Comparative structural evolution under pressure of powder and single crystals of the layered antiferromagnet FePS₃

David M. Jarvis,¹,²,* Matthew J. Coak,²,³ Hayrullo Hamidov,²,⁴ Charles R.S. Haines,⁵,² Giulio I. Lampronti,⁶ Cheng Liu,² Shiyou Deng,⁶ Dominik Daisenberger,⁷ David R. Allan,² Mark R. Warren,² Andrew R. Wildes,¹,³ and Siddharth S. Saxena²,⁴

¹Institut Laue-Langevin, 71 Avenue des Martyrs, 38000 Grenoble, France
²Cavendish Laboratory, Cambridge University, J.J. Thomson Ave, Cambridge CB3 0HE, UK
³Department of Physics, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, UK
⁴Navoi State Mining Institute, 72 M. Tarobiy Street, Navoi, 210100, Uzbekistan
⁵Physics, University of East Anglia, Norwich, NR4 7TJ, UK
⁶Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK
⁷Diamond Light Source, Chilton, Didcot OX11 0DE, United Kingdom

(Dated: March 15, 2022)

The layered antiferromagnet FePS₃ has been shown to undergo a structural transition under pressure linked to an insulator-metal transition, with two incompatible models previously proposed for the highest-pressure structure. We present a study of the high-pressure crystal structures of FePS₃ using both single-crystal and powder x-ray diffraction. We show that the highest pressure transition involves a collapse of the inter-planar spacing of this material, along with an increase in symmetry from a monoclinic to a trigonal structure, to the exclusion of other models. The extent of this volume collapse is shown to be sensitive to the presence of a helium pressure medium in the sample environment, indicating that consideration of such experimental factors is important for understanding high-pressure behaviours in this material.

The layered antiferromagnetic insulators MPS₃, where M is a first-row transition metal, provide an ideal space in which to explore the behaviour of quasi-two-dimensional magnetic systems and the correlated electron physics within them.

The compounds share a common monoclinic structure, space group C2/m, consisting of near-perfect honeycomb layers of transition metal ions in the ab planes[¹, ²]. These planes are weakly coupled to each other by van der Waals forces. Magnetic exchange, partly mediated by the P₂S₆ clusters, is also much stronger within the planes than between them, giving a good approximation of a two-dimensional magnetic system.

Studied extensively since the 1970s, the magnetic exchanges and anisotropies in these materials may be varied by the selection of the transition metal species[¹, ²]. The extreme two-dimensional limit has been approached through delamination towards a single monolayer, with FePS₃ itself found to retain an Ising-type antiferromagnetic order down to the monolayer limit[³–⁵].

Complementary to this, a reduction of the inter-layer spacing may give rise to a more three dimensional structure, providing access to an essential area of interest for both magnetic and transport properties on this crossover.

The application of hydrostatic pressure is an excellent, targeted technique for tuning in this manner, acting primarily to reduce the separation of the weakly-coupled transition metal planes.

Previous high-pressure work[⁶–⁹] has demonstrated the occurrence of two structural transitions under pressure in powder samples of FePS₃. The first, at a critical pressure of 4 GPa, is characterised as a shear of the weakly-coupled ab planes along the crystallographic a direction, maintaining the ambient pressure C2/m space group whilst reducing the angle β to very nearly 90°[⁶].

The second transition, at a pressure of ~14 GPa, has been found to involve a significant volume collapse of the unit cell, which is also coincident with an insulator-to-metal transition in the compound[⁶, ⁷, ¹⁰]. The origin of this volume collapse, however, remains the subject of differing interpretations from powder x-ray diffraction experiments. One model attributes this volume reduction to a collapse of the inter-planar spacing with a simultaneous symmetry increase to a trigonal P31m space group[⁶]: the other to a shrinking of the Fe²⁺ honeycombs, an effect within the ab planes, maintaining a monoclinic structure[¹⁰]. This impact of this higher-pressure structural transition on the magnetism in the system is also the subject of contradictory findings, with indirect results from x-ray emission spectroscopy measurements[¹⁰] contradicted by neutron diffraction[⁹].

The crystal structure of this high-pressure phase provides the starting point for theoretical calculations and models of the novel magnetic and electronic properties, and so the correct identification of the structural transitions in this compound is of vital importance for understanding other behaviours in this and related materials.

