Powder neutron diffraction investigation of the crystal and magnetic structures of NH₄Fe(HPO₄)₂ and its deuterated form.

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Abstract. The NH₄Fe(HPO₄)₂ and its deuterated form, ND₄Fe(DPO₄)₂, were investigated in detail from powder neutron diffraction data allowing a precise determination of the hydrogen positions and low temperature magnetic structures. Below T_C = 17.82 K they order with a ferrimagnetic structure and the magnetic moments lying in the crystallographic plane ac. As the temperature is lowered to T_t = 3.52 K the system undergoes a magnetic phase transition to an equal moment antiphase structure characterized by the propagation vector close to \( \vec{k}_{AF} \approx (1/16, 0, 1/16) \) and a magnetic moment for the Fe³⁺ ions of 4.8 \( \mu_B \) at 1.89 K. The low symmetry of this crystal structure and the complex pattern of competing superexchange pathways are responsible for the existence of this double magnetic phase transition.

1. Introduction
The role of hydrogen in many materials is of paramount relevance such as clay minerals, cements, organometallic compounds, coordination complexes, polymers, hydrogen storage systems, fuel cell components, among others [1, 2]. The determination of the hydrogen positions in the structures of these materials remains cutting edge today as it often governs their physical-chemical properties and, hence, the potential applications.

In particular, iron phosphates have been extensively investigated because they show a complex structural chemistry and a large variety of crystal structures that can give rise to original magnetic behaviors [3, 4, 5]. These features can be attributed to the ability of iron to adopt a variety of coordination and to exhibit mixed valence. A large number of open-framework iron phosphates have been investigated with most of them exhibiting antiferromagnetism [7, 8, 9, 10], less ferrimagnetism [11], with ordering temperature in the 3 – 40 K range.

Recently, interest in NH₄Fe(HPO₄)₂ and its deuterated form has been renewed owing to the existence of two magnetic phases at low temperatures. Magnetic and specific heat measurements reveal that this material orders below T_C = 17.82 K ferrimagnetically and it undergoes a magnetic phase transition below T_t = 3.52 K for adopting an antiferromagnetic arrangement [12]. The
ferrimagnetic phase is quite special in phosphates systems where the superexchange interactions are mainly responsible for the existence of antiferromagnetic ordering. To better understand these macroscopic properties in NH$_4$Fe(HPO$_4$)$_2$ and its deuterated form we require a probe of the microscopic electronic ordering phenomena. We report herein on a structural study for locating the hydrogen and hydrogen bonds, and for determining the low temperature magnetic structures. It is worth noting that both NH$_4$Fe(HPO$_4$)$_2$ and ND$_4$Fe(DPO$_4$)$_2$ materials behaves similarly as the ordered temperatures and magnetization response is almost the same within the experimental uncertainty.

2. Experimental details
The experiments were performed on D2B (λ = 1.594 Å) and on D1B (λ = 2.52 Å) diffractometers at the Institute Laue Langevin (ILL). Data were collected at several selected temperatures (on D2B at 50, 12 and 2 K for the deuterated and hydrogenated compounds, and on D1B every 1 K below 30 K only for the deuterated compound). Rietveld refinements of the crystal and magnetic structures were also carried out using the FULLPROF program [13].

3. Results
The nuclear patterns collected at 50 K on D2B were fitted in $P\bar{1}$ space group. Cell parameters reported from single-crystal x-ray experiments on NH$_4$Fe(HPO$_4$)$_2$ by Yakubovich were used as starting point [6] (see Fig. 1).

![Figure 1](https://example.com/figure1.png)

**Figure 1.** (Color online) Powder neutron diffraction refinement for ND$_4$Fe(DPO$_4$)$_2$ (left side) and NH$_4$Fe(HPO$_4$)$_2$ (right side). Observed (points) and calculated (solid line) collected on D2B at 50, 12 and 2 K. Bragg reflection positions are represented by vertical bars. The first (second) raw of Bragg diffraction reflections corresponds to the nuclear (magnetic) peaks. The observed-calculated difference is depicted at the bottom of each pattern.
Table 1. Cell parameters at 50 K for ND$_4$Fe(DPO$_4$)$_2$ (a) and NH$_4$Fe(HPO$_4$)$_2$ (b) at 50 K.

