Polarized-Neutron Diffraction from Spin-Polarized Protons: A Tool in Structure Determination?*

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We have observed the spin-dependent diffraction of slow neutrons by differentially polarized nuclei in single crystals of lanthanum magnesium nitrate. The effects are accompanied by enhanced Bragg diffraction and reduced incoherent scattering at high proton polarizations. The diffraction pattern is very sensitive to selective depolarization of nuclei, and proton resonances have been observed through changes in the diffracted intensities when the sample is irradiated at the Larmor frequencies.

We report diffraction experiments using polarized slow neutrons and spin-polarized nuclei. A crystal of lanthanum magnesium nitrate (LMN), $La_2Mg_3(NO_3)_{12}\cdot 24H_2O$, was doped with 1% $^{142}Nd^{3+}$ and the protons polarized dynamically[1] by the Abragam-Jeffries "solid" effect. A polarization of about 40% could be routinely obtained at 1.5°K by using only 300 μW of 4-mm microwave power in a resonant TE_{01n} cylindrical aluminum cavity.[2] Much higher polarizations (indicated by many lines in the NMR spectrum) were also obtained by carefully reducing the power to obtain an optimum balance between saturation of the resonance and minimum heating of the sample. The experiments were performed at the polarized-neutron diffractometer, PN2, on the PLUTO reactor hole 7H1L at the Atomic Energy Research Establishment, Harwell. The magnet used was a superconducting asymmetric split pair, specially designed to minimize depolarization of the incident and diffracted neutron beams, while at the same time giving a sample volume of about 1 cm^3 where the field homogeneity was better than a few parts in 10^5 at 1.9 T.[3] Depolarization of the beam [measured by using a standard cobalt-iron ($Fe_{0.08}Co_{0.92}$) crystal in place of the sample] was always less than 1% and usually about 0.5%. Figure 1 shows a schematic diagram of the experiment. The magnetic field at the sample was perpendicular to the neutron scattering plane and the incident neutrons were polarized parallel or antiparallel to the field direction, flipping being achieved by a rf coil at the Larmor frequency.

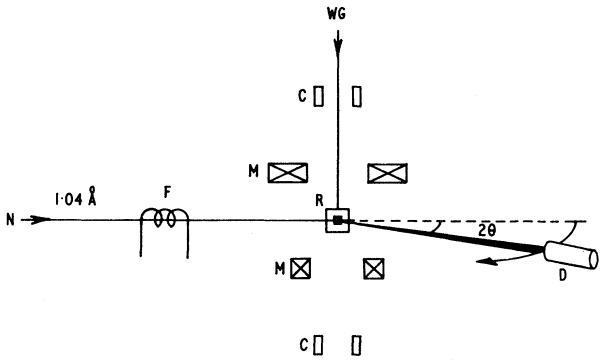

FIG. 1. Schematic diagram of the experiment: N, polarized neutron beam ($\lambda_0 = 1.04$ Å); F, neutron spin flipper; M, C, main and field-trimming coils of superconducting magnet, giving field perpendicular to the scattering plane; WG, R, wave guide and resonant cavity; D, boron trifluoride neutron detector at scattering angle 2θ.

The elastic scattering cross sections for the polarized sample can be estimated from the formulas of Schermer and Blume[4] for coherent and incoherent nuclear scattering from a monoisotopic sample. With the consideration of only the z components of the nuclear magnetization[5] their Eqs. (12) or (20) when applied to LMN, and for a fully polarized neutron beam, reduce to the following:

$$[\partial\sigma(\pm,p)/\partial\Omega]_{coh} = N_0|f_H(\vec{K})(A_H \pm \tfrac{1}{2}B_H p) + f_N(\vec{K})A_N + f_O(\vec{K})A_O + \ldots|^2 , \quad (1)$$

$$[\partial\sigma(\pm,p)/\partial\Omega]_{inc} = N_0[144a_{H\,inc}{}^2(1 - \tfrac{1}{3}p^2 - \tfrac{2}{3}p) + 36a_{N\,inc}{}^2 + 180a_{O\,inc}{}^2 + \ldots], \quad (2)$$

where $f_H(\vec{K})$ is the structure factor for the 144 protons in the hexagonal unit cell[6] (three times the fundamental rhombohedral cell), N_0 is the number of hexagonal cells in the crystal, and the momentum transfer $\vec{K} = \vec{k} - \vec{k}_0$. The $f_N(\vec{K})$, $f_O(\vec{K})$, etc., are the corresponding structure factors for nitrogen, oxygen, etc., whose scattering lengths A_N, A_O are either truly polarization independent or, for the present, are assumed to be so compared with hydrogen. The signs refer to the incident-neutron spin up

(+) or down (−) and p is the proton spin polarization, assumed the same for all the hydrogen in the crystal.

$$A_{\mathrm{H}}=\tfrac{3}{4}a^{+}+\tfrac{1}{4}a^{-},\quad B_{\mathrm{H}}=\tfrac{1}{2}(a^{+}-a^{-}), \tag{3}$$

$$a_{\mathrm{H\ inc}}{}^{2}=\tfrac{3}{16}(a^{+}-a^{-})^{2}, \tag{4}$$

a^{+} and a^{-} being the triplet and singlet scattering lengths for neutron-proton collisions. A_{N}, $a_{\mathrm{N\ inc}}{}^{2}$, etc., are defined in a corresponding manner. The peaks whose structure factor is dominated by hydrogen were of most interest in this experiment. They were classified by comparing the powder diffraction patterns of hydrogenous and deuterated specimens.

