Precise Location of Hydrogen Atoms in Complicated Structures by Diffraction of Polarized Neutrons from Dynamically Polarized Nuclei

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Precise location of hydrogen atoms in complicated structures by diffraction of polarized neutrons from dynamically polarized nuclei

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The first results are reported on the precise location of hydrogen atoms in a complicated crystal structure by using diffraction of polarized neutrons from dynamically polarized protons in the sample. Two methodologies exploiting the spin-dependent scattering power of protons are briefly illustrated.

Introduction

A method equivalent to isomorphous substitution techniques in X-ray diffraction can be used for locating hydrogen atom positions in complex crystals as a result of the strong spin-dependent scattering length of the hydrogen atom (Hayter *et al.* 1974). This technique has now been developed to determine precisely the positions of the hydrogen atoms in lanthanum magnesium nitrate hydrate, a crystal that was chosen to display the methodological aspects of this technique.

The crystal of lanthanum magnesium nitrate hydrate ($La_2Mg_3(NO_3)_{12} . 24H_2O$) was grown from extremely pure solutions of the chemicals and of water with a 1% substitution of $^{142}Nd^{3+}$. This gave a high-grade crystal (typical mosaic block spreads of the order of fractions of a minute of arc) containing about 0.1% of neodymium atoms randomly occupying the lanthanum sites of the crystal. In a conventional dynamic nuclear polarization apparatus (Jenkin *et al.* 1976) this gave enhancements of the proton polarization of factors of 600 with the use of the solid state effect (Abragam & Goldman 1978), that is to say, dynamic nuclear polarization of greater than 90%. This is an indication of the high quality of the crystal and its freedom from other impurity ions.

So the crystal represents an ideal subject on which to test the methodological aspects of the use of dynamic polarization to detect hydrogen positions because the polarization can be varied over a wide range to allow this to be used as a variable in the crystallographic measurements, and because the effects on the polarization and on the flip ratio measurements due to extinction, multiple scattering, etc., are likely to be worst for this crystal than for most crystals on which it might subsequently be wished to apply this technique. In this case, if it can be shown that the results are valuable and interpretable, then it can be expected that under the correct conditions the technique of using nuclear polarization and polarized neutron scattering may be of more general applicability. In a more detailed report, the description of the way in which multiple scattering, extinction and other crystallographic effects have been treated to produce the results shown in this brief report will be given.

For the experiment a crystal of the order of 1 mm³ in volume was mounted in an all-aluminium multi-mode microwave cavity operating at approximately 4 mm wavelength. The cavity and crystal were placed in a superconducting coil magnet and could be refrigerated to temperatures as low as 0.7 K. Dynamic nuclear polarization was obtained by adjusting the field and frequency conditions for saturation of the forbidden electron spin resonances in the dipolar electron nuclear coupled system, and the polarization was monitored by using nuclear magnetic resonance and an integrator system. Continuous digital readout of polarization and field conditions were maintained throughout the experiment and were taken into account in the assessment of data. The whole experiment was mounted in a cryostat such that a polarized neutron beam could be scattered from the sample (Hayter *et al.* 1974) and reflexions from the dynamically polarized crystal at two polarizations were collected, both in the zero layer (xz) plane and in the first layer. In order to have a check of the correct crystal structure for lanthanum magnesium nitrate, which should be available from the refinement procedure, the full neutron diffraction determination of the hydrogen positions in the same crystal was made by using conventional neutron scattering techniques (Anderson *et al.* 1977). For the actual experiment, flip ratios at the maxima in the structure factor were recorded for the incident neutron spin up or down with respect to the polarization direction of the polarized nuclei. Nuclear polarization of 20% was used, although some runs were made at 40% nuclear polarization. In all, a data set comprising some 500 independent flip ratio measurements on 500 independent reflexions was measured.

RESULTS

For a preliminary inspection of the data, a difference Fourier synthesis was made by using the spin flip data. This was achieved by taking the known 4 K structure determined by neutron diffraction as a basis and using the known spin dependent scattering length for hydrogen $b^+ = 1.08 \times 10^{-14}\,M$, $b^- = -4.74 \times 10^{-14}\,M$. The expected neutron spin up structure factors were calculated from this basic information. The neutron spin down structure factors were then calculated by using the measured flip ratios in the experiment and a hydrogen nuclear scattering density Fourier pattern for the xz plane calculated. This is shown in figure 1*a*, and for comparison (figure 1*b*) the similarly calculated Fourier pattern generated from the known low-temperature structure without including the neutron spin flip measurements.

