

Local nuclear and magnetic order in the two-dimensional spin glass  $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$ J. N. Graham<sup>1,2,3,\*</sup> M. J. Coak<sup>4</sup> S. Son,<sup>5,6,7</sup> E. Suard,<sup>2</sup> J.-G. Park,<sup>5,6,7</sup> L. Clark,<sup>1,3</sup> and A. R. Wildes<sup>2</sup><sup>1</sup>*Department of Chemistry and Materials Innovation Factory, University of Liverpool, 51 Oxford Street, Liverpool L7 3NY, United Kingdom*<sup>2</sup>*Institut Laue-Langevin, 71 Avenue des Martyrs, CS20156, 38042 Grenoble Cédex 9, France*<sup>3</sup>*School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom*<sup>4</sup>*Department of Physics, University of Warwick, Coventry, West Midlands CV4 7AL, United Kingdom*<sup>5</sup>*Center for Correlated Electron Systems, Institute for Basic Science, Seoul 08826, Republic of Korea*<sup>6</sup>*Department of Physics and Astronomy, Seoul National University, Seoul 08826, Republic of Korea*<sup>7</sup>*Center for Quantum Materials, Seoul National University, Seoul 08826, Republic of Korea*

(Received 19 June 2020; accepted 13 July 2020; published 3 August 2020)

We present a comprehensive study of the short-ranged nuclear and magnetic order in the two-dimensional spin glass,  $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$ . Nuclear neutron scattering data reveal a random distribution of  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  ions within the honeycomb layers, which gives rise to a spin glass state through inducing competition between neighboring exchange interactions, indicated in magnetic susceptibility data by a cusp at the glass transition,  $T_g = 35$  K. Analysis of magnetic diffuse neutron scattering data collected for both single-crystal and polycrystalline samples gives further insight into the origin of the spin glass phase, with spin correlations revealing a mixture of satisfied and unsatisfied correlations between magnetic moments within the honeycomb planes, which can be explained by considering the magnetic structures of the parent compounds,  $\text{MnPS}_3$  and  $\text{FePS}_3$ . We found that, on approaching  $T_g$  from above, an ensemble-averaged correlation length of  $\xi = 5.5(6)$  Å developed between satisfied correlations, and below  $T_g$ , the glassy behavior gave rise to a distance-independent correlation between unsatisfied moments. Correlations between the planes were found to be very weak, which mirrored our observations of rodlike structures parallel to the  $c^*$  axis in our single-crystal diffraction measurements, confirming the two-dimensional nature of  $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$ .

DOI: [10.1103/PhysRevMaterials.4.084401](https://doi.org/10.1103/PhysRevMaterials.4.084401)

## I. INTRODUCTION

Low-dimensional materials, such as graphene, continue to captivate the scientific community due to the wide range of potential applications they naturally lend themselves to, from optoelectronics to nanocatalysis [1–5]. Whilst their chemical and electronic properties have been studied extensively, examples of two-dimensional magnetic materials that can be exfoliated down to a monolayer, remain relatively scarce [6,7]. Yet lowering the dimensionality of certain compounds, and combining with, for example, the application of pressure, has resulted in the formation of unconventional electronic and magnetic states of matter [8–13] that are rarely encountered in their bulk counterparts. Another potential route to attain unconventional magnetic states is to study frustrated magnets [14,15]. In recent years, there has been a surge of research focused around novel ways to induce frustration on networks of magnetic ions that would not usually show such behavior. One example is the Kitaev model [16,17], where highly anisotropic interactions between neighboring spins generate frustration on a  $S_{\text{eff}} = 1/2$  honeycomb network. The search for the theoretically predicted Kitaev quantum spin liquid resulting from such frustrated interactions has so far centered around two main material families,  $\alpha\text{-RuCl}_3$  [18–21] and  $A_2\text{IrO}_3$  ( $A = \text{Li}, \text{Na}$ ) [22–24], where ultimately deviations from the ideal honeycomb and direct exchange between the transition-metal

ions lead these materials to order. Alternatively, frustration may also be induced by increasing the strength of competing ferromagnetic and antiferromagnetic exchange interactions within the honeycomb network, such as in the Heisenberg antiferromagnet  $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$  [25–28]. One family of materials that may link these fields are the honeycomb layered metal thiophosphates,  $\text{MPS}_3$ .

The  $\text{MPS}_3$  compounds adopt a monoclinic  $C2/m$  structure in which honeycomb networks of transition-metal ( $M$ ) ions form in the  $ab$  planes [30,31] [Fig. 1(a)]. Each transition-metal ion is contained within an octahedron of sulfur atoms with a pair of phosphorous atoms found at the center of each honeycomb ring, stacked in an ABC sequence, similar to the  $\text{CdCl}_2$  structure [2]. These layers are weakly bound by van der Waals interactions [30] [Fig. 1(b)], allowing the layers to either be intercalated [31–33] or delaminated to a single monolayer [34,35].

The magnetic structures of two members of this series,  $\text{MnPS}_3$  and  $\text{FePS}_3$ , have been well characterized in a number of earlier studies [2,31,33,36,37]. Although both are quasi-two-dimensional antiferromagnets, the precise details of their respective magnetic structures are deeply reliant on the choice of transition-metal ion residing within the honeycomb layers. Notably, in  $\text{MnPS}_3$ , all nearest-neighbor magnetic moments are coupled antiferromagnetically in the  $ab$  planes, whereas in  $\text{FePS}_3$ , there are two ferromagnetic nearest-neighbors and one antiferromagnetic neighbor for every  $\text{Fe}^{2+}$  ion within the plane [38–42]. Furthermore,  $\text{MnPS}_3$  is well modelled

\*Corresponding author: JNG909@student.bham.ac.uk

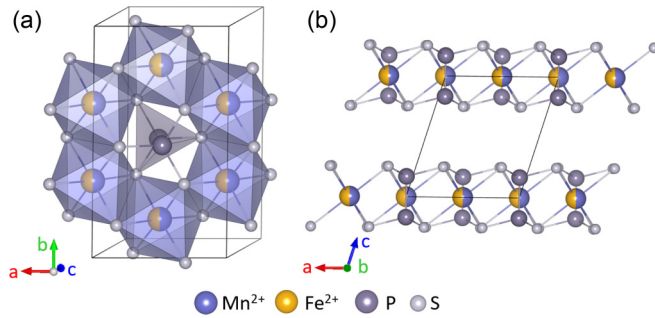


FIG. 1.  $Mn_{0.5}Fe_{0.5}PS_3$  adopts a  $C2/m$  crystal structure where (a) honeycomb layers of transition metal ions form in the  $ab$  planes and are (b) weakly bound by van der Waals interactions along the  $c$  axis. Figures produced in VESTA [29].

by a Heisenberg Hamiltonian, whilst the magnetic moments in  $FePS_3$  are more appropriately described as Ising-like [36,39,41].