Experimental reports of the high-pressure crystal structures of FePS₃ have thus far been determined from powder samples, whereas reports of high-pressure bulk properties, such as measurements of resistivity, have been performed using single-crystals[⁶, ¹⁰]. Verification of the high-pressure behaviour of the crystal structure in single crystals is therefore a necessary step for consolidating
understanding of behaviours in the system.

We report here a study examining the evolution of the crystal structure under pressure of FePS₃ by diffraction of synchrotron radiation. We show new data from both single crystal and powder samples in diamond anvil cells with a helium pressure transmitting medium, and compare these new data with previously published measurements[6] of powder samples without a pressure medium. The highest-pressure transition is found in all cases to include an increase in symmetry to a trigonal $P31m$ structure and a collapse of the inter-planar spacing in both powder and single crystal studies. The extent of this $c$-axis collapse is found to be sensitive to the presence of a helium pressure-transmitting medium, being greatest in experiments without such medium, showing that careful consideration of the sample environment is necessary for the understanding of the high-pressure behaviour of this material.

**Methods**

Single crystals of FePS₃ were grown by a vapour transport method as described in detail in reference [11] using stoichiometric quantities of Fe, P and S powders (all of purity ≥ 99.998 %).

Samples of FePS₃ were manually delaminated down to a thickness of ~15 µm and cut by scalpel and razor blade to squares of side length ~80 µm. Single crystal x-ray diffraction data was collected at the I19-2 beamline at the Diamond Light Source. An incident beam of wavelength 0.4859 Å ($E = 25$ keV) was used to collect diffraction patterns using a Dectris Pilatus 300K detector. The platelet samples were mounted such that the $c^*$ axis was approximately parallel to the incident beam. Data was then collected as the crystal was rotated about $\phi$ and $\omega$ in a standard configuration. The data was analysed using Crystalis Pro software[12].

Powder samples were prepared by grinding the as-grown crystals under liquid nitrogen in order to mitigate the noted tendency towards strong preferred orientations in these materials, arising from the formation of small platelets from shear of the $ab$ planes. This preparation is identical to that used in previous work[6] in order to allow for accurate comparison of other experimental factors in powder experiments.

High-pressure powder x-ray diffraction measurements were performed on the I15 Extreme Conditions beamline at the Diamond Light Source. X-rays of wavelength 0.4246 Å ($E = 29.2$ keV) were used with a MAR345 area detector. Powder data were initially processed using DAWN software[13] and Rietveld and Le Bail refinements were performed using TOPAS[14] and GSAS-II[15].

In both experiments, the gasket material used with the diamond anvil cells was rhenium, and the cells were loaded with helium gas as a pressure-transmitting medium, which was not used for the previously published experiment[6]. The pressure inside the sample space was determined by measurement of the fluorescence of ruby spheres inserted alongside the sample in the pressure region[16].

Diffraction peaks arising from the diamond anvils were identified by fitting the known diamond unit cell and removed from subsequent treatment. Furthermore for the single-crystal experiment, regions of detector images containing powder-like rings from the rhenium gasket were also excluded. Such features remain visible in the generated diffraction images but were excluded from refinements.

**Results**

Both the new powder diffraction (using a helium pressure medium) and single crystal data confirm the presence of two structural phase transitions. The first transition from the ambient to the first high-pressure phase, hereinafter referred to as HP-0 and HP-I respectively, occurred at 4 GPa. The transition to the second phase, denoted HP-II, occurred at 14 GPa. Unlike the powder data without a pressure medium[6], all the transitions were abrupt with no clear evidence of phase coexistence. The powder data and refinements are shown in the supplementary information.

Analysis of both the new powder data and the single crystal data confirmed the conclusions of reference [6], that the HP-I phase had a space group $C2/m$ with $\beta$ close to 90° and the HP-II phase had a higher symmetry trigonal $P31m$ space group. Unit cell parameters for each phase are given in the supplementary information.

The (00$l$) peaks were not accessible in the single crystal measurements due to the experimental geometry. To verify the indexing of the single crystal Bragg peaks, and to independently verify the pressure evolution of the lattice parameters, slices of the (0kl) planes were extracted. The $0k0$ and $00l$ directions are orthogonal in all the considered space groups. The $0kl$ Bragg peaks thus give unambiguous measures of the inter-planar spacing, and of a characteristic intra-planar spacing, of the lattice as a function of pressure.

