>O molecules with the atomic coordinates:

oxygen— $\frac{1}{3}, \frac{2}{3}, \frac{1}{6}; \frac{1}{3}, \frac{2}{3}, \frac{7}{6}; \frac{2}{3}, \frac{1}{3}, \frac{9}{6}; \frac{2}{3}, \frac{1}{3}, \frac{15}{6};$   
hydrogen— $0, \frac{1}{2}, \frac{1}{2}; 0, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, 0, 0; \frac{1}{3}, \frac{2}{3}, \frac{1}{4};$   
 $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0; \frac{2}{3}, \frac{1}{3}, \frac{3}{4}.$

In 1933 Bernal and Fowler<sup>5</sup> proposed a structure for ice in which the H<sub>2</sub>O molecules maintain in the crystal approximately the same structure that they have in the vapor state. The free H<sub>2</sub>O molecule is known from dipole moment and spectroscopic data to have an angle between hydrogen bonds of about 105° and an O—H distance of about 0.96Å. These molecular groups are placed in the crystal with one hydrogen atom along each of the tetrahedral lines joining neighboring oxygen atoms and there are then two hydrogen atoms close (~0.96Å) to each oxygen atom. The existence of molecular groups in the crystal is in line with data on the vibrational frequencies associated with the O—H bond which indicate that the O—H distance is increased by only about 3 percent in going from isolated H<sub>2</sub>O molecules to ice. In this proposed structure the hydrogen molecules are assigned a definite arrangement which involves a unit cell of 12 molecules. (See original paper for atomic coordinates and see also, the note added in proof.)

It has been shown by Pauling<sup>6</sup> that the structure proposed by Bernal and Fowler in which the crystal is assumed to have a unique configuration with respect to the location of the hydrogen atoms is not in accord with the experimentally known fact that the entropy of the crystal does not tend to zero as the crystal is cooled to very low temperatures. Pauling assumes, as do Bernal and Fowler, that each water molecule is so oriented that its two hydrogen atoms are directed approximately toward two of the four surrounding oxygen atoms and that

TABLE I. Comparison of observed and calculated intensities in the neutron diffraction powder pattern of heavy ice. The calculated intensities are on an absolute scale and have been obtained using 5.2 and 4.2 barns for the coherent scattering cross sections of deuterium and oxygen, respectively.

sinθ/λ	Bernal Fowler		hkl	Barnes		Rotating molecule		Pauling or half- hydrogen		Ob- served
	hkl	P <sub>hkl</sub>		P <sub>hkl</sub>	P <sub>hkl</sub>	P <sub>hkl</sub>	P <sub>hkl</sub>	P <sub>hkl</sub>		
0.1271	110	406	100	363	767	304	647	386	835	830
0.1358	002	240		899		202		166		
0.1442	111	253	101	212	79	177	97	230	104	118
0.1860	112			128		102		14		
0.2206	300		199	110	72	131	140	130		
0.2401	113		212	103	14	101	70	95		
0.2542	220	57	200	41	201	14	70	6	111	98
0.2590	302	47		112		15		47		
0.2639	221	66	304	201	67	9	63	41		
0.2717	004	32		004	78	0	0	41		
0.2745	311	102								
0.2836	213	29								
0.2885	222	35	104	202	199	6	6	77	106	97
0.3000	114	40	104	54	253	0	6	29		

only one hydrogen atom lies along each oxygen-oxygen line, but contrary to Bernal and Fowler he assumes that the crystal can exist in any of the many configurations which satisfy these conditions. He also assumes that the crystal can change from one configuration to another by rotation of some of the molecules or by motion of some of the hydrogen nuclei from a position near (~0.96Å) one oxygen atom to a corresponding position near an adjacent oxygen atom. Such motions would involve several hydrogen atoms simultaneously in order to satisfy the condition that there are always two hydrogen atoms near a given oxygen atom. The fact that at temperatures above about 200°K the dielectric constant of ice is of the same order of magnitude as that of water suggests that the molecules can orient themselves with considerable freedom. On the assumption that the crystal upon being cooled to very low temperatures is frozen into any one of the large number of configurations all of