The relative scale of the coherent and incoherent terms depends upon $|f_{\mathrm{H}}(\vec{\mathrm{K}})|^{2}/144$ which may vary by orders of magnitude and from one Bragg peak to another.

In LMN the observed flipping ratio R, defined as

$$R=\frac{\text{(scattered-neutron intensity with incident-neutron spin up)}}{\text{(scattered-neutron intensity with incident-neutron spin down)}},$$

naturally depends on the contribution of unpolarized atoms to the Bragg intensity, so that changes in the polarization of protons (for example) at definite lattice sites have an effect on the diffraction pattern similar to that of the isomorphous replacement method for solving complex structures.

To produce polarization in LMN the c axis was aligned in the scattering plane perpendicular to the steady field B_0. All Bragg peaks in this plane fall, because of selection rules, into four groups given by (in hexagonal notation)

$$(-2k, k, 2n-k),\ (h, 0, 3n+h),\ (h, h, 3n),\ (0, k, 3n-k).$$

In general $-h+k+l=3n$ for a rhombohedral cell, where n is an integer. Several of the peaks in the second and fourth class have structure factors with strong hydrogen contributions. Using the x-ray structure[6] as a guide, we calculated the expected neutron structure factors and their hydrogen contributions and then performed polarization-dependence experiments.

The most obvious effect of nuclear spin polarization is that the scattering cross section becomes dependent on the incident-neutron spin direction, and for one spin configuration the Bragg scattering intensity is enhanced.[7,8] These results confirm earlier experiments with 8-mm microwaves.[9] A nuclear polarization giving a flipping ratio of 8.5/1 at the maximum of the (0, −3, 12) reflection was first produced by saturating one of the "forbidden" transitions. Then the microwave power was turned off, allowing the polarization to decay, and the intensity at the Bragg maximum was measured continuously with an alternation of incident-neutron polarization every 4.5 min. Figure 2 shows the results of this experiment. The flipping ratio decays with a time constant of 25.0 ± 0.2 min, in good agreement with the proton nuclear spin-lattice relaxation time for this system at 1.8 T and 1.5°K found by Jeffries and Schmugge.[10] The same decay time has been found for all the other peaks investigated to date at this temperature. The (2, 0, 8) peak has a decay envelope which demonstrates cancelation of the structure-factor contributions from other atoms by the hydrogen contribution at a particular polarization during the decay.

From the intensities of Bragg peaks dominated by hydrogen, measurements with and without proton polarization should allow the sample polarization to be estimated from Eq. (1). When this was done by using the atomic positions known from x-ray crystallography[6] and a set of Bragg peaks at constant but unknown polarization, values rang-

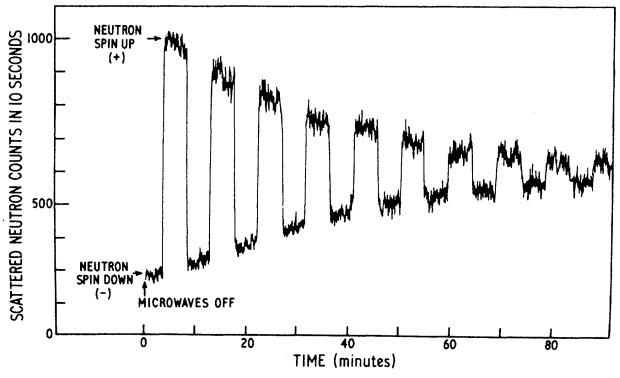

FIG. 2. Decay of the flipping ratio and coherent scattering intensity for the (3, 0, 12) Bragg peak after turning off the microwave power used to maintain nuclear polarization. The nuclear relaxation time was 25 min.

TABLE I. Experimental flipping ratios for Bragg peaks in the a^*-c^* plane of a weakly polarized LMN crystal.