Creating a solid solution of these compounds, therefore, presents another way to generate magnetic frustration on a honeycomb network. Here, the source of frustration originates from the first nearest-neighbor exchange interaction, which is antiferromagnetic for  $MnPS_3$  [41] and ferromagnetic for  $FePS_3$  [39]. This frustration may be further compounded by the competition between spin and exchange anisotropies that exist within the magnetic structures of the two end members. Previous magnetization and specific heat capacity measurements of  $Mn_{0.5}Fe_{0.5}PS_3$  have revealed a spin glass phase exists with the glass transition,  $T_g$ , occurring at 35 K [43–46]. This glassy phase, where frustrated moments are randomly frozen, is thought to arise as a result of the competing magnetic exchange interactions combined with the random site occupancy of the transition-metal ions within the honeycomb layers. The presence of such chemical disorder has been verified using techniques such as Mössbauer spectroscopy [45]. Other sister compounds have also been reported, for instance  $Mn_{0.5}Fe_{0.5}PSe_3$  [47], which despite the presence of chemical disorder and similarity to our material, is not a spin glass due to the very strong spin anisotropy arising from ligand spin-orbit contributions. This results in short-range magnetic order existing between nanoclusters of  $MnPSe_3$  and  $FePSe_3$ -type structures.

However, in the case of  $Mn_{0.5}Fe_{0.5}PS_3$ , there are still a number of important details surrounding the spin glass phase that remain to be understood, in particular, the nature of its local nuclear and magnetic correlations. In this paper, we address these issues through a series of neutron scattering and magnetization measurements.

## II. EXPERIMENTAL METHODS

Single crystals of  $Mn_{0.5}Fe_{0.5}PS_3$  were grown via a three-step process to maximize the homogeneous mixing of manganese and iron constituents. Stoichiometric quantities of elemental powders - Fe (99.998%, Alfa Aesar), Mn (99.95%, Alfa Aesar), P (red phosphorous, 99.99%, Sigma Aldrich), and S (99.998%, Alfa Aesar) were ground under an argon atmosphere until fine and sealed in quartz tubes, which were evacuated to a 10 mbar Ar gas pressure. Quartz tubes used in

each step had an 18 mm inner diameter and were 100 mm in length. The sealed tubes were annealed at 500 °C for 2 days. The powder from this initial heating stage was then reground in an Ar glove box. The ground powder was sealed in a quartz tube as per the first synthesis step, and annealed at 600 °C for a further 2 days. Single crystals were grown from the powder via chemical vapor transport. The powder was reground and loaded into quartz tubes with an iodine powder flux agent (50 mg of  $I_2$  per 1 g of reactants). The tubes were evacuated to  $\sim 10^{-3}$  mbar vacuum using a molecular diffusion pump and sealed. The sealed tubes were placed in a two-zone furnace and heated to 730 °C/630 °C over 12 hours and held for 7 days before cooling to room temperature over 24 hours. The grown crystals formed shiny black flakes with typical dimensions, 1 cm  $\times$  1 cm  $\times$  50  $\mu$ m. The sample stoichiometry and quality were verified with energy dispersive x-ray (EDX) spectroscopy and powder x-ray diffraction (XRD). EDX was performed on a Bruker QUANTAX system combined with a scanning electron microscope (COXEM, EM-30). The quality of single crystals were verified via x-ray Laue diffraction, using an Imaging Plate x-ray Diffraction (IP-XRD) Laue Camera (IPX Co. Ltd).

Constant wavelength neutron powder diffraction (NPD) data were collected at room temperature on the high-resolution D2B diffractometer [48] at the Institut Laue-Langevin (ILL), Grenoble [49]. The incident wavelength was  $\lambda = 1.59432$  Å and the scattering was measured over an angular range of  $10^\circ < 2\theta < 160^\circ$ . Nuclear refinements were completed using the GSAS package [50]. The powder used in these measurements was the powder produced from step two of the growth process. Like previous members of the  $MPS_3$  family [51], preferred orientation had to be accounted for due to the platelike nature of  $Mn_{0.5}Fe_{0.5}PS_3$  which makes grinding an isotropic powder difficult, and was corrected for via the spherical harmonics (ODF) method.

Magnetization measurements were carried out on single-crystal samples in MPMS3 and MPMS SQUID magnetometers, Quantum Design. DC measurements were carried out in a fixed-0.1 T field, both cooled in zero applied field (ZFC) and field cooled (FC) cycles over a temperature range of 2 to 300 K. To avoid causing strains, the sample was not held in any epoxy or grease, and was instead held between sheets of plastic film.

Single crystals were aligned in orientations parallel and perpendicular to the  $c^*$  axis on the three-axis spectrometer IN3 at the ILL. Neutron scattering measurements were performed on powder and single-crystal samples using the polarized diffuse scattering D7 diffractometer [52] at the ILL [53]. The incident neutron wavelength was  $\lambda = 4.8718$  Å, giving a reciprocal space range of  $0.15 \leq Q \leq 2.5$  Å<sup>-1</sup>. Single-crystal data were measured as a function of the sample rotation about the normal to the scattering plane. The samples were rotated over a total range of 210 degrees. The technique of  $xyz$ -polarization analysis was used to separate the magnetic, nuclear-coherent (NC) and nuclear spin-incoherent (NSI) components [52,54]. Full calibration measurements included measurements of an empty and cadmium-filled sample can to estimate the instrumental background, a quartz standard to correct for polarization inefficiencies and a vanadium standard to normalize the detector efficiencies. Data were placed on an absolute intensity scale (with units b/ster/f.u.) by normalising to the incoherent scattering from the vanadium standard. We

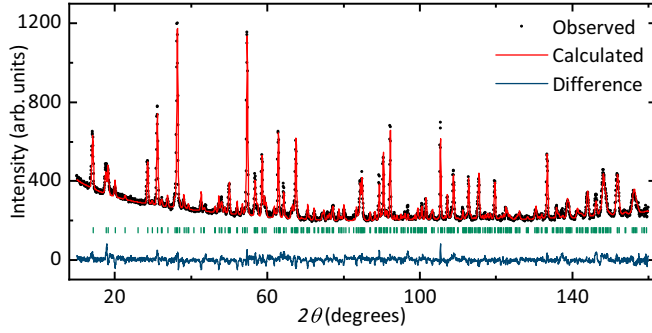


FIG. 2. Rietveld refinement of the  $C2/m$  model ( $\chi^2 = 5.273$ ,  $R_{wp} = 4.54\%$ ) describing the structure of  $Mn_{0.5}Fe_{0.5}PS_3$  using data collected on the D2B instrument at 300 K.

verified our normalization process was correct through Rietveld analysis of the NC cross-sections using FULLPROF [55]. Magnetic diffuse scattering data were analysed using the programs SPINVERT [56,57], SPINCORREL, and SCATTY [58]. These software produce refinements to experimental data based on reverse Monte Carlo (RMC) spin simulations. SPINVERT calculations were repeated 10 times to average out statistical noise.