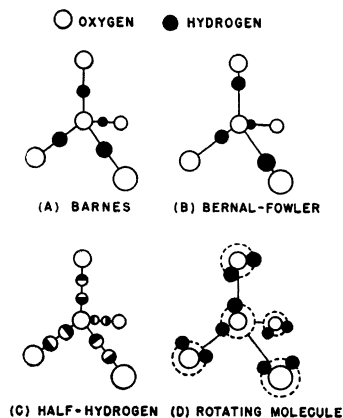


FIG. 2. Schematic diagram of four structural models which are used in calculating pattern intensities for various proposed structures of ice.

<sup>5</sup> J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1**, 515 (1933).

<sup>6</sup> L. Pauling, *J. Chem. Soc.* **57**, 2680 (1935).

which satisfy the above mentioned conditions, the entropy of the crystal will tend towards a finite value as the temperature approaches zero. Pauling's calculation of this residual entropy leads to a value of 0.806 cal. per mole degree and this compares very favorably with the experimental values of 0.82 cal. per mole degree for ordinary ice and 0.77 cal. per mole degree for heavy ice.

The postulated models described above for the ice structure are shown schematically in Fig. 2. The oxygen atoms are at the center and corners of a tetrahedron. In the Barnes model (A) the hydrogen atoms are located midway between oxygen atoms whereas in the Bernal-Fowler model (B) there are two hydrogen atoms near each oxygen atom in a fixed repeating pattern which would require a larger cell to illustrate. For the Pauling model, which assumes a random molecular grouping, the expected intensities can be calculated on the basis of a half-hydrogen model (C) in which half the scattering amplitude of each hydrogen (or deuterium) nucleus is associated with the sites shown in (C). Calculations for a rotating molecule are based on the structure shown in (D) of the figure.

#### COMPARISON OF NEUTRON DIFFRACTION DATA WITH PROPOSED STRUCTURES

The results of the neutron diffraction measurement will now be considered by comparing the observed intensities for the heavy ice pattern with the calculated intensities for the various suggested structures. This comparison has been made for the structures proposed by Barnes, by Bernal and Fowler, for the case of  $D_2O$  molecules rotating about the oxygen atoms as centers and for the structure proposed by Pauling.

The smallest unit cell which accounts for the oxygen atom positions contains four  $D_2O$  molecules. This cell is satisfactory for the Barnes, rotating

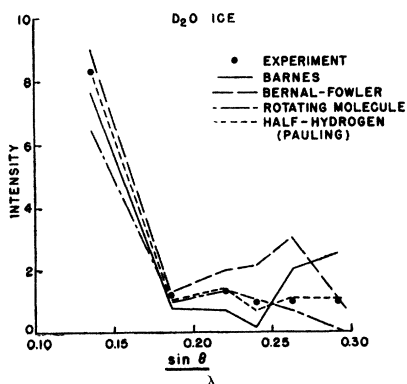


FIG. 3. Comparison of experimental intensities for  $D_2O$  ice with those calculated according to four proposed structures. The six observed intensity values listed in the last column of Table I are plotted as the experimental points in this figure. The lines joining the calculated intensity values are of no significance except for being a visual aid.

molecule and Pauling structures. The Miller indices for this cell are given in the fourth column of Table I. The Bernal-Fowler structure involves a larger cell of 12  $D_2O$  molecules and the Miller indices corresponding to this structure are listed in the second column of the table. For this larger cell there are many more possible reflections over a given range of  $\sin\theta/\lambda$  than for the Barnes cell. The structure factors\*\*\* and corresponding intensities have been calculated for all the possible reflections in the range of angles considered but in the case of those values of  $(hkl)$  not listed, the calculated intensities came out to zero or nearly zero.

