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LETTER TO THE EDITOR

True two-dimensional magnetic ordering in $MnPS_3$

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Abstract. Neutron powder diffraction studies as a function of temperature on $MnPS_3$ have revealed temperature-dependent features inconsistent with the previously quoted magnetic ordering. The features vanish at ~ 12 K, a temperature well above the accepted Néel temperature of 78 K. The features are consistent with a true Ising-like two-dimensional ordering with the moments being antiferromagnetically coupled and pointing along the (010) direction.

Manganese thiophosphate ($MnPS_3$) is reported to be a layered quasi-two-dimensional Heisenberg-like antiferromagnet. Its structure and lattice parameters were first determined by Von Klingen *et al* (1973), and later refined by Ouvrard *et al* (1985). These studies show $MnPS_3$ to have a monoclinic structure of space group $C2/m$, with the manganese atoms forming a honeycomb-like structure in the layer planes (see figure 1(*a*)). The lattice parameters are given by Ouvrard *et al* (1985) as $a = 6.077$ Å, $b = 10.524$ Å, $c = 6.796$ Å, and $\beta = 107.35°$. The quoted magnetic structure, as determined from neutron powder diffraction by Kurosawa *et al* (1983), is antiferromagnetic with the manganese having moments of magnitude $(4.1 \pm 0.3)\mu_B$ pointing perpendicular to the layer planes (see figure 1(*b*)). A small field dependence in the Néel temperature of $dT_N/dH_{ext} \simeq +2.6 \times 10^{-4}$ K G^{-1} at $H_{ext} \simeq 10^4$ G has been measured (Torre and Ziolo 1989), but is unimportant in the context of this work. The Néel temperature at zero field is approximately 78 K.

In the course of experiments on disordered $(Mn_xMg_{1-x})PS_3$, the authors repeated the powder neutron scattering measurements on $MnPS_3$ with greater temperature variation and to a larger scattering vector than Kurosawa *et al* (1983). These measurements appear to reveal a second magnetic structure with a transition temperature of approximately 120 K, the temperature of maximum susceptibility (Okuda *et al* 1986, Joy and Vasudevan 1992).

Samples of $MnPS_3$ were prepared by a vapour deposition technique. Stoichiometric ratios of 99.99% purity manganese, 99.995% purity phosphorus, and 99.99% purity sulphur were sealed in an evacuated quartz tube. A temperature gradient from 690 °C to 700 °C was maintained over the length of the tube for a period of one month with the aid of a horizontal two-zone furnace. The crystals were collected, ground and pressed to give cylindrical pellets. Neutron powder diffraction was carried out on the medium-resolution powder diffractometer (MRPD) at HIFAR, Lucas Heights Research Laboratories (Kennedy and Davis, to be published). Rietveld analysis of room temperature scans confirmed the atomic space group and lattice parameters of Ouvrard *et al* (1985). Temperatures down to 17 K were achievable with the aid of a closed-cycle helium cryorefrigerator.

Powder diffraction scans at $\lambda = 1.664$ Å as a function of temperature in the range $17 \text{ K} \leqslant T \leqslant 165$ K are shown in figure 2. The observed temperature dependence of the Bragg peaks

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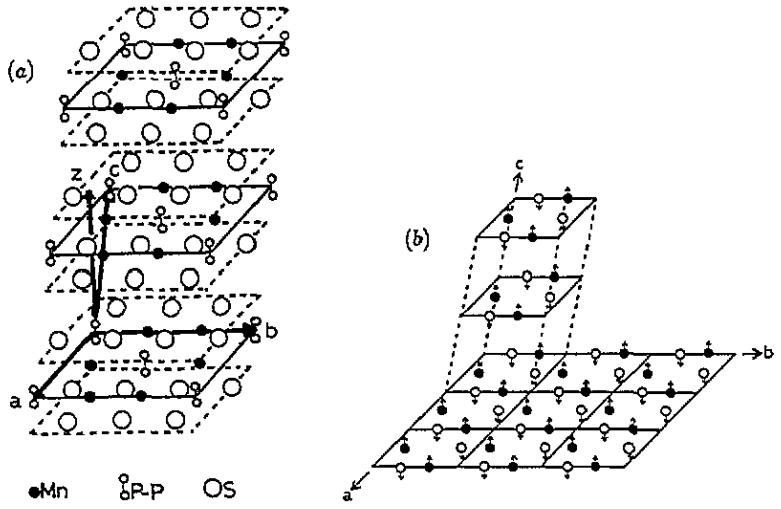

Figure 1. (*a*) Crystal structure of $MnPS_3$. Z is perpendicular to the *ab* plane, and shows the quoted direction of the Mn moments (after Okuda *et al* 1986). (*b*) The quoted magnetic structure of $MnPS_3$. Closed and open circles denote up and down moments, respectively (after Okuda *et al* 1986).

appears to correspond well to the quoted magnetic structure, showing an antiferromagnetic contribution that vanishes at $T \simeq 80$ K. From fitting Gaussian profiles to these peaks the magnetic moment for Mn is calculated to be $(4.5 \pm 1)\mu_B$, which agrees well with the value of Kurosawa *et al* (1983).