### III. RESULTS

#### A. Nuclear structure

Figure 2 shows the Rietveld refinement of the monoclinic  $C2/m$  model against high-resolution NPD data of  $Mn_{0.5}Fe_{0.5}PS_3$  collected at 300 K on the D2B instrument at the ILL. The refined parameters can be found in Table I. Refinement of the transition-metal occupancies confirmed that the sample has the expected stoichiometry whereby the honeycomb network is comprised of an approximately equal amount of  $Mn^{2+}$  and  $Fe^{2+}$  ions. Within error, this is in agreement with the EDX results of 47(1)% and 53(2)% for  $Mn^{2+}$  and  $Fe^{2+}$  respectively. The respective neutron scattering lengths for  $Mn^{2+}$  and  $Fe^{2+}$  are  $b_{Mn} = -3.73$  fm and  $b_{Fe} = +9.45$  fm, which yield excellent contrast. The absence of any diffuse structure within the flat background of the NPD data indicates a lack of any short-range ordering between the  $Mn^{2+}$  and  $Fe^{2+}$  ions, and therefore implies a random distribution of the magnetic ions throughout the average structure.

Experimental powder neutron scattering data recorded on D7 at the ILL are presented in Fig. 3. An example of the NC and NSI components are shown in Fig. 3(a), which were collected at 1.5 K. The expected NC is slightly lower than

TABLE I. Refined nuclear structure parameters for the  $C2/m$  model fitted to NPD data collected at 300 K, where the refined lattice parameters are  $a = 6.0137(2)$  Å,  $b = 10.4174(2)$  Å,  $c = 6.7591(2)$  Å, and  $\beta = 107.129(2)^\circ$ .

Atom	Site	$x$	$y$	$z$	Occ	$U_{iso}$ (Å <sup>2</sup> )
Mn1	4g	0	0.3354(9)	0	0.520(4)	0.022(2)
Fe1	4g	0	0.3354(9)	0	0.480(4)	0.022(2)
P1	4i	0.0542(8)	0	0.1619(5)	1.0	0.0188(7)
S1	4i	0.738(1)	0	0.2442(8)	1.0	0.0051(5)
S2	8j	0.2358(7)	0.1661(4)	0.2503(6)	1.0	0.0051(5)

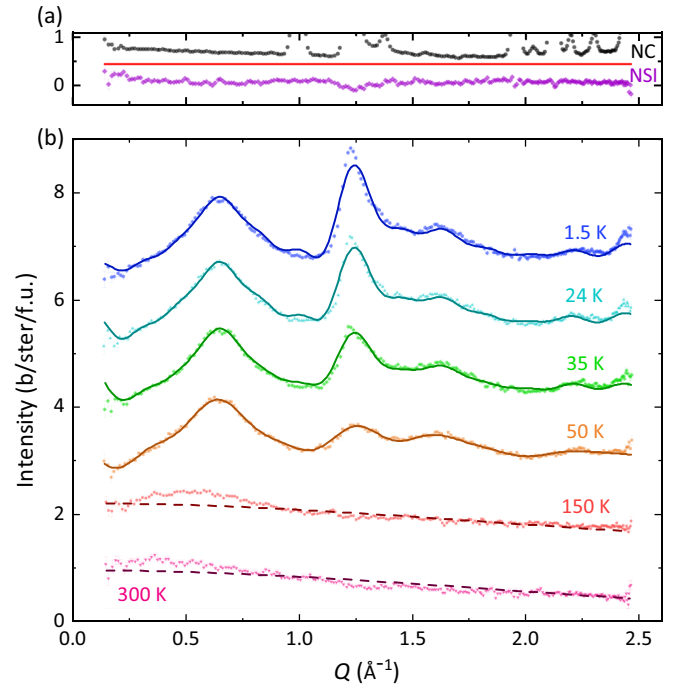


FIG. 3. Experimental powder neutron scattering data from D7. (a) NC and NSI components measured at 1.5 K. The expected NC is highlighted by the red line and is slightly lower than the measured value. (b) Magnetic diffuse scattering contributions. These data have been vertically shifted by 1.25 b/ster/f.u. for clarity. Fits produced by a RMC refinement assuming moments lie along the  $c^*$  axis are shown by the solid lines and fits considering just the paramagnetic contribution of  $Mn^{2+}$  ions are shown by the dashed lines.

the measured values, as shown by the red line, and this may be due to a small systematic error in the estimation of the background. This is possible when using the  $xyz$  method, although it is noteworthy that any residual background will only appear in the NC and NSI contributions as it is self-subtracted from the magnetic contributions. Similarly to the D2B data, there is a nearly flat background in the NC measurement, which further confirms the absence of any substantial short-range order and therefore an essentially random distribution of  $Mn^{2+}$  and  $Fe^{2+}$  ions exists within the honeycomb layers.

#### B. Magnetic susceptibility

Single-crystal magnetization data are presented in Fig. 4 and reveal features concomitant with spin glass behavior. First, the data show a sharp cusp at 35 K, which corresponds to the glass transition,  $T_g$ , and is in accordance with other reports [43,46]. Splitting between the FC and ZFC magnetization occurs below  $T_g$ , which is particularly prominent when the applied field is parallel to the  $c^*$  axis. These data have been fit between 100 and 300 K with a modified Curie-Weiss law,  $\chi = \frac{C}{T-\theta} + \chi_0$ , where  $\chi_0 = -1.0631 \times 10^{-9}$  m<sup>3</sup> mol<sup>-1</sup> is a temperature independent background term describing the inherent diamagnetic contribution of  $Mn_{0.5}Fe_{0.5}PS_3$  [59]. When the  $c^*$  axis is parallel and perpendicular to the applied field, the extracted Curie-Weiss constants are  $\theta_{||} = -105(4)$  K and  $\theta_{\perp} = -267(4)$  K, respectively. These values are both large and negative, indicating that the



