

# Interlayer Mn–Mn exchange parameter MnPS<sub>3</sub> from x-ray diffraction data

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Received July 15, 2011, revised December 23, 2011

The interlayer distance in MnPS<sub>3</sub> was measured by x-ray diffraction as a function of the temperature in the vicinity of the Néel point of 78 K. A well detectable magnetic striction of about 0.0185% has been documented. Using the known values of the external-pressure driven compression and reasonable estimates of the range parameter of the separation dependence of the relevant Mn–Mn exchange parameter  $J'$ , we have estimated  $J'$  to be about 1.0 K. From our analysis of the interlayer magnetic coupling, an inference is drawn that the Mn–Mn interlayer exchange can be strongly directional.

PACS: 61.05.cp X-ray diffraction;  
64.70.–p Specific phase transitions;  
75.50.Ee Antiferromagnetics;  
75.80.+q Magnetomechanical effects, magnetostriction.

Keywords: manganese thiophosphate, Mn–Mn ferromagnetic exchange parameter, powder x-ray diffraction, magnetic phase transitions.

## 1. Introduction

As a new candidate for revealing ferrotoroidicity, thiophosphate MnPS<sub>3</sub> again attracts keen interest [1–6]. Although the structure (both positional and magnetic) of MnPS<sub>3</sub> was known [7–10], recently its magnetic structure below the Néel temperature of  $T_N = 78$  K has been studied anew to a higher accuracy [5] and the skew angle of the Mn spins with respect to the  $(a,b)$  plane accurately determined. The magnetic structure in the magnetically ordered state becomes three-dimensional due to the weaker interlayer ferromagnetic coupling. The values of the strong in-plane antiferromagnetic exchange parameter  $J$  do not differ considerably from author to author [1,10–12], varying from 8.1 to 9.5 K. The only exclusion is the value of 19.2 K as evaluated from the high-temperature expansion of the magnetic susceptibility [13]. As to the value of the interlayer ferromagnetic exchange parameter  $J'$ , there is a very large (by more than two orders of magnitude) difference between the relevant estimates: compare 0.015 K (assuming  $z = 2$ ) [12] and 0.022 K [1] with 3.8 K [10].

Our aim was to evaluate the magnitude of the interlayer exchange parameter  $J'$  from diffraction structure data

close to the phase transition point, where a magnetostriction effect can be detectable. A similar approach was employed in studies of magnetostriction in chlorides [14,15].

## 2. Experimental results and discussion

The structure of MnPS<sub>3</sub> is monoclinic, space group  $C2/m$ , with the following room-temperature lattice parameters [9]:  $a = 6.077$  Å;  $b = 10.524$  Å;  $c = 6.796$  Å;  $\beta = 107.35^\circ$ . Traditionally, we will designate as  $c^*$  the axis normal to the  $(a,b)$  plane as well as the respective lattice parameter. The unusual honey-comb motive of the manganese atoms coupled via antiferromagnetic exchange within the  $(a,b)$  plane repeats itself in adjacent manganese-containing layers, the interlayer exchange being of ferromagnetic nature. Part of the overall structure related to the Mn subsystem is depicted in Fig. 1.

To obtain the necessary structure data, we used a standard x-ray powder diffraction machine DRON-3 equipped with a liquid-helium cryostat. Since our main concern was the Mn–Mn interlayer distance as a function of the temperature varying across the phase transition point, we did not collect a complete set of reflections but monitored to a

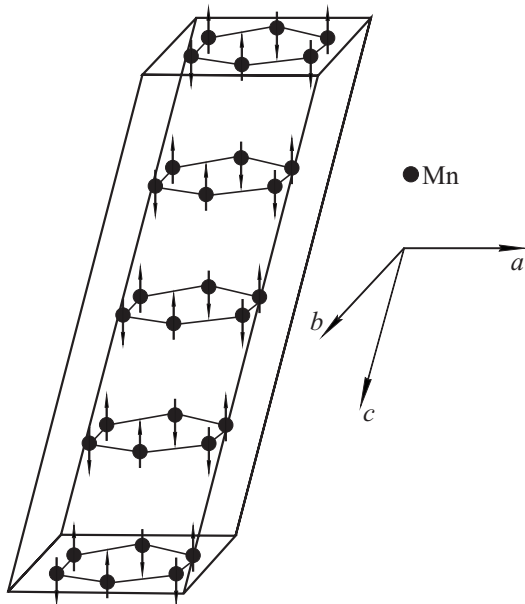


Fig. 1. The structure motive of magnetic ordering of Mn spins in MnPS<sub>3</sub> below the Néel temperature. A small tilt [5] of about 8° of Mn spins respective the *c*\*-axis is not shown.

possibly higher accuracy the 002 reflection from a rather big single crystal with dimensions 5×5×0.1 mm which provides information on the interlayer distance *d*. Our room-temperature value of *c* = (6.795±0.003) Å is in good agreement with the value obtained by Ouvrard *et al.* [9].

