# The Elusive Magnetic Structure of $FePS_3$

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Laue diffraction patterns from a single crystal of $FePS_3$ were recorded at temperatures above and below the Néel temperature $T_N$ = 120 K on the new thermal Laue diffractometer VIVALDI at the Institut Laue Langevin. Magnetic peaks were weaker and more extended than the nuclear peaks. The directions in reciprocal space of the magnetic reflections were found by reference to the nuclear peaks, and the magnetic reflections could then be readily located on the monochromatic diffractometer D19. The strongest magnetic peaks were found at 0.5, -0.5, 0.34 and 1.5, -0.5, 0.34 and symmetry related positions.

## 1. Introduction

Iron thiophosphate, $FePS_3$ is a member of the transition-metal thiophosphate group, $MPS_3$, which has been a focus in recent years for two-dimensional investigations. It is the structure of these materials (see Fig. 1a) that makes them two-dimensional both crystallographically and magnetically. The transition-metal elements form a honeycomb lattice within the *ab*-plane, while two layers of sulphur and phosphorus atoms separate each pair of metal layers. The sulphur atoms in adjacent layers are in turn separated by a relatively weak van der Waals gap which is the basis for the low dimensionality.

A magnetic structure of the antiferromagnet $FePS_3$ has been accepted since 1983 [1]. First proposed by Le Flem et al. [2] this model has the moments collinear and perpendicular to the *ab*-plane and consists of ferromagnetic chains coupled antiferromagnetically within the plane as well as between planes, as seen in Fig. 1b. Kurosawa et al. [1] performed neutron diffraction on pseudo-single crystals of $FePS_3$ and claimed that their results supported Le Flem et al's proposed structure.

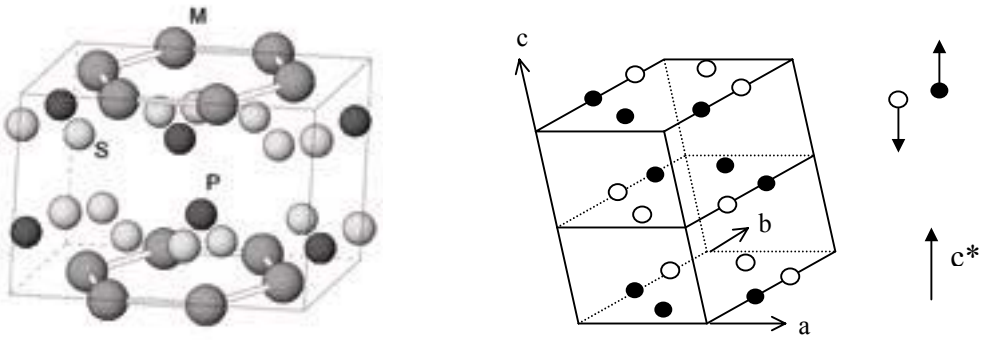


Fig. 1a) Crystallographic structure of $MPS_3$ and b) the previously accepted magnetic structure of $FePS_3$ [1]. Arrows represent magnetic moment directions parallel to c*.

A recent review of this work found inconsistencies in Kurosawa et al's neutron diffraction data. The most recent neutron diffraction studies by Rule et al. [3] were performed on powdered samples and displayed many more magnetic peaks at lower scattering angles than the data of Kurosawa et al. Furthermore, their magnetic propagation vector of [0,0,½], did not link magnetic reflections to the observed nuclear reflections in either set of neutron

diffraction data. The current research investigates the magnetic reflections of $FePS_3$ using two different, complementary neutron diffraction techniques. The aim was to find and classify magnetic peaks and determine possible propagation vectors.

## 2. Experimental Method

Crystals were produced via the vapour deposition method. Stoichiometric quantities of high purity starting materials were sealed in a quartz ampoule and heated for two weeks with a temperature difference of 690°- 630°C. The crystals formed as thin platelets with maximum dimensions of about 10 x 10 x 0.1 mm. A large, well-formed crystal with a nearly hexagonal shape was used for both experiments conducted at the Institut Laue-Langevin.

The sample was mounted on a pin-like sample holder and placed in a He cryostat on VIVALDI (Very Intense Vertical Axis Laue DIffractometer). VIVALDI uses a white beam of neutrons in the wavelength range from 0.8 – 3.0 Å. Laue diffraction patterns were collected at a variety of sample positions at both 5K and 140K to obtain a set of diffraction data below and above the Néel temperature of 120K.

The sample, on the same sample holder, was then transferred to D19, a monochromatic four-circle diffractometer. Using the data from VIVALDI, the orientation of the crystal was quickly verified and the sample was then re-cooled to below the ordering temperature. The magnetic peaks were found by scanning along the reciprocal space directions indicated in the Laue diffraction patterns.

## 3. Results

The Laue diffraction patterns of VIVALDI were recorded on an image-plate detector and analysed using the analysis program, Lauegen [4]. Fig. 2 shows Laue patterns taken at the same sample orientation at the two temperatures. Although much fainter than the nuclear peaks, streaky magnetic reflections can be seen at low scattering angles (especially close to the straight through beam in the centre of the pattern). A monoclinic reciprocal lattice for the space group C2/m was superimposed on the pattern and refined until each nuclear reflection matched a predicted reflection. Two domains were observed in the sample with the second domain rotated 60° from the first. The two domains had a common $c^*$ direction, perpendicular to the face of the sample.