For the calculation of the absolute structure factors and the corresponding integrated intensities (listed as  $P_{hkl}$  in the table) the sign and magnitude of the coherent scattering amplitudes for the oxygen and deuterium nuclei must be known. In the case of oxygen it has been shown that the scattering is not spin dependent and that the phase of scattering is positive. Direct measurements of the coherent scattering by oxygen nuclei in crystals as well as measurements of the total scattering give 4.2 barns for the bound scattering cross section of oxygen. For the case of deuterium, recent unpublished powder crystal measurements with  $ThD_2$  give a coherent scattering cross section of 5.2 barns for deuterium and this value has been used in the ice calculations. The phase of the deuterium scattering was shown to be positive in measurements with  $NaD$ .<sup>7</sup> This cross section is measurably smaller than the total scattering cross section of 7.5 barns for bound nuclei found by Rainwater and Havens and this difference indicates a spin dependent scattering for deuterium. On this basis a diffuse scattering caused by spin incoherence would be expected in the diffraction pattern along with the coherent and other diffuse scattering features.

Using these values for the coherent scattering cross sections, the integrated intensities (on an absolute scale) have been calculated using the structure factors for the various models. The comparison of the observed intensities with those calculated for the various models is given in Table I and also in Fig. 3 where the points represent the measured values and the lines show the trend of the calculated results. Column 3 in Table I lists the calculated intensities for the Bernal-Fowler structure, and these are to be compared with the observed intensities listed in the last column. It is seen that this model predicts intensities two and three times the observed intensity for the intermediate angle reflections and hence is not too suitable for describing the structure.

\*\*\* For a cell of this size the structure factor calculations are quite laborious and we have been assisted in these calculations by Miss E. A. Forbes.

<sup>7</sup> Shull, Wollan, Morton, and Davidson, Phys. Rev. **73**, 830 (1948).

The intensities calculated for the Barnes model, in which the deuterium atoms are assumed to be located half way between oxygen atoms, are listed in the fifth column of the table. The intensities of the reflections at the larger angles are seen to be very much higher than the measured values whereas at the smaller angles they are smaller than measured.

The intensities calculated for a rotating molecule in which the positional relationship present in the water molecule is maintained during rotation are shown in the sixth column of the table. A calculation for the case of deuterium nuclei rotating independently and at random on a shell of radius  $r=0.96\text{\AA}$  about the oxygen atoms gives essentially the same result. It is to be expected that this randomness in the orientation of the deuterium nuclei with respect to specific directions in the lattice will cause the coherent scattering to fall off with increasing angle of reflection, as is seen to be the case for the calculated values in the table. In any case the calculated intensities appear too small for both the small and large angle reflections.

The determination of the integrated intensities to be expected for the Pauling model of the ice crystal would require one to calculate the intensities for each of the many possible configurations which the crystal could assume under the previously mentioned assumptions that two and only two hydrogen atoms are at any given time located close to a given oxygen atom. When the problem is set up in this way it becomes evident that the solution with respect to the Bragg scattering by the crystal is just that which would be obtained by assuming the crystal to possess a substitution disorder with respect to hydrogen atoms in which half of the sites available for these atoms are unoccupied. This assumes that the occupied and unoccupied sites are randomly distributed and the requirement of molecular ( $\text{D}_2\text{O}$ ) groups is disregarded. It is hence evident that the diffraction measurements are only capable of determining that on the average two hydrogen atoms will be found close to a given oxygen atom. The intensities calculated for what might now be called the half-hydrogen model in which an average scattering amplitude of  $f_D/2$  has been taken for the  $2N$  sites available to the  $N$  deuterium nuclei are listed in the seventh column of the table. The agreement of these calculated values of  $P_{hki}$  with those observed experimentally is seen to be good, there being only one value which might be considered somewhat outside the experimental error. The fact that the measured peaks at the larger values of  $(\sin\theta)/\lambda$  are lower than the calculated values can be due to a temperature effect or some of it may be due to the uncertainty in the deuterium scattering cross section.

This agreement constitutes strong evidence for the correctness of the Pauling structure. The

neutron measurements cannot, however, in themselves prove the absence of any  $(\text{D}_4\text{O})^{++}$ ,  $(\text{D}_3\text{O})^+$ ,  $(\text{OD})^-$  or  $\text{O}^-$  groups in the crystal. That the number of such groups is small is borne out by the agreement of the calculated and experimentally determined residual entropy. A random distribution of the various possible groups would lead to a value of the residual entropy about three times greater than the measured value.