In Fig. 2 we show the temperature dependence of the interlayer spacing *d*<sub>002</sub> in the vicinity of the magnetic phase transition. A transition-related spontaneous magnetostriction contraction of about 0.0185% is clearly seen. It should be noted here that the lattice reaction along axis *c* stretches well below the critical point, the separation *d*<sub>002</sub> leveling finally off to its low-temperature value about 30 K below *T<sub>N</sub>*. It should be noted here that, given the nominal absolute error of 2·10<sup>-3</sup> Å was actually by a factor of 2 or 3 smaller because we measured a relative variation of *d*<sub>002</sub>.

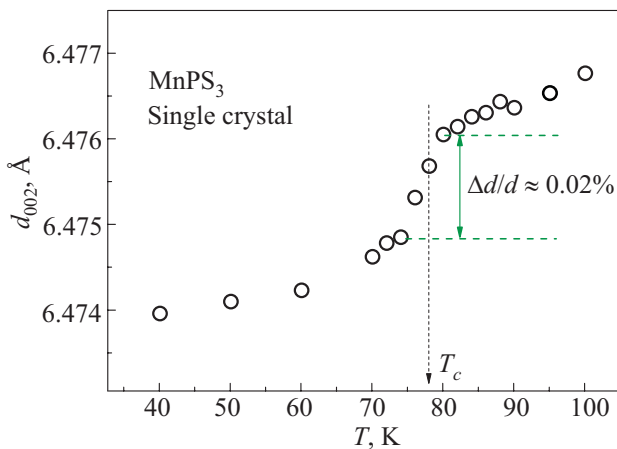


Fig. 2. Temperature dependence of the interplane distance *c*\* = *c* cos(β - π/2).

In Fig. 3 we show the variation of the width of the 002 reflection with temperature. It is quite common that local distortions in samples with a comparatively high concentrations of defects increase in magnitude as an additional ordering due to anisotropic forces sets in.

The total interlayer interaction energy per Mn atom can be represented as a sum of three terms

$$E = E_{el} + E_{pr} + E_{mag}. \quad (1)$$

Here

$$E_{el} = \frac{\epsilon}{2}(c - c_0)^2 \quad (2)$$

is the static elastic energy related with the deviation of the actual lattice parameter *c* (which is the distance between two equivalent Mn positions in adjacent planes) from its equilibrium value *c*<sub>0</sub> just above the transition temperature, assuming that at that point the striction due to the magnetic order is absent or insignificant. If the sample is compressed normal to plane (*a*,*b*) with pressure *P*, the corresponding energy per Mn atom will be

$$E_{pr} = Pcs_0, \quad (3)$$

where *s*<sub>0</sub> is the area per Mn atom within plane (*a*,*b*), which for the actual crystal structure amounts to *s*<sub>0</sub> = *ab*/4. The last term in Eq. (1) is the magnetic energy due to the interlayer ferromagnetic ordering, which in the Heisenberg approximation can be cast in the form

$$E_{mag} = \frac{S(S+1)}{2} \sum_n J'_{0n} \sigma_n. \quad (4)$$

Here *S* = 5/2 is the spin of the manganese atom in the title compound; *J*'<sub>0*n*</sub> is the ferromagnetic part of the exchange energy of two Mn spins, one of which is the “reference” center and the other sits at site *n* in an adjacent layer; σ is the sign function, which is +1 if the two interacting spins are parallel and -1 if they are antiparallel.

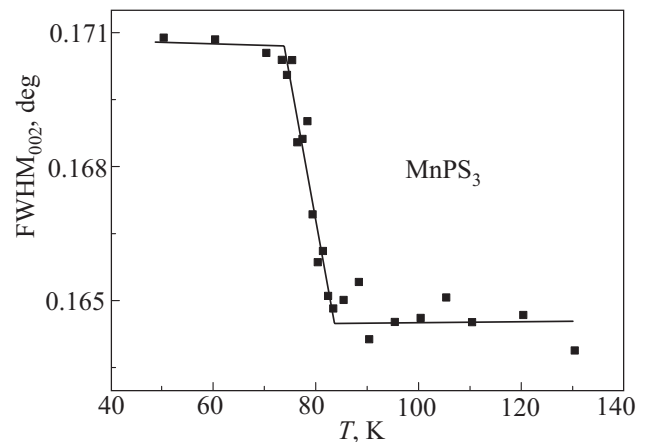


Fig. 3. Temperature dependence of the FWHM of the 002 reflection in the vicinity of the magnetic phase transition.