Peak	Unpolarized structure factor	Proton part of structure factor	Flipping ratio R	Polarization (%)
(0, −1, 4)	18.4	0.654	4.22	23
(0, −2, 8)	− 0.89	−0.785	1.91	
(0, −3, 12)	−29.92	2.253	5.19	15
(0, −4, 16)	14.86	0.271	7.58	57
(0, −5, 20)	41.16	0.0165	0.799	
(0, −6, 24)	− 8.83	−0.4729	1.30	
(0, −7, 28)	28.94	0.152	2.14	
(0, −8, 32)	−37.46	0.124	1.43	

ing from $p = 13\%$ to $p = 57\%$ were obtained. A minimum estimate from the incoherent scattering, using Eq. (2), gave $p \approx 25\%$. This variability probably reflects the sensitivity of the calculation to the hydrogen-atom positions.

Accurate relative flipping ratios were obtained by programming the diffractometer to "visit" cyclically a sequence of Bragg peaks and their nearly flat backgrounds, repeating the operation as many times as were necessary to get good statistics or until the polarization changed noticeably. Positioning accuracy was $\pm 0.01°$. Scans of 8 h at constant polarization were possible and Table I shows some of the different flipping ratios. The results demonstrate the sensitivity of Bragg diffraction to the proton, and possibly other, nuclear polarizations. They suggest that difference analyses (for example the difference Patterson method) may be useful for obtaining parts of a crystal structure, such as the hydrogen positions, to high accuracy without the need to solve the complete structure.

For very complex crystals it is attractive to minimize the amount of data to be refined in order to get the atomic positions of interest. One way is to selectively depolarize nuclei whose Larmor frequencies differ either because of their magnetic moments or because of their proximity to paramagnetic ions in the crystal. In this way one can control and vary the contribution to the structure factor of individual nuclei within the unit cell.

Figure 3 shows the proton magnetic resonance in LMN at about 40% polarization observed by measuring the change in scattered-neutron intensity at the (3, 0, 12) Bragg peak. An oscillator, feeding a coil correctly wrapped around the sample, was swept through the proton Larmor frequencies synchronously with a chart recorder which displayed the Bragg-peak intensity. Strong depolarization of the sample occurred at 77.67 MHz, the expected frequency for proton resonance in the mainly diamagnetic crystal, but the depolarization spectrum has some poorly resolved shoulders indicating that separated nuclear spin packets might be depolarized sequentially. The microwave pumping power was left on during the scan to compete with the depolarizing transitions. The resonance covers about 80 kHz which corresponds to the 20 G calculated.[10]

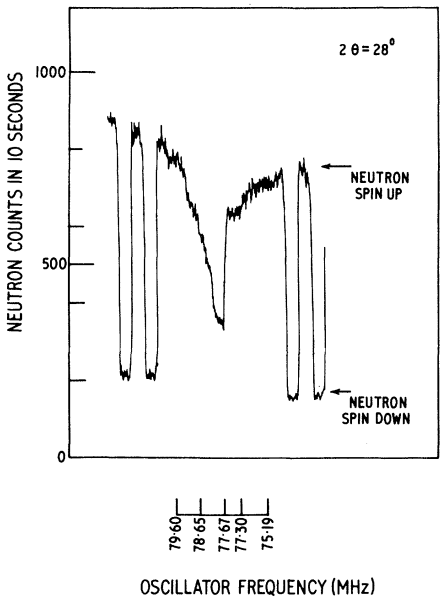

FIG. 3. Proton-magnetic-resonance spectrum of LMN crystal observed by a change in intensity of the (3, 0, 12) Bragg peak as an exciting frequency was swept through the resonance. (The neutron spin direction was "up" continuously throughout the scan.)

Neutron spin-up–spin-down measurements were made before and after the scan and show that the polarization recovered effectively. Selective depolarization of nuclei effectively combines diffraction and electron-nuclear double resonance[11] greatly expanding the information available from each Bragg peak. For sufficiently distinguishable resonances it performs a partial analysis of the diffraction pattern.

Other rf frequencies were fed into the coil corresponding to the nitrogen and lanthanum resonance values but no effect of their nuclear polarization was found either on the "hydrogenous" Bragg peaks or on "nonhydrogenous" peaks such as (0, 1, 2).

The nuclei may be polarized by other means than dynamic polarization, but the dynamic method has the advantage that a change from positive to negative nuclear polarization can be made easily. We think that the method may have some virtues for studying chemically interesting sites in complex crystals such as proteins.

We are planning to refine the evaluation of the position of the hydrogens in LMN by using a four-circle neutron-diffraction experiment, and to use the polarization data as a further refinement.

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Evidence of Optical Transitions in X-Ray Inelastic Scattering Spectra: Li Metal*

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We report results of x-ray Compton-Raman scattering experiments. In addition to the expected Compton and Raman scattering, there is a prominent feature in the form of a peak near $E/E_F = 1$. The new peak can be explained qualitatively by considering the conduction band of lithium metal to be composed of hybridized orbital electrons, and it furnishes the first evidence of an L-x-ray Raman band.

The strongly interacting electron gas is one of the most interesting systems in solid-state physics, and it may soon be expected to form a rigorous testing ground for approximations and theories. The numerous difficulties involved in the theoretical calculations render it one of the areas