That there is a randomness in the location of the deuterium nuclei in the crystal is shown also by the magnitude of the diffuse scattering. With an average coherent scattering amplitude of  $f_D/2$  for the  $2N$  deuterium sites in the crystal, the average coherent cross section per deuterium nucleus will be  $(4\pi/N)\sum_{2N}(f_D/2)^2 = \frac{1}{2}(4\pi f_D^2)$ . The coherent scattering cross section in a crystal with no randomness in the location of deuterium nuclei would be  $4\pi f_D^2$  and the difference  $4\pi f_D^2 - \frac{1}{2}(4\pi f_D^2)$  will appear for the ice crystal as a diffuse scattering arising from the random character of the lattice. In addition to the diffuse scattering arising from this cause there will be diffuse scattering arising from spin dependence and a small amount from the usual Debye temperature effect. In addition to these true sources of diffuse scattering there is always present in our neutron experiments a small background which arises from multiple scattering of Bragg diffracted radiation.

Although, as yet, no real effort has been made to make an accurate determination of the diffuse scattering by ice, the measurements agree quite well with the calculated values. An approximate correction can be made for multiple scattering and the temperature diffuse scattering is negligible at small angles. The spin scattering per deuterium nucleus is given by  $4\pi f_D^2(\text{total}) - 4\pi f_D^2(\text{coherent}) = 7.5 - 5.2 = 2.3$  barns and the corresponding random disorder scattering is, as we have shown above, equal to  $\frac{1}{2}(4\pi f_D^2(\text{coherent})) = 2.6$  barns. The sum of these cross sections, 4.9 barns per deuterium nucleus, agrees within experimental error with the observed value after correction for the multiple scattering. Thus the diffuse scattering constitutes an additional check on the random nature of the lattice.

We are not in a position at this time to discuss the relation of our results to the diffuse streaks which Owston and Lonsdale<sup>8</sup> has observed in their x-ray Laue photographs of ice. We hope, at a later date, to see whether or not this effect will also be observed with neutrons. The ice measurements represent the first real effort at applying neutron diffraction to the study of the location of hydrogen (or deuterium) nuclei in crystals and they show the potentialities of this technique in such structure analyses.

<sup>8</sup> P. G. Owston and K. Lonsdale, *J. Glaciology* **I**, 118 (1948).

*Note added in proof:* Since this paper went to press, Lonsdale and Owston have pointed out to us by correspondence that the parameters given by Bernal and Fowler, namely,  $y=0.105$  and  $Z=0.037$ , are incorrect and should be changed to  $y=0.115$  and  $Z=0.0435$ . This change in the value of the parameters would affect somewhat the intensity calculations given in column 3 of Table I but this change could almost certainly not produce good agreement between this model and our observed results since the coherent scattering by the hydrogen atoms in a model in which these atoms are fixed at definite sites will always be twice as great as that produced by the

Pauling model. The calculated intensities given in Table I for the Bernal-Fowler model are all higher than the observed intensities given in column 7 of the table and it would not be expected that a revision of the parameters would alter this situation.

#### ACKNOWLEDGMENTS

We are indebted to Dr. H. M. James for valuable discussions in connection with the calculations of the intensities for the Pauling Model.

## The Scattering of High Energy Neutrons by Nuclei

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The experiments of Cook, McMillan, Peterson, and Sewell on the cross sections of nuclei for neutrons of about 90 Mev indicate that the nuclei are partially transparent to high energy neutrons. It is shown that the results can be explained quite satisfactorily using a nuclear radius  $R=1.37A^{\frac{1}{3}} \times 10^{-13}$  cm, a potential energy for the neutron in the nucleus of 31 Mev, and a mean free path for the neutron in nuclear matter of  $4.5 \times 10^{-13}$  cm. This mean free path agrees with that estimated from the high energy  $n$ - $p$  cross section, but the results are not sensitive to the choice of mean free path.