The structure factor of the quoted antiferromagnetic structure, F_M, is given by

$$F_M \simeq \mu_\perp 4\mathrm{i} \sin\left(\frac{2\pi}{3}k\right)$$

where k is a Miller index and $\mu_\perp$ is the component of the moment perpendicular to the scattering vector. The above structure factor is calculated assuming that the fractional atomic coordinates for Mn are approximately $(0, \frac{1}{3}, 0)$. Thus, magnetic Bragg reflections of the type $(h\ 3nk\ l)$, with n integral, are forbidden. Kurosawa *et al* (1983) justify the direction of the ordered moments below 78 K as perpendicular to the layer planes (i.e. the (001) direction) by pointing out that there are no $(00l)$ reflections. This is obviously an invalid argument, as according equation (1) the magnetic structure factor for $(00l)$ reflections is zero and therefore there can be no $(00l)$ reflections. However, the quoted moment direction appears justified as measurements using other techniques (e.g. susceptibility (Joy and Vasudevan 1992, Okuda *et al* 1986), and our own susceptibility measurements) appear to confirm the moment direction proposed by Kurosawa *et al* (1983).

In addition to the Bragg peaks from the quoted magnetic structure, a distinct temperature variation in a peak at large angle ($2\theta \approx 66°$) was observed. This peak corresponds to an overlap of four Bragg peaks: (i) $(33\bar{3})$; (ii) (331); and (iii) (062), and appears to undergo a phase transition at 120 K. This peak not only has a transition temperature different to the quoted Néel temperature, but by examination of equation (1) it also has a magnetic structure factor equal to zero. A subtraction of the scattering at 165 K from the scattering at 100 K reveals additional peaks at lower angle that have been attributed to the presence of a second magnetic phase, and is shown in figure 3.

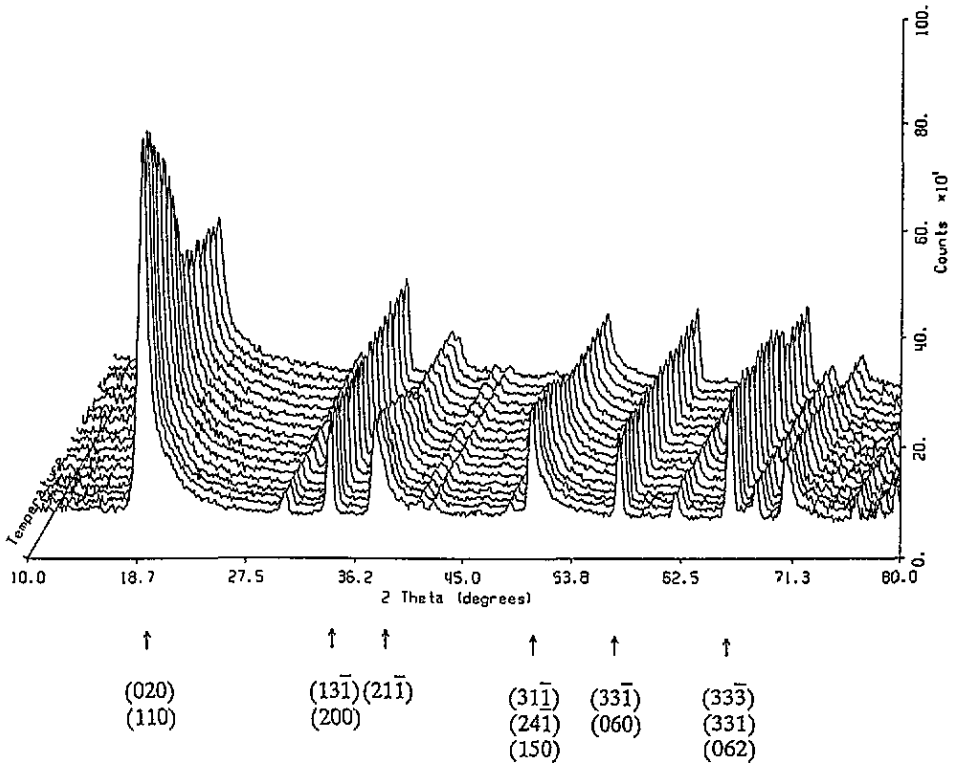

Figure 2. Neutron powder diffraction scans of $MnPS_3$ at 1.66 Å as a function of temperature. Some important peaks are labelled. The nearest scan was measured at 17 K. The scans are then increasing in temperature to the furthest scan, measured at 165 K.