Figure 1 shows slices of the (0kl) scattering planes generated from single crystal diffraction data at three pressures corresponding to the determined HP-0, HP-I and HP-II phases. The strong monoclinic (06l) and (06l) peaks for $l = -1, 0, 1$ which are instead indexed in HP-II as $(0, \pm 3, l)$, are visible alongside powder rings from the rhenium gasket. Smearing of the strongest Bragg peaks along the $00l$ direction is attributable to stacking faults and the quasi-two-dimensional nature in this family of materials which have been previously observed[17–19]. These slices show a distinct increase in the separation of the peaks along the (00l) direction between the HP-I
and HP-II phases, corresponding to a reduction in the distance between the transition metal planes, without a similar change in the (0k0) distances. This is immediate evidence that the volume reduction upon the transition to HP-II is due to changes between the planes, rather than an intra-planar change of the honeycombs themselves.

To allow for effective quantitative comparison of the crystal structure across the transitions and in different space groups, two key quantities are determined from both powder and single crystal to characterise changes in distances both between the van der Waals planes and between individual Fe$^{2+}$ ions within them.

Inter-planar distance may be determined from powder diffraction patterns directly from observation of the (001) diffraction peak. Such analysis however relies on the correct indexation of diffraction peaks. Indexation of powder diffraction patterns of the HP-II phase is found to be possible using a $C2/m$ space group as for the lower pressure phases, but this leads to a misidentification of the important (001) peak and of the overall structure which is clearly incompatible with the structure identified from single-crystal. This is demonstrated fully in the supplementary information, as is the quantitative treatment of reciprocal space images such as those in Figure 1 for the determination of an equivalent inter-planar distance.

Figure 2 shows this inter-planar spacing in FePS$_3$ as a function of pressure across the three distinct structural phases from: automated refinements of our single crystal data using CrysAlis Pro; as determined from analysis of 0kl reciprocal space slices; and from Le Bail refinements of powder diffraction data both with and without a helium pressure medium. The transition from HP-0 to HP-I is not clearly observed as this transition involves a shear along the a-axis, with a minimal change in the inter-planar spacing, but it is apparent in a shift in intensities around the (131) and (202) peaks as shown in the supplementary information in Figure S4. The transition to HP-II is observed at similar pressures across the different experiments, and in all cases this transition involves a reduction of the inter-planar distance. The extent of this collapse differs between experiments. The powder measurement without pressure-transmitting medium shows the greatest change of 13.5%, from 5.718 Å to 4.948 Å, whilst the powder measurement with helium medium shows a reduction of 11.7 %, from 5.794 Å to 5.114 Å. The single crystal measurement, also with helium medium, shows a reduction between 7.0% and 11.3%.

The structural evolution within the ab planes may be characterised in terms of a nearest-neighbour distance between Fe ions in the honeycombs which is shown in Figure 3. For single crystal data this distance is derived from the position of the (060) and (060) peaks as indexed in the monoclinic unit cell, or the (030) and (030) in the trigonal HP-II cell. The Fe atoms form an almost perfect honeycomb lattice in the HP-0 phase[1] and as shown in the inset of Figure 3, in the limit of a perfect honeycomb structure the spacing of these (0k0) planes is equal to half the side length of the Fe ion hexagons. Due to correlations observed in refinements for the powder measurement with helium medium (see supplementary information), only values for the HP-II phase are shown.

Figure 3 shows that the characteristic intra-planar spacing does not display a significant discontinuity across...
FIG. 3. Average intra-planar nearest neighbour distance between Fe ions as a function of pressure as determined from (cyan) single crystal refinement; (red) single crystal as determined from (0kl) and equivalent images; (green) powder sample with a He pressure medium; (blue) powder diffraction without pressure medium. (Inset) view along c* of the monoclinic and trigonal unit cells, with the spacing of the (060) monoclinic or (030) trigonal lattice planes in red.

Discussion

These results verify the occurrence of the two structural transitions under pressure in FePS$_3$. The first transition involves a shear of $\sim a/3$ along the $a$ direction and the second an increase in symmetry to a $P31m$ space group. The results verify the model proposed by Haines et al.\cite{6} attributing the volume collapse to a reduction of inter-layer separation.

The magnitudes of the lattice parameters show differences between the data sets. This is particularly evident for the powder data with a helium pressure medium in Figure 3, and is also true for data $\leq 20$ GPa in the HP-II phase in Figure 2. The observed differences between the experiments suggest that both the presence of a helium pressure medium and the form of the sample used are both important factors in the high-pressure structural behaviour of FePS$_3$. There are multiple possible origins for this. One is the intended effect of the pressure-transmitting medium to allow a more hydrostatic pressure distribution in the sample. Fractions of the sample experiencing a different local pressure may explain the observation of phase coexistence only in the no medium data, but the effect of a more significant uniaxial component of pressure on the inter-planar spacing and volume collapse requires further investigation.