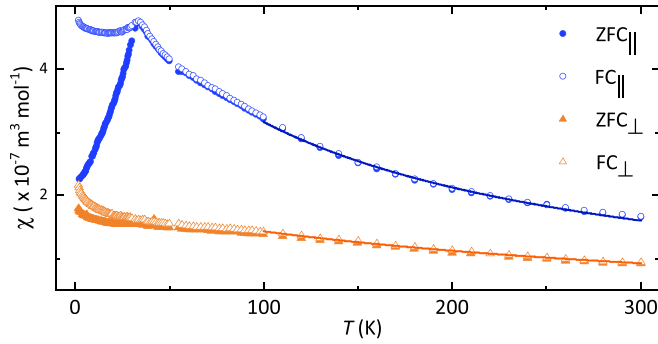


FIG. 4. DC susceptibility data for  $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$  in a 0.1 T magnetic field. Curie-Weiss fits were conducted over a range of 100 to 300 K and are shown by the blue and orange lines for when the  $c^*$  axis is parallel and perpendicular to the applied field respectively.

dominant interactions in  $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$  are antiferromagnetic. The Curie constants,  $C_{\parallel} = 6.5(1) \times 10^{-5} \text{ m}^3 \text{ K mol}^{-1}$  and  $C_{\perp} = 5.29(5) \times 10^{-5} \text{ m}^3 \text{ K mol}^{-1}$ , give effective magnetic moments,  $\mu_{\text{eff}} = 6.43(1)\mu_{\text{B}}$  and  $\mu_{\text{eff}} = 5.80(3)\mu_{\text{B}}$  when the applied field is parallel and perpendicular to the  $c^*$  axis respectively. This is slightly larger than the expected spin-only effective moment,  $\mu_{\text{eff}} = 5.41\mu_{\text{B}}$ , assuming an average  $S = 2.25$  from the mixture of  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  ions. Although previous magnetization studies of  $\text{MnPS}_3$  have shown that the system can be well modelled by a spin-only effective moment, the high-spin state of  $\text{Fe}^{2+}$  ions results in a sizable spin-orbit contribution, seen in both magnetization [36] and neutron [39] studies of  $\text{FePS}_3$ . The large difference in the measured susceptibility when the field is applied in different orientations indicates that  $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$  is highly anisotropic, similar to the measured magnetic susceptibility of  $\text{FePS}_3$  with pronounced Ising anisotropy parallel to the  $c^*$  axis.

### C. Magnetic diffuse scattering

The magnetic cross-sections recorded on D7 are presented in Fig. 3(b) and have been vertically shifted by 1.25 b/ster/f.u. for clarity. The high-temperature data ( $\geq 150$  K) have been fit using an analytical approximation of the magnetic form factor for  $\text{Mn}^{2+}$  ions [60], as shown by the dashed lines. This function describes the expected nature of  $\text{Mn}^{2+}$  ions when in a purely paramagnetic state. In the paramagnetic regime, the analytical approximations of  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  are roughly equivalent, therefore to simplify the analysis only one magnetic ion has been used. This function compares with the data reasonably well, however, the associated paramagnetic moment at  $Q = 0 \text{ \AA}^{-1}$  is  $\mu_{\text{eff}} = 4.45\mu_{\text{B}}$  which is a little low when compared to the expected  $\mu_{\text{eff}} = 5.41\mu_{\text{B}}$ . This can occur when there is some additional inelastic scattering at energies outside the integration window of D7, which may be attributed to persistent critical fluctuations that extend beyond 20 meV, similar to those found in  $\text{FePS}_3$  [61]. The noticeable deviation between the function and data, particularly at low  $Q$ , indicates that some residual short-range correlations are still present, even at 300 K.

Below 50 K, there are a mixture of broad and sharp features which are reminiscent of the parent compounds,  $\text{MnPS}_3$  and  $\text{FePS}_3$ . For instance, the broad feature centered around  $Q =$

$0.6 \text{ \AA}^{-1}$  is similar to that observed in  $\text{FePS}_3$  [39,62–64]. The magnitude of this feature has little variation below 50 K and therefore suggests that  $\text{FePS}_3$ -type correlations are more or less fully developed above  $T_g$ . Furthermore, the sharp peak at  $Q = 1.2 \text{ \AA}^{-1}$  is similar to that observed in  $\text{MnPS}_3$  [64,65]. This feature continues to evolve with temperature, thus implying that  $\text{MnPS}_3$ -type correlations are still developing below  $T_g$ . These data were fit using the SPINVERT program. A box size of  $12 \times 12 \times 12$  unit cells were constructed with the moments constrained to lie either parallel or antiparallel to the  $c^*$  axis. The resultant reverse Monte Carlo (RMC) fits are shown in Fig. 3(b) by the solid lines. The assumption that moments lie along the  $c^*$  axis is supported by the anisotropy in the paramagnetic susceptibility and the fact that the orientation of ordered moments in the parent compounds align approximately along the  $c^*$  axis. Specifically in  $\text{MnPS}_3$  the moments are canted  $7^\circ$  from the  $c^*$  axis, whereas in  $\text{FePS}_3$  ordered moments lie directly along the  $c^*$  axis [37,38]. The SPINVERT fits compare to the powdered data well, as they maintain a good balance between fitting all the features, both broad and sharp, within the data. The simplicity of this model is particularly appealing, by allowing the moments to lie only collinear to the  $c^*$  axis, we were able to not only model these data well but also extend this to our single-crystal study. Modeling with more complex models, with more free parameters such as larger box sizes or more rotational degrees of freedom for the magnetic moments, did not produce as good results as the ones presented here, as these additional parameters began to fit the statistical noise. We notice some small anomalies to the fit, such as the small peak emerging at  $Q = 0.9 \text{ \AA}^{-1}$  and that the intensity of the sharp peak at  $Q = 1.2 \text{ \AA}^{-1}$  is lower than the measured value, however we are confident in this model as the extracted magnetic moment from SPINVERT,  $\mu_{\text{eff}} = 5.23(8)\mu_{\text{B}}$  [ $S = 2.15(4)$ ] is in good agreement with the expected moment,  $\mu_{\text{eff}} = 5.41\mu_{\text{B}}$  ( $S = 2.25$ ). Additionally, the quality of our later reconstruction of single-crystal data indicates that this model is a reliable estimate of the magnetic diffuse scattering of  $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$ .