Figure 3 shows a relatively strong broad peak under the first magnetic Bragg peak (i.e. (020), (110)). Similar peaks can also be seen at (21$\bar{1}$), and the (31$\bar{1}$), (24$\bar{1}$), and (150) positions. To confirm the presence of a second magnetic phase, this peak was fitted at the different temperatures with a combination of Gaussians—one narrow to reflect the quoted three-dimensional antiferromagnetic phase, and one broad to reflect the newly discovered peak. The integrated intensities of these Gaussians are shown in figure 4.

The temperature dependences of the two peaks are obviously different. As expected, the integrated intensity of the narrow Gaussian firstly reduces with temperature and then becomes stable above 78 K, the Néel temperature of the quoted magnetic structure. The broad Gaussian, however, does not reduce and stabilize until ~120 K. This is strong evidence of a second magnetic phase in $MnPS_3$ with a phase transition temperature of ~ 120 K.

Previous authors (Joy and Vasudevan 1992, Okuda *et al* 1986) have discovered that $MnPS_3$ has a small Ising or single-ion anisotropy within the layer planes, and this suggests that the second magnetic phase is a 2D Ising-type order. In reciprocal space a true two-dimensional lattice becomes a lattice of rods, and these would take the form of *Bragg rods* in a neutron diffraction pattern. The lineshape of a peak produced from a powdered sample of a two-dimensional lattice would be far more complex than a simple Gaussian. The random orientation of the crystallites in a powder is reflected in reciprocal space in the rods. This means that the lineshape would be spread in scattering vector, and as the scattered intensity depends on the length and overlap of the rods, the peaks will be asymmetric.

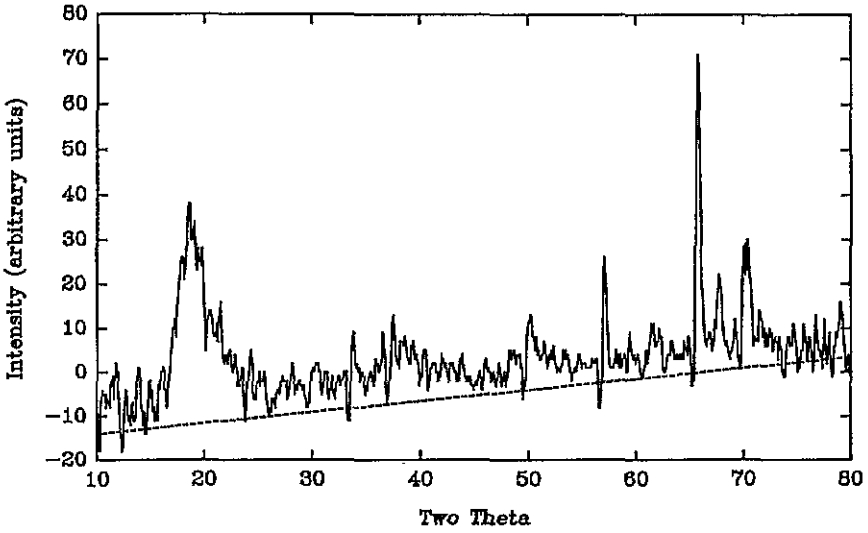

Figure 3. A plot showing the subtraction of the scan of $MnPS_3$ at 165 K from the scan at 100 K. The dotted line is a guide to the eye, to assist in the observation of the broad features at $2\theta \approx 20°$, 37° and 52°. The data have been three-point averaged.