A more subtle effect may be the interaction of helium itself with FePS$_3$. The intercalation of MPS$_3$ materials with elements such as lithium\cite{20} has been found to strongly affect both the electronic and magnetic properties. Differences in behaviour between the single crystal and powder, both with a helium medium, such as those seen in Figure 3, could then arise from differing amounts of intercalation of helium into the material due to the sample form. The impact of such factors is important for cases of other layered compounds such as the intercalation of graphite with Li\cite{21} or Yb\cite{22}, in which intercalation is limited to the layer edges of samples. In this way intercalation in FePS$_3$ may be more complete in the powder sample, giving rise to observed differences in behaviour.

Regardless of its microscopic origin, a change in the extent of the reduction of inter-planar spacing accompanying the symmetry increase between the experiments presented here is important. It is direct evidence that the high-pressure properties of this material and others in the same family are sensitive to experimental factors which may not be considered by calculations. These theoretical predictions themselves must make careful consideration when using previous experimental observations of crystal structure as a basis for the determination of properties such as band structure calculations.

We verify that the structural transition linked to metallisation and a new magnetic state in FePS$_3$ involves a symmetry increase from space group $C2/m$ to $P31m$ and...
that the volume collapse is due to a reduction of inter-planar spacing rather than intra-planar effects. We find that the extent of this collapse is sensitive to the presence of a helium pressure-transmitting medium, and note that consideration must be given to this such factors in future experiments and calculations.

Acknowledgements

This research was supported by United Kingdom Research and Innovation Global Challenges Research Fund COMPASS Grant No. ES/P010849/1 and Cambridge Central Asia Forum, Jesus College, Cambridge. This project has received funding from the UK Department of Business, Environment and Industrial Strategy to support collaboration between Cavendish Laboratory and Navoi Mining Institute.

This work was carried out with the support of the Diamond Light Source through the award of beamtime for proposals EE15949 and CY23524.

* Corresponding author: jarvis@ill.fr
† Corresponding author: wildes@ill.fr
‡ Corresponding author: sss21@cam.ac.uk

