[1] Reid, I., Reichle, M., Brune, J., and Bradner, H., *Geophys. J. R. astr. Soc.* (in the press).
[2] Sykes, L. R., Oliver, J., and Isacks, B., *The Sea*, **4** (edit. by Maxwell, A. E.), 353 (Interscience, New York, 1971).
[3] Evernden, J. F., *Bull. seism. Soc. Am.*, **59**, 1365 (1969).
[4] Francis, T. J. G., and Porter, I. T., *Nature*, **240**, 547 (1972).
[5] Spiess, F. N., and Mudie, J. D., *The Sea*, **4** (edit. by Maxwell, A. E.), 205 (Interscience, New York, 1971).
[6] Le Pichon, X., Ewing, J., and Houtz, R. E., *J. geophys. Res.*, **73**, 2597 (1968).
[7] Macdonald, K. C., and Mudie, J. D., *Geophys. J. R. astr. Soc.* (in the press).
[8] Sykes, L. R., *J. geophys. Res.*, **75**, 6598 (1970).
[9] Brune, J. N., and Allen, C. R., *Bull. seism. Soc. Am.*, **57**, 277 (1967).
[10] Francis, T. J. G., *Earth planet. Sci. Lett.*, **4**, 39 (1968).
[11] Wilson, J. T., *Nature*, **207**, 343 (1965).
[12] Menard, H. W., and Atwater, T., *Nature*, **219**, 463 (1968).
[13] Sykes, L. R., *J. geophys. Res.*, **72**, 2131 (1967).

Location of Hydrogen Atoms in ADP by Neutron Powder Profile Refinement

NEUTRON diffraction is a powerful tool for the location of light atoms, especially hydrogen, because the neutron scattering power of these atoms is comparable to that of the heavier elements. In particular, the study of hydrogen bonding and its effect on the physical properties of molecular crystals is well suited to neutron diffraction techniques. Unfortunately, because of the relatively low flux of thermal neutrons available, even from the best reactors, rather large single crystals are required, together with expensively long periods of time for data collection. Even when large crystals can be grown, multiple scattering (extinction effects) introduce systematic errors which limit the precision with which atoms can be located. It would be important then, if some way could be found to eliminate the need for large single crystals and long periods for data collection.

The powder diffraction method solves some of these problems, but it is usually thought that neutron powder patterns contain too little information to allow the solution of any but the most simple crystal structures. I argue that provided we abandon the traditional method of structure refinement based on the measurement of structure factors, there is much more useful information in a neutron powder pattern than is immediately obvious.

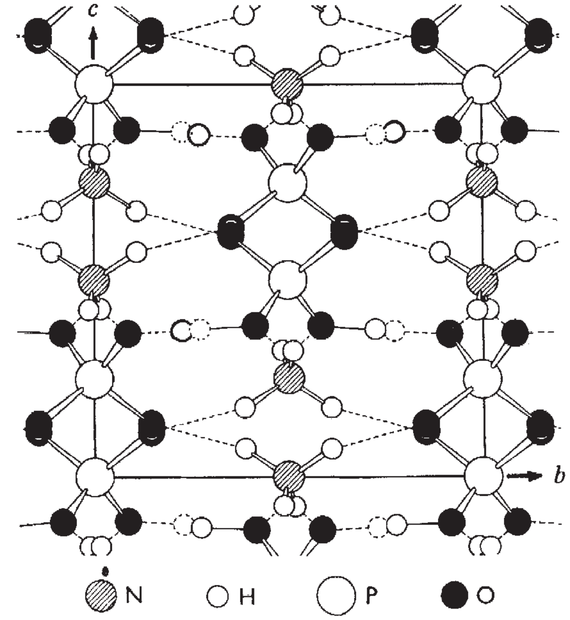

Fig. 1 The [100] projection of the $NH_4H_2PO_4$ structure showing the two positions between which the hydrogen atom linking PO_4 groups can tunnel (after Tenzer *et al.*[4]).