|       | a (Å)   | b (Å)   | c (Å)   | α (deg) | β (deg) | γ (deg) |
|-------|---------|---------|---------|---------|---------|---------|
| (a)   | 8.83860(5) | 9.73954(5) | 9.21292(5) | 117.8573(5) | 133.6068(4) | 80.6736(5) |
| (b)   | 8.83906(9) | 9.7419(1)   | 9.21435(9) | 117.849(2)  | 133.5947(8) | 80.6970(8) |

It should be pointed out that the quality of the data (even for the hydrogen sample, where the incoherent scattering of neutrons by hydrogen leads to high backgrounds, noisy data and therefore very long-counting-time experiments) allows us the determination of up to eleven H/D positions. Final cell parameters, atomic positions and isotropic displacement parameters are given in Table 1 and 2. The reliability factors are 5.83 % for the hydrogenated sample and 3.39 % for the deuterated.

Table 2. Final atomic positions and isotropic displacement parameters (Å$^2$) for ND$_4$Fe(DPO$_4$)$_2$ / NH$_4$Fe(HPO$_4$)$_2$ at 50 K on D2B.

| Atom  | x        | y        | z        | B        |
|-------|----------|----------|----------|----------|
| Fe1   | 0.50000  | 0.50000  | 0.00000  | 0.00 / 0.03(1) |
| Fe2   | 0.3701(5)/0.3734(9) | 0.9501(4)/0.9493(6) | 0.6534(5)/0.6512(9) | 0.16(2)/0.17(8) |
| P1    | 0.8477(10)/0.8420(14) | 0.7813(7)/0.7797(11) | 0.1925(10)/0.188(2) | 0.28(2)/0.23(8) |
| P2    | 0.2703(10)/0.2697(14) | 0.7778(7)/0.7790(11) | 0.8255(10)/0.829(2) | 0.28(2)/0.23(8) |
| P3    | 0.4748(10)/0.4789(15) | 0.7687(7)/0.7705(10) | 0.3531(10)/0.360(2) | 0.28(2)/0.23(8) |
| O1    | 0.5037(8)/0.5037(9) | 0.7951(7)/0.7972(11) | 0.5491(9)/0.546(2) | 0.43(2)/0.31(3) |
| O2    | 0.9179(9)/0.9160(13) | 0.1886(6)/0.1928(9) | 0.6768(9)/0.681(2) | 0.43(2)/0.31(3) |
| O3    | 0.3450(9)/0.3389(14) | 0.9377(6)/0.9396(9) | 0.0337(10)/0.031(2) | 0.43(2)/0.31(3) |
| O4    | 0.6163(9)/0.6215(13) | 0.9097(6)/0.9077(9) | 0.4339(10)/0.4419(14) | 0.43(2)/0.31(3) |
| O5    | 0.3460(9)/0.3492(12) | 0.7868(6)/0.7834(10) | 0.7217(9)/0.7190(13) | 0.43(2)/0.31(3) |
| O6    | 0.7892(9)/0.7882(13) | 0.6459(7)/0.6455(10) | 0.2003(9)/0.2022(14) | 0.43(2)/0.31(3) |
| O7    | 0.5312(9)/0.5329(13) | 0.6131(6)/0.6155(9) | 0.2698(10)/0.2781(14) | 0.43(2)/0.31(3) |
| O8    | 0.7766(8)/0.7759(12) | 0.9277(7)/0.9280(10) | 0.2604(10)/0.260(2) | 0.43(2)/0.31(3) |
| O9    | 0.6628(8)/0.6695(13) | 0.3582(6)/0.3547(9) | 0.1209(9)/0.1219(13) | 0.43(2)/0.31(3) |
| O10   | 0.2709(9)/0.2686(13) | 0.2860(6)/0.2809(9) | 0.0683(9)/0.0729(13) | 0.43(2)/0.31(3) |
| O11   | 0.9864(9)/0.9789(13) | 0.2597(6)/0.2591(9) | 0.3588(9)/0.3549(14) | 0.43(2)/0.31(3) |
| O12   | 0.7674(9)/0.7687(12) | 0.2516(7)/0.2470(9) | 0.8548(9)/0.8501(13) | 0.43(2)/0.31(3) |
| N1    | 0.00000  | 0.00000  | 0.94(2)/0.84(8) |
| N2    | 0.1828(6)/0.1825(10) | 0.4680(4)/0.4684(7) | 0.3487(6)/0.3469(10) | 0.94(2)/0.84(8) |
| D/H1  | 0.4116(10)/0.417(3) | 0.2577(7)/0.252(2) | 0.1537(11)/0.151(3) | 1.74(2)/1.57(9) |
| D/H2  | 0.8426(10)/0.858(3) | 0.2317(7)/0.228(2) | 0.8039(11)/0.801(3) | 1.74(2)/1.57(9) |
| D/H3  | 0.2255(10)/0.237(3) | 0.4151(8)/0.418(2) | 0.2557(11)/0.267(3) | 1.74(2)/1.57(9) |
| D/H4  | 0.5926(9)/0.592(2) | 0.5919(7)/0.586(2) | 0.4364(10)/0.435(2) | 1.74(2)/1.57(9) |
| D/H5  | 0.9824(10)/0.983(3) | 0.5653(7)/0.558(2) | 0.7645(10)/0.760(3) | 1.74(2)/1.57(9) |
| D/H6  | 0.0657(10)/0.073(2) | 0.2933(7)/0.289(2) | 0.5168(11)/0.520(3) | 1.74(2)/1.57(9) |
| D/H7  | 0.2588(9)/0.267(2) | 0.4311(7)/0.442(2) | 0.4691(10)/0.484(3) | 1.74(2)/1.57(9) |
| D/H8  | 0.108(2)/0.135(5) | 0.9706(14)/0.987(4) | 0.998(2)/1.049(5) | 1.74(2)/1.57(9) |
| D/H9  | 0.872(2)/0.871(5) | 0.9013(14)/0.914(4) | 0.095(2)/0.095(6) | 1.74(2)/1.57(9) |
| D/H10 | 0.070(2)/0.086(5) | 0.0451(15)/0.065(4) | 0.183(2)/0.191(5) | 1.74(2)/1.57(9) |
| D/H11 | 0.077(2)/0.069(5) | 0.9170(15)/0.915(4) | 0.040(2)/0.030(5) | 1.74(2)/1.57(9) |