[1] G. Ouverard, R. Brec, and J. Rouxel, Structural determination of some MPS₃ layered phases (M = Mn, Fe, Co, Ni and Cd), Materials Research Bulletin 20, 1181 (1985).
[2] R. Brec, Review on structural and chemical properties of transition metal phosphorous trisulphides MPS₃, Solid State Ionics 22, 3 (1986).
[3] J.-U. Lee, S. Lee, J. H. Ryoo, S. Kang, T. Y. Kim, P. Kim, C.-H. Park, J.-G. Park, and H. Cheong, Ising-Type Magnetic Ordering in Atomically Thin FePS₃, Nano Lett. 16, 7433 (2016).
[4] C.-T. Kuo, M. Neumann, K. Balamurugan, H. J. Park, S. Kang, H. W. Shiu, J. H. Kang, B. H. Hong, M. Han, T. W. Noh, and J.-G. Park, Exfoliation and Raman Spectroscopic Fingerprint of Few-Layer NiPS₃ Van der Waals Crystals, Sci. Rep. 6, 1 (2016).
[5] X. Wang, K. Du, Y. Y. F. Liu, P. Hu, J. Zhang, Q. Zhang, M. H. S. Owen, X. Lu, C. K. Gan, P. Sengupta, C. Kloc, and Q. Xiong, Raman spectroscopy of atomically thin two-dimensional magnetic iron phosphorus trisulphide (FePS₃) crystals, 2D Mater. 3, 031009 (2016).
[6] C. R. S. Haines, M. J. Coak, A. R. Wildes, G. I. Lampronti, C. Liu, P. Nahai-Williamson, H. Hamidov, D. Daisenberger, and S. S. Saxena, Pressure-Induced Electronic and Structural Phase Evolution in the van der Waals Compound FePS₃, Phys. Rev. Lett. 121, 266801 (2018).
[7] Y. Zheng, X.-x. Jiang, X.-x. Xue, J. Dai, and Y. Feng, Ab initio study of pressure-driven phase transition in FePS₃ and FePSe₃, Phys. Rev. B 100, 174102 (2019).
[8] R. A. Evarestov and A. Kuzmin, Origin of pressure-induced insulator-to-metal transition in the van der Waals compound FePS₃ from first-principles calculations, J. Comput. Chem. 41, 1337 (2020).
[9] M. J. Coak, D. M. Jarvis, H. Hamidov, A. R. Wildes, J. A. M. Padddson, C. Liu, C. R. S. Haines, N. T. Dang, S. E. Kichanov, B. N. Savenko, S. Lee, M. Kratochvilová, S. Klotz, T. C. Hansen, D. P. Kozenko, J.-G. Park, and S. S. Saxena, Emergent Magnetic Phases in Pressure-Tuned van der Waals Antiferromagnet FePS₃, Phys. Rev. X 11, 011024 (2021).
[10] Y. Wang, J. Ying, Z. Zhou, J. Sun, T. Wen, Y. Zhou, N. Li, Q. Zhang, F. Han, Y. Xiao, P. Chow, W. Yang, V. V. Struzhkin, Y. Zhao, and H.-k. Mao, Emergent superconductivity in an iron-based honeycomb lattice initiated by pressure-driven spin-crossover, Nat. Commun. 9, 1 (2018).
[11] D. Lançon, H. C. Walker, E. Ressouche, B. Oulad-diaf, K. C. Rule, G. J. McIntyre, T. J. Hicks, H. M. Rønnow, and A. R. Wildes, Magnetic structure and magnon dynamics of the quasi-two-dimensional antiferromagnet FePS₃, Phys. Rev. B 94, 214407 (2016).
[12] Crysalis PRO, Agilent Technologies Ltd (2014).
[13] J. Filik, A. W. Ashton, P. C. Y. Chang, P. A. Chater, S. J. Day, M. Drakopoulos, M. W. Gerring, M. L. Hart, O. V. Magdysyuk, S. Michalik, A. Smith, C. C. Tang, N. J. Terrill, M. T. Wharmby, and H. Wilhelm, Processing two-dimensional X-ray diffraction and small-angle scattering data in DAWN 2, J Appl. Cryst 50, 959 (2017).
[14] A. A. Coelho, TOPAS and TOPAS-Academic: An optimization program integrating computer algebra and crystallographic objects written in C++, J Appl. Cryst 51, 210 (2018).
[15] B. H. Toby and R. B. Von Dreеле, GSAS-II: The genesis of a modern open-source all purpose crystallography software package, J Appl. Cryst 46, 544 (2013).
[16] H. K. Mao, J. Xu, and P. M. Bell, Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions, J. Geophys. Res. Solid Earth 91, 4673 (1986).
[17] D. J. Goossens, D. James, J. Dong, R. E. Whitfield, L. Norén, and R. L. Withers, Local order in layered NiPS₃ and Ni₀₇Mg₀₃PS₃, J. Phys.: Condens. Matter 23, 065401 (2011).
[18] A. R. Wildes, V. Simonett, E. Ressouche, G. J. McIntyre, M. Avdeev, E. Suard, S. A. J. Kimber, D. Lançon, G. Pepe, B. Moubarak, and T. J. Hicks, Magnetic structure of the quasi-two-dimensional antiferromagnet NiPS₃, Phys. Rev. B 92, 224408 (2015).
[19] C. Murayama, M. Okabe, D. Urushihara, T. Asaka, K. Fukuda, M. Isobe, K. Yamamoto, and Y. Matsushita, Crystallographic features related to a van der Waals coupling in the layered chalcogenide FePS₃, Journal of Applied Physics 120, 142114 (2016).
[20] V. Grasso and L. Silipigni, Low-Dimensional Materials: The MPX₃ Family—Physical Features and Potential Future Applications, ChemInform 34, 10.1002/chin.200311221 (2003).
[21] Y. Guo, R. B. Smith, Z. Yu, D. K. Efetov, J. Wang, P. Kim, M. Z. Bazant, and L. E. Brus, Li intercalation into graphite: Direct Optical Imaging and Cahn–Hilliard Reaction Dynamics, J. Phys. Chem. Lett. 7, 2151 (2016).
[22] T. E. Weller, M. Ellerby, S. S. Saxena, R. P. Smith, and N. T. Skipper, Superconductivity in the intercalated graphite compounds Cs₀Yb and Cs₀Ca, Nature Phys 1, 39 (2005).