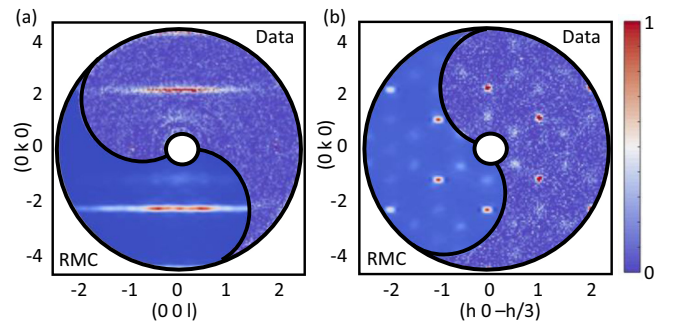


FIG. 5. Magnetic component of single-crystal neutron scattering data measured at 1.5 K compared against the RMC SPINVERT model. (a) Data in the  $(0\ 0\ l)$ ,  $(0\ k\ 0)$  plane reveal rodlike structures that reflect the two-dimensionality of  $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$  and (b) data in the  $(h\ 0\ -h/3)$  plane, which is orthogonal to the plane in part (a), shows strong magnetic intensity at nuclear Bragg peak positions. The intensity of these data have been normalized to the maximum of the measured intensity as given by the color bar.

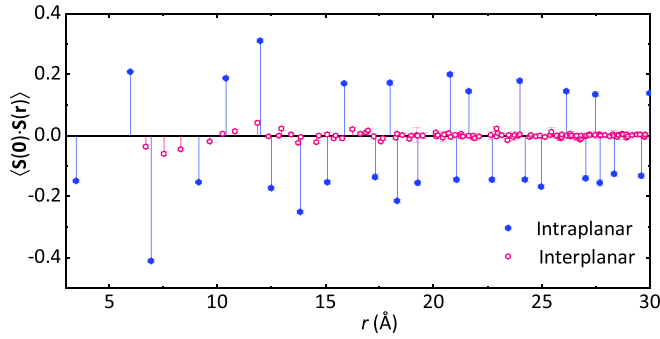


FIG. 6. Normalized spin-spin correlation function  $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$  values for increasing interatomic distances at 1.5 K. Correlations have been separated into intra- and interplanar by blue and pink markers respectively.

Figure 5 shows the measured single-crystal data from D7 at 1.5 K. Figure 5(a) shows rodlike scattering parallel to the  $c^*$  axis. These observations coincide with the main feature in our low-temperature powder data, the sharp peak at  $Q = 1.2 \text{ \AA}^{-1}$ . Both of these features are synonymous with two-dimensional structures and thus reflect the two-dimensional nature of  $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$ . When the  $c^*$  axis is normal to the scattering plane, as in Fig. 5(b), we observe strong magnetic intensity, approximately  $60^\circ$  apart, which correspond to the expected magnetic Bragg positions for ordered  $\text{MnPS}_3$  [38]. Additional magnetic Bragg spots are observed at low temperatures, with the same sixfold rotation, but their intensity is weaker. Single-crystal diffraction patterns were produced from fits of our powder data by the SCATTY program. A comparison between the experimental data and scattering predicted from the RMC fits is shown in Fig. 5, the good agreement indicates that the fit results will give a reliable estimate of the spin correlations in  $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$ .

#### D. Spin correlations

The radial spin correlation functions,  $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$ , were calculated by SPINCORREL, where  $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$  is the scalar product of a normalized spin with its neighbor at a vector separation,  $\mathbf{r}$  [57]. The function  $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$  is normalized to

equal +1 if all the neighbors at a distance  $\mathbf{r}$  are ferromagnetically coupled, and equal to  $-1$  if all the neighbors are antiferromagnetically coupled. Figure 6 shows  $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$  at 1.5 K split between intra- and interplanar correlations by blue and pink markers respectively.

Figure 7(a) shows the magnitude,  $|\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle|$ , of the intraplanar correlations where two trends are apparent. The first set of correlations, highlighted by the orange markers, are approximately constant as a function of interatomic spacing,  $\mathbf{r}$ . The second, shown by the blue markers, decrease in magnitude with increasing  $\mathbf{r}$ . These two distinct trends in the data were analysed using two different functions. The orange points were averaged out to give a constant,  $|\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle| = A$ , and the blue markers were fit with an exponential function,  $|\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle| = \exp(-\frac{r}{\xi}) + A$ , where  $\xi$  is the characteristic spin-spin correlation length ( $\text{\AA}$ ). The fits for the 1.5 K data are shown in Fig. 7(a). Intraplanar correlations were found to be temperature dependent, and the fit values of  $\xi$  and  $A$  as a function of temperature are shown in Figs. 7(b) and 7(c), respectively.

Figure 7(d) shows the magnitude of the interplanar correlations for those neighbors closest to the  $c^*$  axis, that is the nearest neighbors between parallel planes. The magnitude of these correlations showed no noticeable change with temperature. These correlations are very weak, only the first nearest-neighbor, at  $\mathbf{r} = 6.71 \text{ \AA}$ , has a magnitude significantly greater than zero and that is small at  $|\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle| = 0.035$ . This weak interaction between adjacent planes reflects the two-dimensional nature of  $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$ .

#### IV. DISCUSSION

One plausible explanation as to why these two trends exist in Fig. 7(a) can be understood by considering the magnetic structures of  $\text{MnPS}_3$  and  $\text{FePS}_3$ . In  $\text{MnPS}_3$ , all the nearest-neighbor interactions within the  $ab$  planes are antiferromagnetic, whereas in  $\text{FePS}_3$ , there are two ferromagnetic neighbors and one antiferromagnetic neighbor. This is illustrated in Figs. 8(a) and 8(b) for  $\text{MnPS}_3$  and  $\text{FePS}_3$  respectively, where closed circles represent a spin-up orientation and open circles represent a spin-down orientation of the magnetic moments