It is immediately apparent that the resolution on the data with the measured spin flip information included is lower than that generated from conventional neutron diffraction measurements alone. This is the first indication of the effects of polarization distribution in the spin polarized crystal and will be discussed in more detail later. Nevertheless, it is apparent that, by using the relatively small number of reflexions taken in the spin flip data, all of the hydrogen atoms seen in the conventional structure can, in principle, also be seen by the use of the spin slip information.

The approach next adopted was more akin to that which would be used for solving an unknown structure, but given some basic information from X-ray diffraction. It is our belief that, for using this technique, a good point of departure at this stage should be a good X-ray structure which would find atoms such as oxygen and nitrogen in enzyme crystals, for example. It is not worthwhile to use neutron scattering to determine these positions since the X-ray method is faster and cheaper.

The structure $Ce_2Mg_3(NO_3)_{12}.24H_2O$ was therefore taken as a point of departure, the structure determined from X-rays by Zalkin *et al.* (1963). By comparison with our own low-temperature diffraction work, this structure is not completely correct for $La_2Mg_3(NO_3)_{12}.24H_2O$,

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especially in the location of hydrogen atoms, which they did by a difference Fourier synthesis on the X-ray patterns. Nevertheless, the oxygen and nitrogen, lanthanum, magnesium and other atomic positions except hydrogen are a reasonable basis for departure in our second approach. Here, the hydrogen positions were guessed on the basis of chemical knowledge of OH bond lengths and of hydrogen bond lengths. It was reckoned that these guesses might be good to a few tenths of an ångström† in all cases.

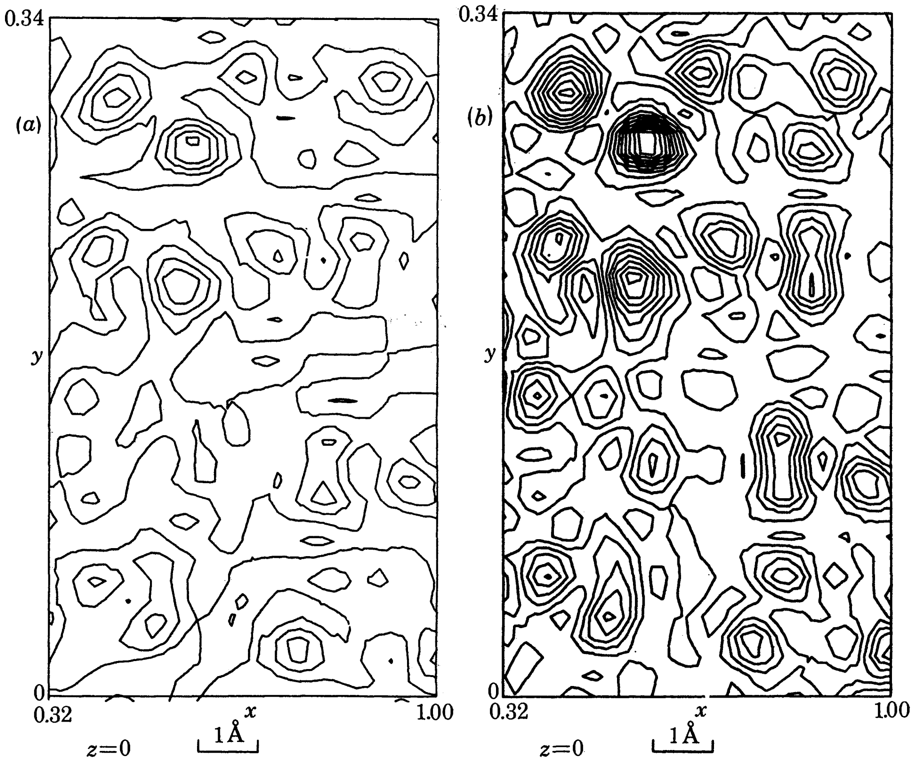

FIGURE 1. (*a*) The difference Fourier synthesis locating the hydrogen atoms in the *xy* projection of the structure of lanthanum magnesium nitrate hydrate at 1.2 K. (*b*) The difference Fourier map of the hydrogen positions obtained from classical neutron diffraction data.