The patterns collected between 3.8 K and 17.8 K (see Fig. 1 for the patterns on D2B) have no additional peaks compared to those measured at 50 K, indicating the existence of a ferrimagnetic arrangement of the three Fe magnetic moments within the crystallographic cell, having an
arrangement $\uparrow \downarrow \uparrow$, and the magnetic moments lying in the $ac$-plane of the crystal structure with an amplitude of 4.2 $\mu_B$, $R_{mag} = 5\%$ on D1B at 4 K. Comparing the powder patterns measured above $T_C$ and that below 3.8 K, new additional magnetic reflections became evident (see Fig. 1 for the patterns on D2B). The propagation vector was determined to be $\vec{k}_{AF} \equiv (1/16, 0, 1/16)$. The powder diffraction data were successfully fitted, $R_{mag} = 11.8\%$ on D1B at 1.89 K, with a magnetic model based on the high-temperature ferrimagnetic arrangement $\uparrow \downarrow \uparrow \uparrow \uparrow \uparrow$ adopting an antiphase ordering following the sequence $+ - + -$, where $+ (-)$ means $\uparrow \downarrow \uparrow \downarrow \downarrow \downarrow \downarrow \uparrow \downarrow \downarrow \downarrow \downarrow$. The magnetic moments are found to be also in the $ac$–plane, and the magnitude of the magnetic moments at 1.89 K were refined to be of 4.8 $\mu_B$, which is in good agreement with that expected for a free–ion Fe$^{3+}$ ($5 \mu_B$). The patterns collected at 12 K and 2 K on D2B, for both NH$_4$Fe(HPO$_4$)$_2$ and ND$_4$Fe(DPO$_4$)$_2$, confirm the main results found from the experiments carried out on D1B.

4. Conclusions

In summary, the present results suggest in NH$_4$Fe(HPO$_4$)$_2$ the presence of a particular competition of superexchange interactions that are responsible for the unusual existence of two magnetic phase transitions, a ferrimagnetic ordering below $T_C = 17.82$ K that evolves to a an antiphase one below $T_t = 3.52$ K.

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