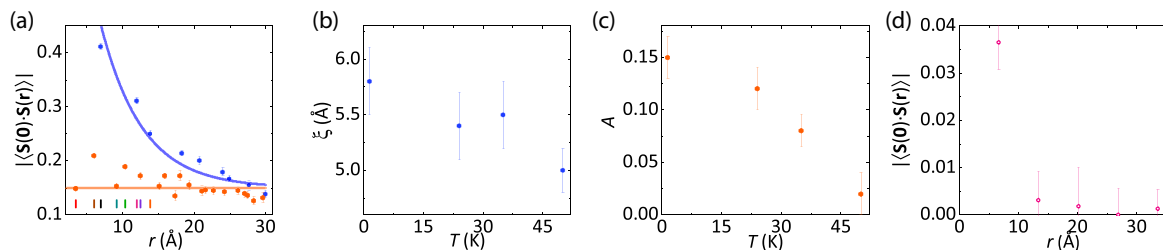


FIG. 7. (a) Magnitude of intraplanar correlations,  $|\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle|$  at 1.5 K. Blue markers highlight correlations that decrease in magnitude with increasing  $\mathbf{r}$  and orange markers highlight correlations that remain roughly constant in magnitude with increasing separation. These data have been fit with an exponential and linear function as shown by the blue and orange lines respectively. The first eight correlations have an associated colored tickmark which links to a corresponding arrow in Fig. 8. (b) Extracted correlation length,  $\xi$ , from the exponential fit as a function of temperature is roughly constant below  $T_g$ . (c) Linear fits,  $|\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle| = A$ , as a function of temperature decrease in magnitude with increasing temperature, becoming zero above  $T_g$ . (d) Magnitude of interplanar correlations,  $|\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle|$ , lying closest to the  $c^*$  axis at 1.5 K. Measurable intensity is only observed between the first set of adjacent planes.

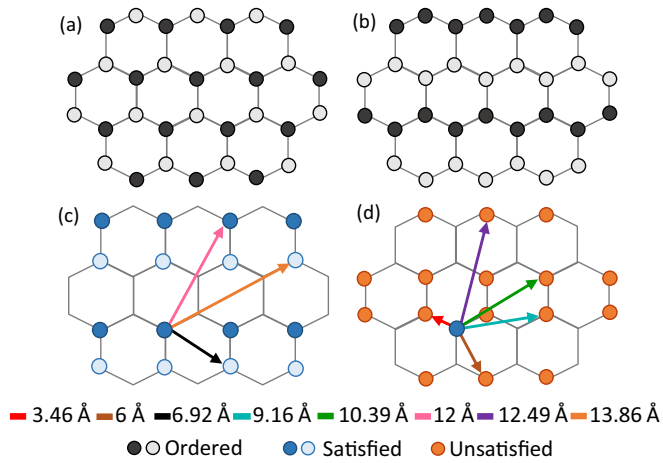


FIG. 8. In-plane magnetic structures of (a)  $\text{MnPS}_3$  and (b)  $\text{FePS}_3$  have conventional long-ranged ordered states. Spin up and spin down moments in these antiferromagnetic structures are indicated by closed and open circles respectively. (c) Common orientations of magnetic moments between  $\text{MnPS}_3$  and  $\text{FePS}_3$  are present in the mixed  $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$ , and the correlations between these moments have been considered as satisfied. (d) All other moment orientations are competing between the two structures, and so the correlations between these moments have been regarded as unsatisfied. The first eight distances have been plotted from an arbitrary point, where the color of the arrow links to a corresponding tickmark in Fig. 7(a).

within the magnetic structures. Despite the differences in the magnetic structures, there are certain magnetic moment orientations that are the same, for which the underlying correlations must be similar. These correlations can thus be considered as satisfied and are illustrated in Fig. 8(c). Each satisfied correlation gives rise to a defined spin orientation between pairs of magnetic moments, just like in a conventionally ordered magnetic ground state, as shown by the open and closed blue circles. The remaining correlations are competing, and therefore unsatisfied, which are represented by the orange circles in Fig. 8(d). Figures 8(c) and 8(d) show the first eight correlations as given by SPINCORREL plotted from an arbitrary site, where it can be seen that these correlations fall into the two aforementioned groups. Some correlations could fit into either group, such as the shortest interatomic distance,  $r = 3.46 \text{ \AA}$ , which has three neighbors. Of the three, one correlation is satisfied and the other two are unsatisfied. All neighbors at the distances marked in Fig. 8(c) have solely satisfied correlations. If any neighbor in a group of equivalent distances has an unsatisfied interaction then it has been assigned to the unsatisfied group in Fig. 8(d), regardless of how many satisfied correlations that distance may have. Therefore the correlation occurring at  $r = 3.46 \text{ \AA}$  has been assigned to the unsatisfied group. These groups are in perfect agreement when compared back to the observed trends in Fig. 7(a). To illustrate this, we have related the color of tickmark for the first eight correlations in Fig. 7(a) with its corresponding arrow in Fig. 8.

The average correlation length between satisfied moments is approximately constant below the freezing temperature as shown in Fig. 7(b). The average correlation length of

these correlations,  $\xi = 5.5(6) \text{ \AA}$  is relatively small, as it does not even stretch one unit cell across in the honeycomb. So although there is some short-ranged magnetic order present, ordered interactions within the plane can only be considered between the very closest neighboring ions, and long-ranged magnetic order does not develop across the honeycomb network. In Fig. 7(c), we observe that the dropoff of  $A$  is more pronounced with increasing temperature, becoming approximately zero just above  $T_g$ . We can therefore relate that the unsatisfied moments give rise to the glassy behavior of  $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$  and observe that they reach a local level of ordering with continued cooling.

To summarize, the correlations can be separated into three groups. The first, interplanar correlations, are very weak, verifying the two-dimensional character of the compound. The intraplanar correlations may be separated into two sub-groups: satisfied correlations, between moments that have the same orientations for all equivalent distances in both the  $\text{MnPS}_3$  and  $\text{FePS}_3$  structures; and unsatisfied correlations, where moments at equivalent distances have at least one pair that differ between the two structures. The unsatisfied correlations are approximately constant with distance and are temperature-dependent, falling to zero above  $T_g$ . The satisfied correlations decrease exponentially with distance, having a characteristic length that is much less temperature-dependent and that persists above the glass temperature.

## V. CONCLUSION

In conclusion, we have presented high-resolution powder neutron diffraction, DC magnetic susceptibility and magnetic diffuse scattering data for the two-dimensional honeycomb spin glass,  $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$ . We have confirmed that no short- or long-ranged nuclear ordering is present within the honeycomb layers from the random distribution of  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  ions. Neutrons were the ideal tool for determining this, as the difference in neutron scattering lengths of  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  provided a clear contrast, which is not resolvable in other methods, like x-ray diffraction. The presence of the spin glass phase has been validated through DC magnetic susceptibility measurements, through the observation of a characteristic sharp cusp at the glass transition. In modeling and interpreting our magnetic diffuse scattering data we have relied upon the nature of the magnetic structure of the parent compounds,  $\text{MnPS}_3$  and  $\text{FePS}_3$ . Whilst the differences produced unsatisfied interactions that cause glassy behavior, similarities were found to be responsible for some local magnetic ordering, both of which are required to understand two emergent trends in the data collected. We confirmed this model through the excellent agreement with measured single-crystal data. We have found that  $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{PS}_3$  is an near-ideal example of a two-dimensional magnetic material through observing rodlike structures in single-crystal data and determining that interactions between the planes were very weak in our analysis of the spin correlations.