The guessed hydrogen positions were then used for a least-squares refinement of the flip ratios as measured. Data from both the zero layer and the first layer were taken, although those data from the first layer were less reliable than those from the zero layer. After a small number of iterations the structure refined to a good minimum ('*R* factor' 12.5 %). Table 1 compares the observed flip ratios, *r*, for several reflexions with those calculated from the structure at $R = 12.5\,\%$. The hydrogen positions had moved to those as determined by the conventional neutron scattering technique. This shows the success of the method and it therefore remains only to demonstrate the degree to which the limited amount of data available on the flip ratios (due to lack of extensive measuring time) can be used to pull in the hydrogen positions from a distance.

To test this point, single hydrogen atoms were moved to various distances from their equilibrium positions along various directions. In all cases, when a single hydrogen atom was moved the refinement procedure produced the correct structure after of the order of 5–15 iterations.

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† 1 ångström (Å) = 10^{-10} m = 10^{-1} nm.

A plot of the refinement factor (on the spin flips) as a function of the displacement of the H_{11} hydrogen atom from its equilibrium position in the z and the y and the x directions is shown in figure 2. It is immediately clear that the hypersurface for the refinement is complicated. This may well be a consequence of the limited data set being used. Figure 3 shows a mapping of this hypersurface, giving the true deep minimum of the correct structural position for this atom and indications of subsidiary minima, which undoubtedly arise because of the lack of high-angle reflexions. (For the particular spectrometer used in these measurements, D3 at the Institut Laue–Langevin, Grenoble, high-angle reflexions were difficult to take because of the small take-off angle of the instrument which makes the resolution rather poor at high angles.)

Table 1

reflexion			r_{obs}	r_{calc}
0	0	33	0.772	0.594
0	0	30	1.542	1.598
0	0	27	15.552	5.380
0	0	24	4.919	4.736
0	0	21	0.248	0.263
0	0	18	0.842	0.777
0	0	15	0.440	0.752
0	0	12	3.278	3.232
0	0	9	0.441	0.529
0	0	6	0.421	0.439
0	0	3	0.336	0.324
1	1	−6	1.586	1.820
1	1	−12	0.629	0.668
1	1	−15	5.512	7.383
1	1	−18	1.141	1.174
1	1	−21	1.405	1.188
1	1	−24	0.194	0.231
1	1	−27	0.741	1.347
1	1	−30	1.029	2.994
1	1	−33	2.283	2.500
1	1	−36	1.246	1.112

If more than one atom is moved at a time, the structure refines to the correct value up to displacements of the order of 0.5 Å from the equilibrium position, so long as all atoms are moved in the same direction. Preliminary indications are that, if atoms are moved in different directions, the structure does not refine as well as this but may find false minima.

Polarization distribution

There is good evidence from other work that the polarization in a dynamically polarized crystal is not uniform (Abragam *et al.* 1972). In our experiment the flip ratio may be written

$$r = \left(\frac{A+Bp}{A-Bp}\right)^2,$$

where A is the conventional structure factor, B the structure factor of hydrogen atoms alone with $b_H = \frac{1}{4}(b_+ - b_-)$, and p the proton polarization.

Clearly, for certain reflexions it may be possible to have $A = Bp$, and hence r should rise to a very large value. In practice, r is limited by such factors as the neutron beam polarization and flipper efficiency, which can be measured by replacing the sample with a FeCo crystal. Multiple scattering will also limit the maximum (or minimum) flip ratio that can be observed.

We have measured r as a function of polarization for several reflexions at two different temperatures. The data for the (0,0,12) reflexion are shown in figure 4. This shows that there is an additional temperature-dependent effect. We attribute this to the distribution of polarization in the crystal. The distribution becomes less homogeneous at the higher temperature and hence the minimum value of r increases.