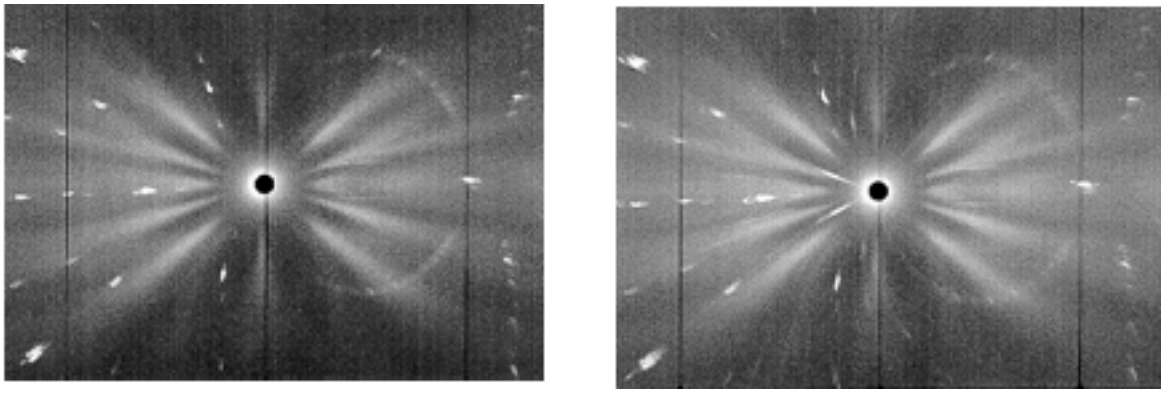

Fig. 2 Laue diffraction patterns from VIVALDI at 140 K (left) and 5 K (right).

The results from D19 were more quantitative yet complementary to those from VIVALDI. The presence of two crystal domains was confirmed and their orientations accurately determined. It was noted that the magnetic peaks observed on D19 were elongated along $z$. This corresponds to the streaky appearance in both the VIVALDI data and the recent MRPD data [3]. Peak intensities were found to be greatest at 0.5, -0.5, 0.34 and 1.5, -0.5, 0.34. Thus a general selection of peaks was measured at positions $h + 0.5$, $k \pm 0.5$, $l +$

0.34. The magnetic peaks from Kurosawa et al's [1] structure were also investigated in both domains, but gave zero intensity.

## 4. Discussion

Results from both VIVALDI and D19 were compared with the previously published MRPD data from Lucas Heights Research Laboratories in Sydney [3]. All predicted peak positions (for both nuclear and magnetic peaks) were generated by Lauegen and superimposed on the VIVALDI patterns. Each observed magnetic peak corresponded to at least one predicted reflections from one of the domains, with the more intense magnetic peaks often corresponding to two predicted reflections (one from each domain). The most intense peaks from the VIVALDI data corresponded to the lowest scattering angle peak from the MRPD data, labelled (-½, ½, -⅓).

Although the propagation vector of (½ ½ ⅓) suggests a commensurate structure, the D19 data indicate that reciprocal lattice positions with $l_{magnetic} = (l_{nuclear} \pm 0.34)$ are more accurate, even though the elongation of the reflections does give intensity at the positions ($l \pm$ ⅓). Analysis of magnetic peak positions from the powder diffraction data also indicated that the $l = 0.34$ is more probable than ⅓.

The powder neutron diffraction patterns of $MnPS_3$ also revealed rod-like structures in reciprocal space. These were in the form of trailing edges on the high scattering-angle side of the magnetic peaks [5]. This elongation, or rod-like structure in reciprocal space, is a result of the quasi-two-dimensional structure of these materials. These rods appear to extend along the *l*-direction in reciprocal space, which corresponds to incomplete long-range order along the *z*-axis in real space. Although the powder diffraction pattern of $FePS_3$ did not show such obvious trailing edges, it is possible that they are present to a lesser extent. The difference in extent of the two-dimensional scattering for $FePS_3$ and $MnPS_3$ is probably due to the different anisotropies of the two transition-metal atoms.

## 5. Conclusion

Although reciprocal space selection rules have been found for the magnetic peaks, a real-space magnetic structure has not yet been determined. The (0.5, 0.5, 0.34) propagation vector implies that the structure is incommensurate, which allows several possible spin models. Mössbauer spectroscopy measurements on $FePS_3$ indicate that the magnetic moments must be oriented along the *z*-axis [6]. This would initially suggest a co-linear structure, unless the moments rotate faster than the Lamor precession frequency. Current analysis is focusing on the possibility of a helical magnetic structure.


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## References


[1] K. Kurosawa, S. Saito, and Y. Yamaguchi, *J. Phys. Soc. Jpn.* **52,** 3919-3926 (1983).

[2] G. Le Flem, R. Brec, G. Ouvrard, A. Louisy, and P. Segransan, *J. Phys. Chem. Solids* **43,** 455-461 (1982).

[3] K. C. Rule, S. J. Kennedy, D. J. Goossens, A. M. Mulders, and T. J. Hicks, *Appl. Phys. A* **74,** S811-S813 (2002).

[4] J. W. Campbell, *J. Appl. Crystallogr.* **28,** 228-236 (1995).

[5] D. J. Goossens, PhD Thesis, Monash University, 1999.

[6] K. C. Rule, J. C. Cashion, A. M. Mulders, and T. J. Hicks, *Hyperfine Interact.* **141,** 219-222 (2002).