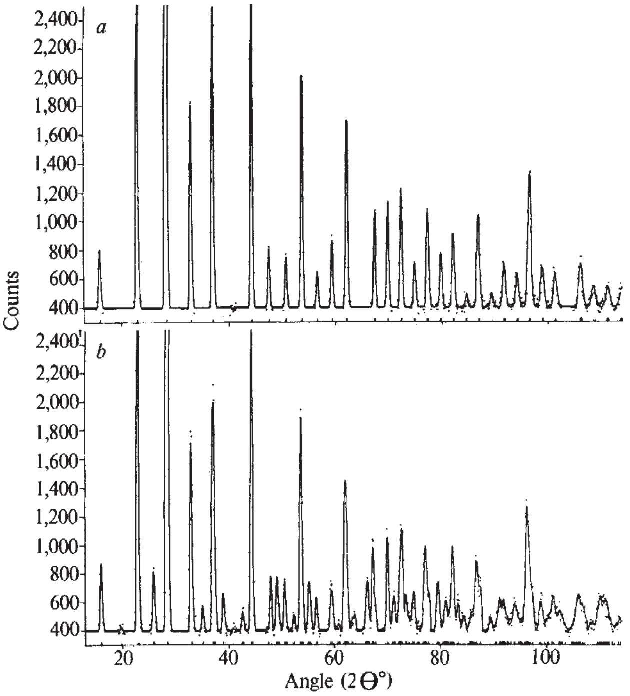

Fig. 2 Observed and calculated powder profiles of deuterated ADP for 1.54 Å neutrons. The positions of the separate Bragg reflexions contributing to these profiles, which were obtained in 22 h on the PANDA diffractometer at Harwell, are marked along the 2θ scattering angle axis. The superlattice lines in the low temperature phase appear because the ordering of the O–H . . . O hydrogen atoms reduces the symmetry from I$\bar{4}$2d at room temperature (*a*) to $P2_12_12_1$ at 77.4 K (*b*).

Information is lost, of course, because the crystalline grains in a powder have all orientations; the intensity scattered into a particular direction is the sum of all reflexions having that particular Bragg angle Because of the finite resolution of a diffractometer, this usually results in a very complicated diffraction pattern from which it is impossible to resolve individual reflexions and to obtain a set of structure factors. Rietveld[1] has shown that in this case it is best to refine the structure to fit directly the observed diffraction pattern, rather than to try to extract the structure factors as an intermediate step. Fortunately, because of the simple radiation spectrum and geometry of a neutron diffractometer, the shape of a single Bragg powder peak is known very precisely for every scattering angle: it is a Gaussian. The positions of all these peaks are fixed by the crystal lattice constants, and so the detailed shape of the entire pattern must be determined solely by the positions of the atom in the crystal lattice; these positions can be refined to obtain the best agreement between the calculated and observed diffraction pattern "profiles".

This profile refinement technique has proved very valuable for the structure refinement of inorganic materials[1,2], but now I apply it to more complicated crystals, especially to hydrogen bonded structures. ADP, ammonium dihydrogen phosphate ($NH_4H_2PO_4$) is a rather single example, but the hydrogen bonds are responsible for a very interesting structural transition which occurs at ~245 K in the deuterated material. The (H_2) hydrogen atoms have two stable positions, close to one or the other of two oxygen atoms in adjacent PO_4 groups[4]. At room temperature these hydrogen atoms have sufficient energy to tunnel between the two stable positions, and the average occupancy of both positions is $\frac{1}{2}$. When the temperature is lowered the hydrogen atoms are presumably caught in one or the other of these positions, but there is no random

Table 1 Fractional Coordinates of the Deuterium Atoms on the O-H ... O Bonds, obtained in this Experiment

	Paraelectric phase I$\bar{4}$2d				Antiferroelectric phase $P2_12_12_1$			
	$a=b=7.502$ Å $T=22°$ C		$c=7.520$ (2) Å* $R=2.8\%$		$a=7.507$ Å $T=77.4$ K	$b=7.529$ (2) Å*	$c=7.445$ (2) Å* $R=2.8\%$	
	x	y	z	Occupation	x	y	z	Occupation
D1	0.277 (3)	0.144 (1)	0.140 (4)	$\frac{1}{2}$	0.275 (3)	0.144 (3)	0.134 (3)	1
D2	0.223	0.144	0.110	$\frac{1}{2}$				0
D3	−0.144	0.277	−0.140	$\frac{1}{2}$	−0.146 (3)	0.277 (3)	−0.145 (3)	1
D4	−0.144	0.223	−0.110	$\frac{1}{2}$				0

* From observed ratios b/a, c/a: the neutron wavelength $\lambda=1.53$ Å was not measured precisely.

In the low temperature antiferroelectric phase, these atoms are ordered on one of the two sites over which they are distributed in the room temperature paraelectric phase (see Fig. 3). The R factors are for separated structure factors, and the numbers in parentheses are the standard deviations for the parameters[1].

distribution; there seems to be an ordering of these hydrogen bonds which results in a distortion of the structure from tetragonal (I$\bar{4}$2d) to orthorhombic $P2_12_12_1$. This mechanism is similar to that found by Bacon and Pease[3] to be responsible for the ferroelectric transition in KH_2PO_4, but in the ammonium salt the transition is antiferroelectric. It is important to find the reason for this difference, but experiments on the low temperature structure of $NH_4H_2PO_4$ are difficult: the crystal shatters when passed through the transition because the different domains distort in different directions. This difficulty has held up the solution of the low temperature structure for twenty years.