IN a previous paper by one of the writers<sup>1</sup> it has been pointed out that to a high energy bombarding particle a nucleus appears partially transparent, since at energies of the order of 100 Mev the scattering mean free path for a neutron or proton traversing nuclear matter becomes comparable to the nuclear radius. This transparency effect is strikingly apparent in the experiments of Cook, McMillan, Peterson, and Sewell<sup>2</sup> on the scattering by nuclei of neutrons of about 90 Mev. In the present paper it will be shown that the observed scattering cross sections can be quite satisfactorily accounted for, using a mean free path of the expected magnitude.

The problem is that of the scattering of the neutron wave by a sphere of material characterized by an absorption coefficient and an index of refraction. The index of refraction is determined by the mean potential energy,  $V$ , of the neutron in the nucleus. If  $k=(2ME)^{\frac{1}{2}}/\hbar$  is the propagation vector of the wave outside the nucleus, its propagation vector inside is  $k+k_1$ , with

$$k_1 = k[(1+V/E)^{\frac{1}{2}} - 1].$$

For  $E=90$  Mev,  $k=2.08 \times 10^{13}$  cm<sup>-1</sup>. The potential  $V$  is generally taken to be about 8 Mev larger than the energy of the Fermi sphere. The latter depends on the assumed nuclear density. If we use for the nuclear radius the value  $R=1.37A^{\frac{1}{3}} \times 10^{-13}$  cm,

deduced by Cook, McMillan, Peterson, and Sewell from the 14-25 Mev scattering results of Amaldi, Bocciairelli, Cacciapuoti, and Trabacchi,<sup>3</sup> and Sherr,<sup>4</sup> we find a Fermi energy of 22 Mev, and  $V=30$  Mev. This gives  $k_1=3.22 \times 10^{12}$  cm<sup>-1</sup>. The absorption coefficient in nuclear matter is equal to the particle density times the cross section for scattering of the neutron by a particle in the nucleus,

$$K = 3A\sigma/4\pi R^3.$$

In terms of the  $n$ - $p$  and  $n$ - $n$  cross sections,

$$\sigma = [Z\sigma_{np} + (A-Z)\sigma_{nn}]/A.$$

Cook *et al.*,<sup>2</sup> give for the scattering of a 90 Mev neutron by a free proton  $\sigma_{np(\text{free})} = 8.3 \times 10^{-26}$  cm<sup>2</sup>. This cross section must be reduced to allow for the effect of the exclusion principle on the scattering by a proton bound in the nucleus; according to Goldberger,<sup>5</sup> the factor is  $\sigma_{np} = \frac{2}{3}\sigma_{np(\text{free})}$ . Assuming a  $1/E$  dependence of the cross sections we find, for  $E=90+30=120$  Mev,  $\sigma_{np} = 4.15 \times 10^{-26}$  cm<sup>2</sup>. If, following Goldberger, we take  $\sigma_{nn} = \frac{1}{4}\sigma_{np}$ , and use the previously quoted radius formula, we obtain  $K = 2.4 \times 10^{12}$  cm<sup>-1</sup> for  $Z/A = \frac{1}{2}$ ,  $K = 2.1 \times 10^{12}$  cm<sup>-1</sup> for  $Z/A = 0.39$  ( $U$ ). It will be seen from these numbers that in the ensuing calculations it will be a reasonable approximation to suppose that  $kR \gg 1$ , but  $k_1/k$  and  $K/k \ll 1$ , so that  $k_1R$  and  $KR$  are of order one.

<sup>3</sup> E. Amaldi, D. Bocciairelli, B. N. Cacciapuoti, and G. C. Trabacchi, *Nuovo Cimento* **3**, 203 (1946).

<sup>4</sup> R. Sherr, *Phys. Rev.* **68**, 240 (1945).

<sup>5</sup> M. L. Goldberger, *Phys. Rev.* **74**, 1268 (1948).

<sup>1</sup> R. Serber, *Phys. Rev.* **72**, 1114 (1947).

<sup>2</sup> L. J. Cook, E. M. McMillan, J. M. Peterson, and D. C. Sewell, *Phys. Rev.* **75**, 7 (1949).