Raw data sets from ILL experiments can be accessed via links provided in Refs. [49,53]. Magnetization data presented in this paper resulting from the UK effort will be made available in Ref. [66].

## ACKNOWLEDGMENTS

J.N.G. and L.C. acknowledge the ILL Graduate School and the EPSRC (DTP) for providing a studentship to J.N.G. This project has received funding from the European Research Council (ERC) under the European Unions Horizon 2020 research and innovation programme (Grant Agreement No. 681260). This work was supported by the Institute for Basic

Science (IBS) in Korea (Grant No. IBS-R009-G1). Work at CQM was supported by the Leading Researcher Program of the National Research Foundation of Korea (Grant No. 2020R1A3B2079375). The authors would like to thank Joe Paddison, Paul Goddard, Siân Dutton, Charles Haines, David Jarvis, Cheng Liu, Siddharth Saxena, Inho Hwang, JungHyun Kim, and Nahyun Lee for their help and useful discussions.

- 
- [1] Q. Tang and Z. Zhou, *Prog. Mater. Sci.* **58**, 1244 (2013).
- [2] F. Wang, T. A. Shifa, P. Yu, P. He, Y. Liu, F. Wang, Z. Wang, X. Zhan, X. Lou, F. Xia, and J. He, *Adv. Funct. Mater.* **28**, 1802151 (2018).
- [3] J. S. Ponraj, Z.-Q. Xu, S. C. Dhanabalan, H. Mu, Y. Wang, J. Yuan, P. Li, S. Thakur, M. Ashrafi, K. Mccoubrey, Y. Zhang, S. Li, H. Zhang, and Q. Bao, *Nanotechnology* **27**, 462001 (2016).
- [4] K. F. Mak and J. Shan, *Nat. Photonics* **10**, 216 (2016).
- [5] A. Kumar and Q. Xu, *ChemNanoMat.* **4**, 28 (2018).
- [6] K. S. Burch, D. Mandrus, and J.-G. Park, *Nature (London)* **563**, 47 (2018).
- [7] J.-G. Park, *J. Phys. Condens. Matter* **28**, 301001 (2016).
- [8] D. A. Dikin, M. Mehta, C. W. Bark, C. M. Folkman, C. B. Eom, and V. Chandrasekhar, *Phys. Rev. Lett.* **107**, 056802 (2011).
- [9] C. Gong, L. Li, Z. Li, H. Ji, A. Stern, Y. Xia, T. Cao, W. Bao, C. Wang, Y. Wang, Z. Q. Qiu, R. J. Cava, S. G. Louie, J. Xia, and X. Zhang, *Nature (London)* **546**, 265 (2017).
- [10] H. Wang, F. Fan, S. Zhu, and H. Wu, *Europhys. Lett.* **114**, 47001 (2016).
- [11] B. Huang, G. Clark, D. R. Klein, D. MacNeill, E. Navarro-Moratalla, K. L. Seyler, N. Wilson, M. A. McGuire, D. H. Cobden, D. Xiao, W. Yao, P. Jarillo-Herrero, and X. Xu, *Nat. Nanotechnol.* **13**, 544 (2018).
- [12] M. J. Coak, D. M. Jarvis, H. Hamidov, C. R. S. Haines, P. L. Alireza, C. Liu, S. Son, I. Hwang, G. I. Lampronti, D. Daisenberger, P. Nahai-Williamson, A. R. Wildes, S. S. Saxena, and J.-G. Park, *J. Phys.: Condens. Matter* **32**, 124003 (2020).
- [13] 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, *Phys. Rev. Lett.* **121**, 266801 (2018).
- [14] L. Balents, *Nature (London)* **464**, 199 (2010).
- [15] L. Savary and L. Balents, *Rep. Prog. Phys.* **80**, 016502 (2017).
- [16] A. Kitaev, *Ann. Phys.* **321**, 2 (2006).
- [17] M. Hermanns, I. Kimchi, and J. Knolle, *Annu. Rev. Condens. Matter Phys.* **9**, 17 (2018).
- [18] A. Banerjee, C. A. Bridges, J. Q. Yan, A. A. Aczel, L. Li, M. B. Stone, G. E. Granroth, M. D. Lumsden, Y. Yiu, J. Knolle, S. Bhattacharjee, D. L. Kovrizhin, R. Moessner, D. A. Tennant, D. G. Mandrus, and S. E. Nagler, *Nat. Mater.* **15**, 733 (2016).
- [19] H.-S. Kim, V. Vijay Shankar, A. Catuneanu, and H.-Y. Kee, *Phys. Rev. B* **91**, 241110(R) (2015).
- [20] J. A. Sears, M. Songvilay, K. W. Plumb, J. P. Clancy, Y. Qiu, Y. Zhao, D. Parshall, and Y.-J. Kim, *Phys. Rev. B* **91**, 144420 (2015).
- [21] L. J. Sandilands, Y. Tian, A. A. Reijnders, H.-S. Kim, K. W. Plumb, Y.-J. Kim, H.-Y. Kee, and K. S. Burch, *Phys. Rev. B* **93**, 075144 (2016).
- [22] S. C. Williams, R. D. Johnson, F. Freund, S. Choi, A. Jesche, I. Kimchi, S. Manni, A. Bombardi, P. Manuel, P. Gegenwart, and R. Coldea, *Phys. Rev. B* **93**, 195158 (2016).
- [23] F. Ye, S. Chi, H. Cao, B. C. Chakoumakos, J. A. Fernandez-Baca, R. Custelcean, T. F. Qi, O. B. Korneta, and G. Cao, *Phys. Rev. B* **85**, 180403(R) (2012).
- [24] X. Liu, T. Berlijn, W.-G. Yin, W. Ku, A. Tsvelik, Y.-J. Kim, H. Gretarsson, Y. Singh, P. Gegenwart, and J. P. Hill, *Phys. Rev. B* **83**, 220403(R) (2011).
- [25] M. Alaei, H. Mosadeq, I. A. Sarsari, and F. Shahbazi, *Phys. Rev. B* **96**, 140404(R) (2017).
- [26] N. Onishi, K. Oka, M. Azuma, Y. Shimakawa, Y. Motome, T. Taniguchi, M. Hiraishi, M. Miyazaki, T. Masuda, A. Koda, K. M. Kojima, and R. Kadono, *Phys. Rev. B* **85**, 184412 (2012).
- [27] M. Matsuda, M. Azuma, M. Tokunaga, Y. Shimakawa, and N. Kumada, *Phys. Rev. Lett.* **105**, 187201 (2010).
- [28] S. Okumura, H. Kawamura, T. Okubo, and Y. Motome, *J. Phys. Soc. Jpn.* **79**, 114705 (2010).
- [29] K. Momma and F. Izumi, *J. Appl. Crystallogr.* **44**, 1272 (2011).
- [30] G. Ouvrard, R. Brec, and J. Rouxel, *Mater. Res. Bull.* **20**, 1181 (1985).
- [31] R. Brec, D. M. Schleich, G. Ouvrard, A. Louisy, and J. Rouxel, *Inorg. Chem.* **18**, 1814 (1979).
- [32] P. J. Foot, T. Katz, S. N. Patel, B. A. Nevet, A. R. Piecny, and A. A. Balchin, *Phys. Status Solidi A* **100**, 11 (1987).
- [33] L. Silipigni, L. Schirò, T. Quattrone, V. Grasso, G. Salvato, L. Monsù Scolaro, and G. De Luca, *J. Appl. Phys.* **105**, 123703 (2009).
- [34] 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, *Sci. Rep.* **6**, 20904 (2016).
- [35] S. Lee, K.-Y. Choi, S. Lee, B. H. Park, and J.-G. Park, *APL Mater.* **4**, 086108 (2016).
- [36] P. A. Joy and S. Vasudevan, *Phys. Rev. B* **46**, 5134 (1992).
- [37] M. A. Susner, M. Chyasnavichyus, M. A. McGuire, P. Ganesh, and P. Maksymovych, *Adv. Mater.* **29**, 1602852 (2017).
- [38] E. Ressouche, M. Loire, V. Simonet, R. Ballou, A. Stunault, and A. Wildes, *Phys. Rev. B* **82**, 100408(R) (2010).
- [39] D. Lançon, H. C. Walker, E. Ressouche, B. Ouladdiaf, K. C. Rule, G. J. McIntyre, T. J. Hicks, H. M. Rønnow, and A. R. Wildes, *Phys. Rev. B* **94**, 214407 (2016).
- [40] C. Murayama, M. Okabe, D. Urushihara, T. Asaka, K. Fukuda, M. Isobe, K. Yamamoto, and Y. Matsushita, *J. Appl. Phys.* **120**, 142114 (2016).
- [41] A. R. Wildes, B. Roessli, B. Lebech, and K. W. Godfrey, *J. Phys. Condens.* **10**, 6417 (1998).
- [42] K. Kurosawa, S. Saito, and Y. Yamaguchi, *J. Phys. Soc. Jpn.* **52**, 3919 (1983).