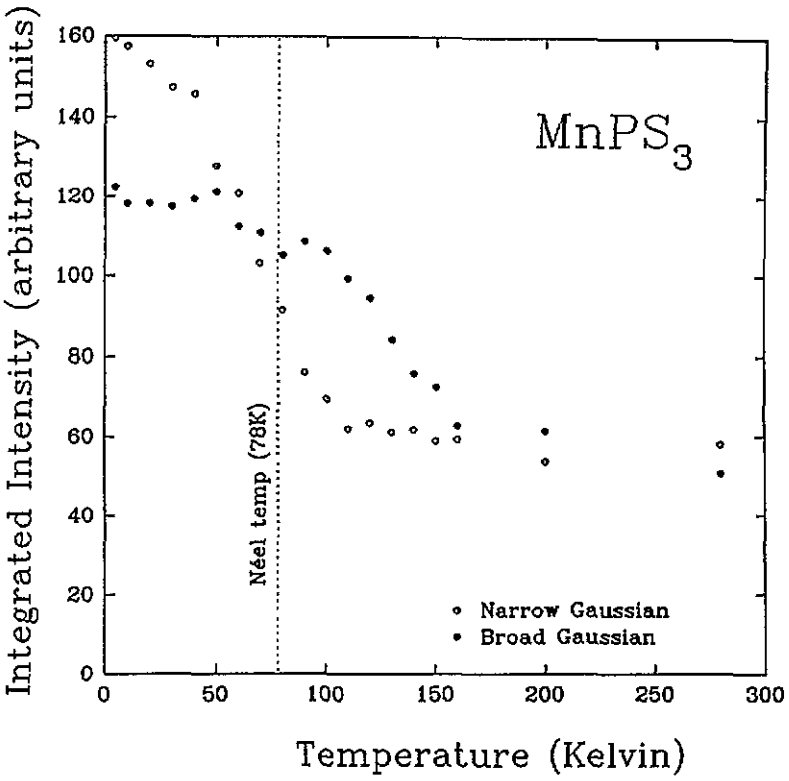

Figure 4. A comparison of the integrated intensities of the narrow and broad Gaussians fitted to the first magnetic Bragg peak of $MnPS_3$ as a function of temperature.

Such lineshapes can be calculated using the theory of Schildberg and Lauter (1989). These authors have presented an algorithm that will give the correct powder lineshape that also accounts for preferred orientation, which is a problem in the scattering from $MnPS_3$ due to the platelet-like nature of the crystals.

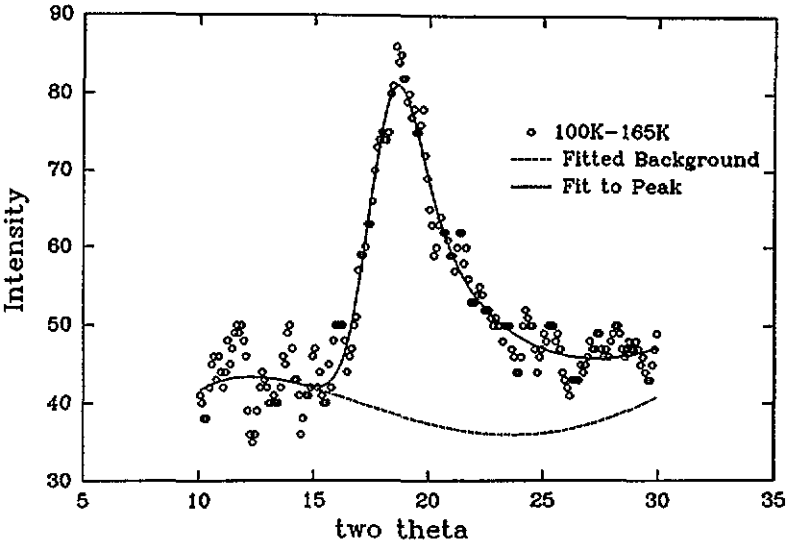

Figure 5. A fit of the lineshape for a 2D powder sample, as given by Schildberg and Lauter (1989), to the first broad peak in figure 3. The background is fitted with a polynomial. The intensity is in arbitrary units.

Lineshapes calculated using the method of Schildberg and Lauter (1989) match well with the observed scattering seen at low angle in the subtraction plots (see figure 5). The Bragg *rods* were assumed to have a Gaussian profile. The width of this profile was fitted to the data, and a typical value for this width was 0.09 $Å^{-1}$. The fact that the *peak* has a much broader width than 0.09 $Å^{-1}$ is due to the length and overlap of the randomly oriented Bragg rods in the powder pattern.

The broad peaks seen in figure 3 are the same positions as the magnetic Bragg peaks resulting from the quoted magnetic structure. This suggests that the moments in the 2D structure are arranged in the same way as the moments in the quoted structure, with each moment being antiferromagnetically coupled to its nearest neighbours within the plane. However, the moment direction in the quoted structure is not necessarily preserved in the 2D structure. Examination of figure 3 shows that the positions of the broad peaks correspond well to the positions of the first three 2D magnetic Bragg peaks: (02) and (11); (04) and (22); and (31), (24) and (15).