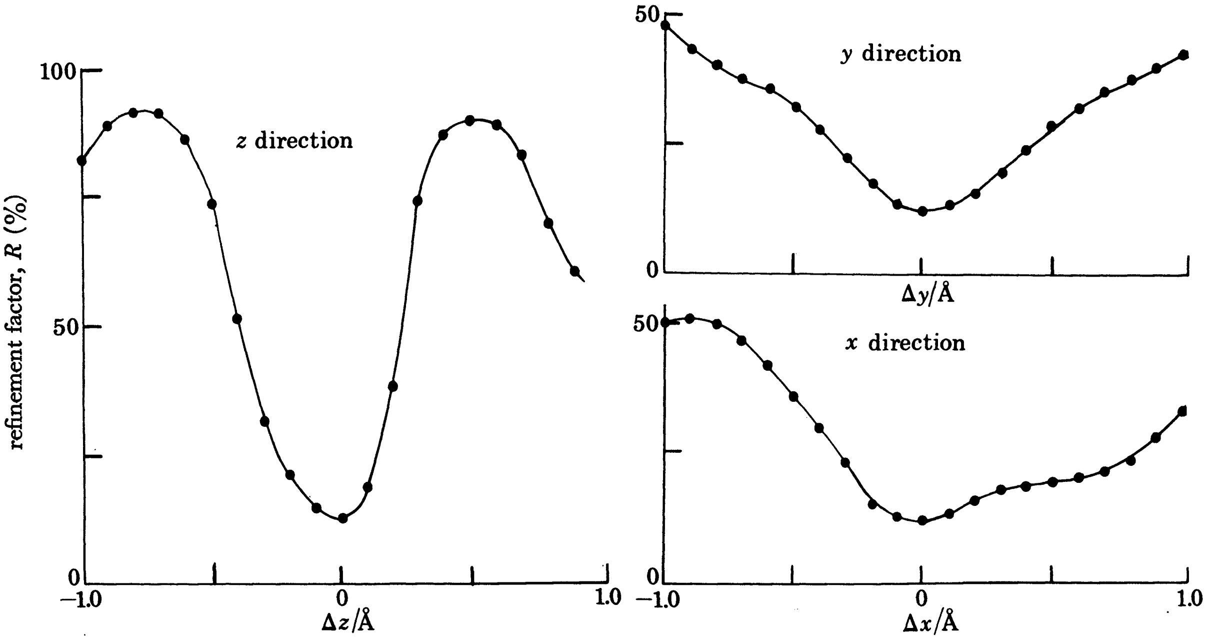

FIGURE 2. Refinement factor (R) obtained from a least-squares refinement of the position of the proton H_{11} against the measured flip ratios in the basal and the first layer plane of the diffraction pattern of lanthanum magnesium nitrate hydrate. The three curves are appropriate for displacements of the proton in the z, x and y directions. Similar behaviour is found for displacements of other single protons in the unit cell.

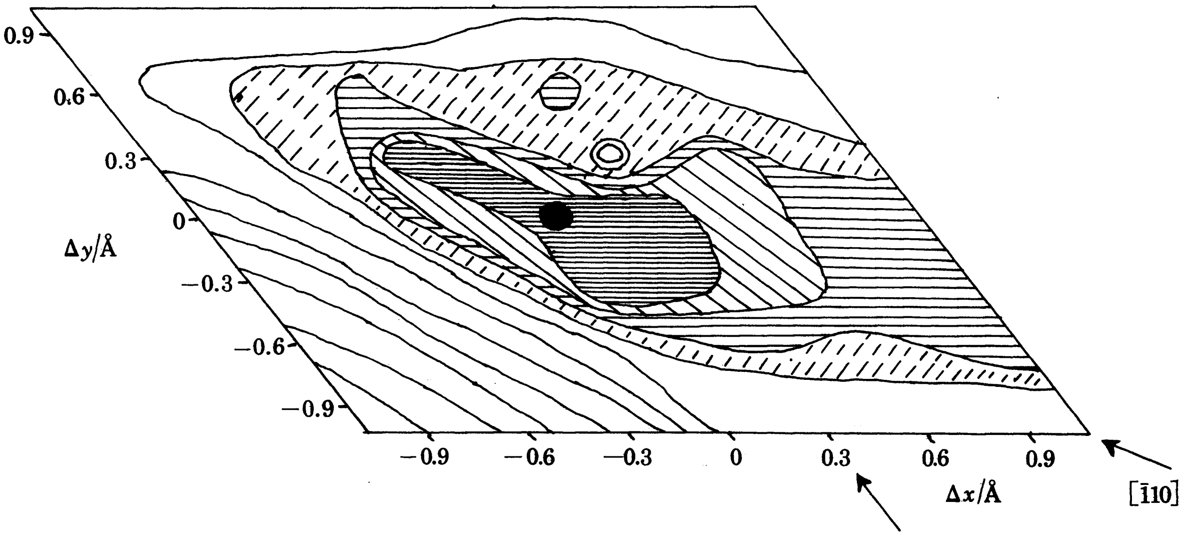

FIGURE 3. Contour diagram showing the true minimum in the xy plane of the lanthanum magnesium nitrate hydrate structure obtained by a least squares refinement against the spin slip ratios.