This experimental problem does not exist for a powdered specimen. In Fig. 2 I show the diffraction pattern obtained in 22 h from 15 g of deuterated ADP, both above (*a*) and below (*b*) the transition temperature. The strong "super lattice" reflexions observed in the low temperature phase reflect the lowering of the symmetry which occurs when the deuterium atoms order on one or the other of the sites available to them, thereby distorting the whole structure. The solid lines in these diagrams represent the calculated profiles which best fit the observed points. In both cases, the fit approaches that expected for purely statistical errors in the count. The coordinates and vibrational amplitudes of all of the atoms in both structures have been obtained, but the structural transition can most simply be described if I refer only to the (H_2) hydrogen positions.

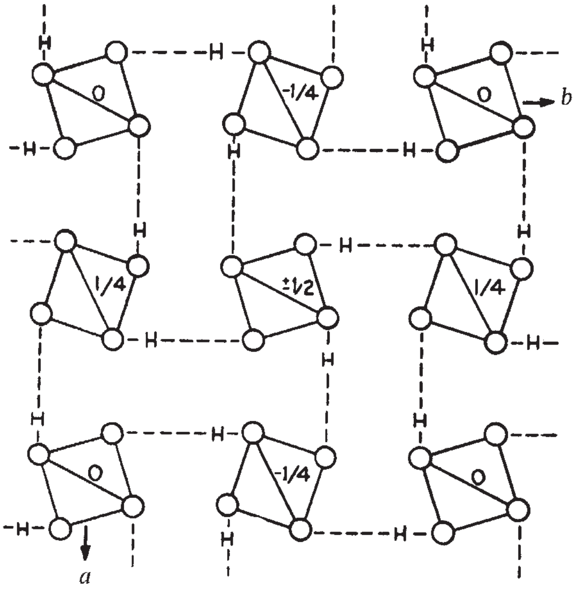

Fig. 3 Ordering of the deuterium atoms (H) on the hydrogen bonds between the phosphate groups, as proposed by Nagamiya[5] and verified in the present experiment.

In Table 1 I give the coordinates obtained for the two equivalent hydrogen sites in the high temperature phase, when each is occupied for half of the time. In the low temperature phase, I find that the diffraction pattern can be explained if I assume that only one of these alternative positions is occupied. When the occupation numbers for the two positions were refined, starting with $\frac{1}{2}$ for both, the one approached unity while the other approached zero within the limits of uncertainty imposed by the data (1.0 ± 0.1). Figure 3 shows how these positions are taken up to produce a perfectly ordered arrangement of hydrogen bonds, but one in which there is no net dipole moment for the complete cell. This result confirms the ordering proposed by Nagamiya[5]. The PO_4 group at ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$), which was equivalent to that at (000) in the high temperature phase, becomes inequivalent in the low temperature phase because of this ordering of hydrogen atoms. These phosphate groups, and the ammonium groups too, are slightly distorted by this hydrogen atom ordering (the ammonium groups are displaced as well), but the resulting dipole moments cancel out over the entire cell and the low temperature structure is antiferroelectric rather than ferroelectric as in KH_2PO_4.

Finally I note that the profile powder method is a technique for structure refinement: it is not intended to compete with methods such as those based on Fourier techniques for the solution of structures about which very little is known. But with neutron diffraction we are almost always trying to refine the details of a structure which has already been solved approximately by X-ray or other techniques—finding more precise positions for the atoms, especially those of hydrogen and the lighter elements, measuring magnetic moments, nuclear and magnetic disorder, defect structures, atomic vibrational amplitudes and so on. For these structure refinement problems the profile refinement of neutron powder patterns often has many advantages over single crystal method. New designs for neutron powder diffractometers, giving greatly increased resolution and intensity, will allow larger structures to be studied with this technique.

I thank Dr B. T. M. Willis for encouragement and Dr H. M. Rietveld of the Reactor Centrum Nederland for a copy of his original profile refinement computer program.

A. W. HEWAT*

Materials Physics Division,
UKAEA Research Group,
Harwell, Berkshire

Received July 6; revised August 7, 1973.

* Now at Institut Laue-Langevin, BP156 Centre de tri, 38042 Grenoble Cedex.

[1] Rietveld, H. M., *J. appl. Crystallog.*, **2**, 65 (1969).
[2] Hewat, A. W., *J. Phys. C.*, **6** (in the press).
[3] Bacon, G. E., and Pease, R. S., *Proc. R. Soc.*, *A*230, 359 (1955).
[4] Tenzer, L., Frazer, B. C., and Pepinsky, Ray, *Acta Crystallog.*, **11**, 505 (1958).
[5] Nagamiya, T., *Progr. theoret. Phys. Japan*, **7**, 275 (1952).