Now we derive an expression which will allow evaluation of  $J'$ . Making use of the known partial compressibility [3] along axis  $c$ ,  $\chi_c \equiv \partial c / \partial P = -9.8 \cdot 10^{-2}$  Å/GPa, we express the elastic parameter  $\varepsilon$  through observable quantities:

$$\varepsilon = s_0 / \chi_c. \quad (5)$$

To proceed further, we need to approximate  $J'$  as a function of the separation  $c$ . We chose for that purpose an exponential function,  $J' = j_0 \exp(c/\lambda)$  with  $\lambda$  as the range parameter of the ferromagnetic exchange interaction. Since the changes in the values of  $c$  close to and across the transition are small, we could take any other functional form, because the quantity we actually need is the first distance derivative of the exchange parameter. Then the interlayer magnetic energy becomes

$$E_{\text{mag}} = \frac{S(S+1)}{2} j_0 \sum_n \sigma_n \exp(-r_n/\lambda), \quad (6)$$

where  $r_n$  is the distance between the reference Mn atom and its  $n$ th neighbor from one of the two adjacent Mn layers. Since we define  $J'$  as  $j_0 e^{-c/\lambda}$ , we rewrite Eq. (6)

$$E_{\text{mag}} = \frac{S(S+1)}{2} J' z_{\text{eff}} \quad (7)$$

with

$$z_{\text{eff}} = \sum_n \exp[-(r_n - c)/\lambda]. \quad (8)$$

We calculated  $z_{\text{eff}}$  taking the  $\lambda$  parameter to be within the range 2 to 2.5 Å, as it follows from the separation dependence of  $J'$  in similar solid systems [16,17]. If the sum is over all Mn spins in the two adjacent layers, the result turns out to be unphysical, the effective number  $z_{\text{eff}}$  being very small (of order 0.1) and even becoming negative below  $\lambda \simeq 1.9$  Å. This happens so because in the actual structure one of the neighbors from an adjacent layer with opposite spin is closer to the reference Mn atom than its nearest neighbor along axis  $c$  with the same spin direction. This strange result makes us turn to the problem of directionality of the interlayer exchange, which is of indirect, intermediate nature. It seems likely that the orbitals of the non-magnetic ions in the “spacer” layers extend along the  $c$ -axis, making up an exchange channel. If so, then the indirect Mn–Mn interlayer exchange is highly anisotropic and cannot be described by a simple Heisenberg Hamiltonian. Hence, in effective exchange coupling are involved only the two ions that are structurally linked through one translation along axis  $c$ . As a result, the effective coordination number for interlayer exchange should be  $z_{\text{eff}} \simeq 2$ .

From the equilibrium equation  $\partial(E_{\text{el}} + E_{\text{mag}}) / \partial c = 0$  in the absence of pressure we find the relative magnetic striction  $\sigma = \Delta c / c = \Delta c^* / c^*$  across the phase transition point

$$\sigma \simeq \frac{2S(S+1)z_{\text{eff}}\lambda J'}{\varepsilon c}, \quad (9)$$

which gives the sought for expression for  $J'$ :

$$J' = \frac{\sigma \lambda c s_0}{2\chi_c S(S+1)z_{\text{eff}}}. \quad (10)$$

Finally, within the span  $2 \text{ Å} \geq \lambda / z_{\text{eff}} \geq 2.5 \text{ Å}$  we find for the ferromagnetic interlayer exchange parameter in MnPS<sub>3</sub>

$$J' = (0.96 \pm 0.11) \text{ K}. \quad (11)$$

This value is closer to that obtained by Okuda *et al.* [10] but is greater by an order of magnitude compared to other estimates [1,12]. We must only remark here that an interlayer exchange of order  $10^{-2}$  K could hardly result in a detectable striction caused by the transition to the magnetically ordered state.

In conclusion the authors thank G.E. Grechnev, V.V. Eremenko, S.L. Gnatchenko, M.I. Kobets, and V.G. Piryatinskaya for helpful discussions.

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