Further evidence for the polarization distribution came from measurements made as the crystal is polarized then depolarized. Figure 5 shows a hysteresis in the measured intensities. The minimum for the spin down case is greater when the crystal is polarizing. This is when the inhomogeneities are expected to be greatest. Finally, for our measurements at constant polarization we assume that a polarization distribution is still present. We define the distribution by a parameter α, such that

$$\bar{p}^2 = (1+\alpha)\,\bar{p}^2,$$

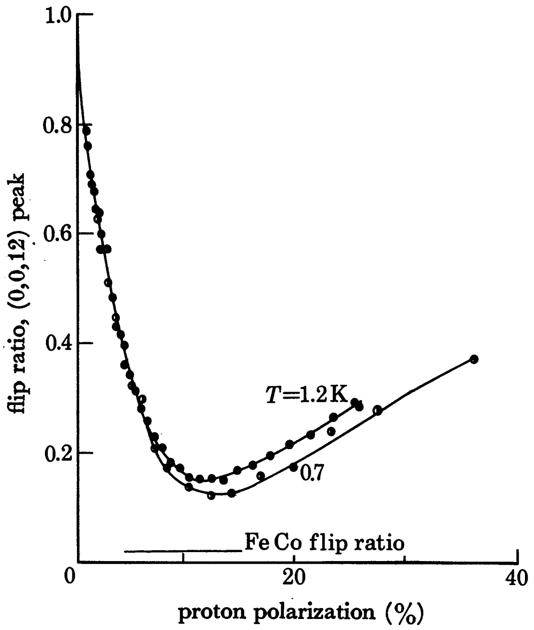

FIGURE 4. Flip ratio of the (0,0,12) reflexion as a function of proton polarization at two temperatures.

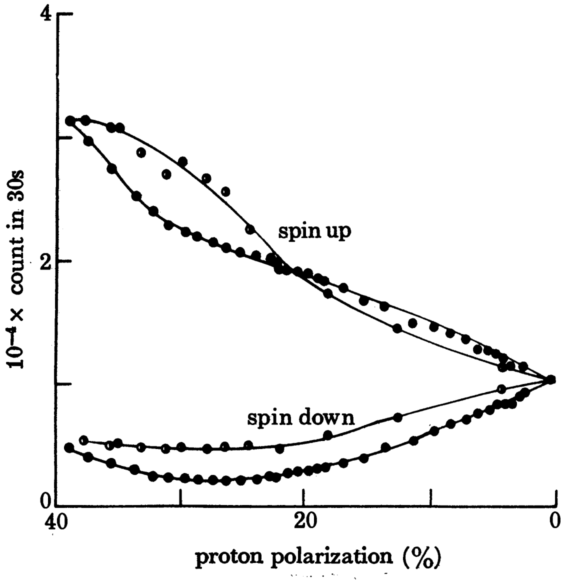

FIGURE 5. Spin up and spin down intensity of the (3,0,12) reflexion at 1.2 K during polarization and depolarization. ◑, Crystal polarizing; ●, crystal depolarizing. All counts corrected for background.

where $\bar{p}$ is the average proton polarization and $\bar{p}^2$ the average of the square of the proton polarization.

The value of α is fitted from our measured flip ratios. Typical values are $\alpha = 0.25$ for $\bar{p} = 40\%$.

Preliminary small-angle neutron scattering experiments have been made to detect the direct scattering of polarized neutrons from the polarization distribution in the crystal.

Discussion

We conclude from these measurements that the use of nuclear polarization as a method of labelling protons in a complicated unit cell may have advantages for determining the proton structure. This would typically be of interest, for example, in determining the proton configuration around the active site in an enzyme. A relatively limited set of data plus the X-ray coordinates of heavier atoms can be used to obtain a refinement of good precision (proton location typically to within 0.05 Å, of the structure determined by classical neutron diffraction measurements at low temperatures). An interesting physical phenomenon discovered is the variation of nuclear spin polarization throughout the crystal. Inevitably this must give rise to a broad background to the diffraction pattern which would, in general, be the Fourier transform of the spin distribution. This broad background in our present measurements leads to a loss of resolution which could, in principle, be recovered by making a model of the spin distribution and refining again the distribution parameter which may be of intrinsic interest itself in a discussion of the physics of highly polarized samples.

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