- [43] T. Masubuchi, H. Hoya, T. Watanabe, Y. Takahashi, S. Ban, N. Ohkubo, K. Takase, and Y. Takano, *J. Alloys Compd.* **460**, 668 (2008).
- [44] V. Manríquez, P. Barahona, and O. Peña, *Mater. Res. Bull.* **35**, 1889 (2000).
- [45] Y. He, Y. D. Dai, H. Huang, J. Lin, and Y. Hsia, *J. Alloys Compd.* **359**, 41 (2003).
- [46] Y. Takano, A. Arai, Y. Takahashi, K. Takase, and K. Sekizawa, *J. Appl. Phys.* **93**, 8197 (2003).
- [47] A. Bhutani, J. L. Zuo, R. D. McAuliffe, C. R. dela Cruz, and D. P. Shoemaker, *Phys. Rev. Materials* **4**, 34411 (2020).
- [48] A. W. Hewat, *Mater. Sci. Forum* **9**, 69 (1986).
- [49] A. R. Wildes and E. Suard, ILL experiment EASY-541 (2019), <https://doi.ill.fr/10.5291/ILL-DATA.EASY-541>.
- [50] B. Toby and R. B. Von Dreele, *J. Appl. Crystallogr.* **46**, 544 (2013).
- [51] A. R. Wildes, V. Simonet, E. Ressouche, G. J. McIntyre, M. Avdeev, E. Suard, S. A. J. Kimber, D. Lançon, G. Pepe, B. Moubaraki, and T. J. Hicks, *Phys. Rev. B* **92**, 224408 (2015).
- [52] J. R. Stewart, P. P. Deen, K. H. Andersen, H. Schober, J.-F. Barthélémy, J. M. Hillier, A. P. Murani, T. Hayes, and B. Lindenau, *J. Appl. Crystallogr.* **42**, 69 (2009).
- [53] A. R. Wildes, M. J. Coak, J. N. Graham, and S. S. Saxena, ILL experiment 5-32-870 (2019), <https://doi.ill.fr/10.5291/ILL-DATA.5-32-870>.
- [54] W. Schweika, *Journal of Physics: Conference Series* **211**, 012026 (2010).
- [55] J. Rodríguez-Carvajal, *Physica B* **192**, 55 (1993).
- [56] J. A. M. Paddison and A. L. Goodwin, *Phys. Rev. Lett.* **108**, 017204 (2012).
- [57] J. A. M. Paddison, J. R. Stewart, and A. L. Goodwin, *J. Phys. Condens.* **25**, 454220 (2013).
- [58] J. A. M. Paddison, *Acta Crystallogr. Sect. A* **75**, 14 (2019).
- [59] G. A. Bain and J. F. Berry, *J. Chem. Educ.* **85**, 532 (2008).
- [60] P. J. Brown, *Electron and Magnetisation Densities in Molecules and Crystals* (Plenum Press N. Y., 1979) Chap. Magnetic Neutron Scattering.
- [61] A. R. Wildes, K. C. Rule, R. I. Bewley, M. Enderle, and T. J. Hicks, *J. Phys.: Condens. Matter* **24**, 416004 (2012).
- [62] D. J. Goossens, A. J. Studer, S. J. Kennedy, and T. J. Hicks, *J. Phys.: Condens. Matter* **12**, 4233 (2000).
- [63] K. C. Rule, S. J. Kennedy, D. J. Goossens, A. M. Mulders, and T. J. Hicks, *Appl. Phys. A* **74**, s811 (2002).
- [64] K. C. Rule, T. Ersez, S. J. Kennedy, and T. J. Hicks, *Physica B Condens. Matter* **335**, 6 (2003).
- [65] A. R. Wildes, S. J. Kennedy, and T. J. Hicks, *J. Phys.: Condens. Matter* **6**, L335 (1994).
- [66] M. J. Coak, Open access data (2020), <https://wrap.warwick.ac.uk/139402>.