A moment direction was determined by comparing the relative heights of the broad peaks in figure 3 with calculated lineshapes. Magnetic contributions were assumed to be solely due to the manganese atoms, and the 2D antiferromagnetic order was assumed to be purely within the planes. This latter assumption is consistent with the findings of Okuda *et al* (1986) who found a single-ion anisotropy within the layer planes. The calculated peak height ratios matched the observed ratios assuming moments in the (010) direction. This direction points to the nearest-neighbour manganese atom—an encouraging result.

It was hoped that a moment magnitude could be determined by fitting the first magnetic Bragg peak with a combination of Gaussians and 2D lineshapes as calculated from the method of Schildberg and Lauter (1989). Unfortunately, due to the nature of the Bragg peak, extraction of the moment magnitude proved to be an extremely difficult exercise. The first magnetic Bragg peak is a conglomeration of many contributions: (i) the (020), (110), and (11$\bar{1}$) nuclear peaks (that also have a magnetic contribution); (ii) the hypothesized (02) and (11) 2D magnetic peak; and as the temperature increases beyond the 120 K transition (iii) a Lorentzian-type 2D short-range order peak that would decrease with increasing temperature. The contributions due to (020) and (110) are easy to extract as they are 3D Bragg peaks of considerable intensity and well defined in κ; hence the calculation above giving the Mn moment in the quoted magnetic structure as $4.5\mu_B$ is valid. The 2D peak, however, is spread over a wide range of κ that includes the (11$\bar{1}$) peak and hence an unambiguous fit to the broad tail on the first magnetic Bragg peak is not possible.

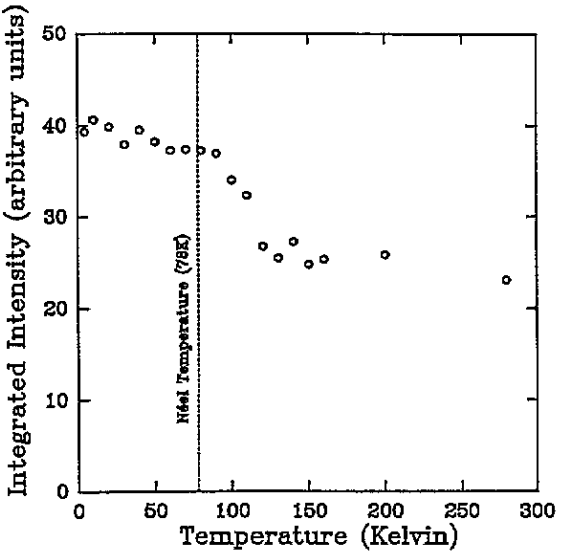

Figure 6. The temperature variation of the peak composed of (33$\bar{3}$), (331), (062), and (06$\bar{2}$), calculated from the integrated intensities of fitted Gaussians.

Figure 6 shows the integrated intensities of fitted Gaussians to the peak at the (33$\bar{3}$) position. This peak has the same temperature dependence as the broad peaks. It has, however, an entirely different shape to the broad peaks, and according to equation (1) it has a magnetic structure factor equal to zero. The temperature dependence of this peak may be due to a dynamic relaxation in the lattice and the subsequent effect on the Debye–Waller factor as the magnetic phase transition occurs. It should be noted that the Mn atoms have maximum contribution to the nuclear structure factor of this peak for the same reason that the magnetic structure factor is zero. Other high-angle peaks show a similar anomaly at 120 K. Unfortunately, no direct measurements exist to prove this hypothesis, although published results on Raman scattering at room temperture (Mathey *et al* 1979) and calculated phonon dispersion curves (Bernasconi *et al* 1988) will form the basis of such a study.

In conclusion, in addition to the established order, a new magnetic order with a transition temperature of $\sim$ 120 K has been discovered by the presence of broad Bragg peaks in neutron

powder diffraction experiments. This order is attributed to an Ising-like anisotropy that causes a two-dimensional antiferromagnetic order. The moment direction was determined to be in the (010) direction, while the moment magnitude proved to be too difficult to determine. The moment direction is in agreement with the findings of Okuda *et al* (1986), who, on the basis of electron spin resonance (EPR) experiments, reported a single-ion anisotropy that would cause the Mn spins to lie in the *ab* plane. The anisotropy would appear to be weak, and it is expected that even weak fields would destroy the order. This would account for the susceptibility measurements, which show no antiferromagnetic characteristics above 80 K. Even so, the susceptibility peaks at $T \approx 120$ K (see Joy and Vasudevan 1992). This is the transition temperature of the proposed 2D order, and thus the remnants of the 2D order are observable.

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