

Dimensionality crossovers in the magnetization of the weakly ferromagnetic two-dimensional manganese alkylphosphonate hydrates  $\text{MnC}_n\text{H}_{2n+1}\text{PO}_3\cdot\text{H}_2\text{O}$ ,  $n=2-4$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 L109

(<http://iopscience.iop.org/0953-8984/7/9/002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.179

The article was downloaded on 13/05/2010 at 12:38

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

**Dimensionality crossovers in the magnetization of the weakly ferromagnetic two-dimensional manganese alkylphosphonate hydrates  $\text{MnC}_n\text{H}_{2n+1}\text{PO}_3\cdot\text{H}_2\text{O}$ ,  $n = 2-4$**

S G Carling<sup>†</sup>, P Day<sup>†</sup> and D Visser<sup>‡</sup>

<sup>†</sup> The Royal Institution, 21 Albemarle Street, London W1X 4BS, UK

<sup>‡</sup> Physics Department, Loughborough University of Technology, Loughborough LE11 3TU, UK

Received 16 January 1995

**Abstract.** Critical exponents of magnetization  $\beta$  below  $T_N$  in the weakly ferromagnetic layer compounds  $\text{MnC}_n\text{H}_{2n+1}\text{PO}_3\cdot\text{H}_2\text{O}$  have been measured by SQUID magnetometry for  $n = 2-4$ . In all three compounds crossovers are observed in  $\beta$  as follows ( $\beta_1, \beta_2$ ): 0.21(2), 0.73(2) ( $n = 2$ ); 0.18(1), 0.42(6) ( $n = 3$ ), 0.18(1),  $\sim 0.6$  ( $n = 4$ ). The crossover occurs at values of the reduced temperature  $\epsilon = (T_N - T)/T_N$  that become smaller as the separation between the magnetic layers increases.

Low-dimensional inorganic and metal-organic compounds have proved valuable in testing models of magnetic critical behaviour in lattices containing localized exchange-coupled moments (de Jongh and Miedema 1974). However, very few such compounds show finite spontaneous magnetization because ferromagnetic exchange between localized moments is quite rare. To our knowledge the only examples known belong to the layer perovskite family  $(\text{RNH}_3)_2\text{MX}_4$  with  $\text{M} = \text{Cr}$  (Bellitto and Day 1992) or  $\text{Cu}$  (de Jongh 1976). An alternative strategy for creating low-dimensional lattices with finite zero-field magnetization is to synthesize compounds in which the metal ions occupy lattice sites of low symmetry so that, although the near-neighbour exchange interaction may be antiferromagnetic, it competes with strong single-ion anisotropy brought about by second-order spin-orbit coupling. Then the equilibrium distribution of moments is not collinear but canted, leading to a weak ferromagnetic moment along one axis. We have been investigating an extensive series of compounds of this type,  $\text{M}^{\text{I}}\text{M}^{\text{II}}\text{PO}_4\cdot\text{H}_2\text{O}$  ( $\text{M}^{\text{I}} = \text{NH}_4, \text{K}$ ;  $\text{M}^{\text{II}} = \text{Mn, Fe, Co, Ni}$ ) (Carling *et al*, to be published) and the related compounds in which the  $\text{M}^{\text{II}}\text{-PO}_4\text{-H}_2\text{O}$  layers are separated, not by  $\text{M}^{\text{I}}$ , but by organic groups (Carling *et al* 1993). In the latter, varying the chain length of an alkyl group leads to wide variation in the interlayer spacing. For example in  $\text{MnCH}_3\text{PO}_3\cdot\text{H}_2\text{O}$  it is 8.82 Å and in  $\text{MnC}_4\text{H}_9\text{PO}_3\cdot\text{H}_2\text{O}$  14.71 Å. Like the ternary metal phosphate hydrates, the alkylphosphonate hydrates are canted antiferromagnets, and hence behave as weak ferromagnets. We studied the critical behaviour of the magnetization of  $\text{NH}_4\text{MnPO}_4\cdot\text{H}_2\text{O}$  and its deuterated analogue by a combination of neutron diffraction and bulk magnetometry, finding that the critical exponent  $\beta$  of the magnetization below  $T_N$  underwent a crossover from a value of 0.20 when the reduced temperature  $\epsilon = (T_N - T)/T_N$  was  $>0.03-0.07$  to a much higher value (0.39–0.40) on approaching  $T_N$  (Carling *et al* 1993). We have therefore examined the alkylphosphonates to see whether there is a corresponding crossover and if so, how it varies with interlayer spacing.

The samples were prepared by the method described by Carling *et al* (1993); all had satisfactory chemical analyses. The variation of magnetization with temperature was measured on polycrystalline samples using a CCL 5600 SQUID magnetometer at the Inorganic Chemistry Laboratory, Oxford. The samples were loaded into quartz buckets suspended on a copper wire. Measurements were made as close as possible to zero field by applying alternately positive and negative fields of successively decreasing magnitude, beginning from a field of 1 kG. In this way the remanent field of the magnet is diminished.

Figures 1(a)–(c) show the magnetization data for the  $n = 2$ –4 Mn alkylphosphonate compounds subtracting the appropriate diamagnetism corrections, while figures 2(a)–(c) present the same data in logarithmic form on a reduced scale. In the latter case, data more remote from  $T_N$  obey the relationship  $M_\epsilon = M_0 e^{\beta}$  with  $\beta$  in the region of 0.20 for all three compounds. Least squares fitted values of  $\beta_1$  are listed in table 1. However, as  $T_N$  is approached from below the exponential relationship changes and a much higher  $\beta$  exponent becomes evident. The value of  $\beta_1$  is close to that found in  $M^I\text{MnPO}_4 \cdot \text{H}_2\text{O}$  ( $M^I = \text{NH}_4, \text{ND}_4, \text{K}$  (Carling *et al* 1993)). Our first important conclusion is that a figure of  $\sim 0.20$  for  $\beta$  is far from any of the estimates of [2d] or [3d] magnetic models. Thus in [3d] the Ising, XY and Heisenberg models predict respectively 0.31, 0.33 and 0.35 while the [2d] Ising model predicts 0.125 (de Jongh and Miedema 1974). However, it is important to note that, from an experimental point of view,  $^1\text{H}$  NMR measurements on the quadratic layer Heisenberg antiferromagnet  $\text{Cu}(\text{HCOO})_2 \cdot 4\text{D}_2\text{O}$  give  $\beta_1 = 0.22(2)$  (Koyama *et al* 1987), confirmed by neutron scattering (Clarke *et al* 1992). Fluorine NMR gives a similar result for the [2d] ferromagnet  $\text{K}_2\text{CuF}_4$  (Ikeda and Hirakawa 1972). The related compound  $\text{Mn}(\text{HCOO})_2 \cdot 2\text{D}_2\text{O}$ , also a quadratic layer Heisenberg antiferromagnet, contains two distinct planes of  $\text{Mn}^{\text{II}}$  ions, one which orders antiferromagnetically while the other remains paramagnetic: again  $^1\text{H}$  NMR gives  $\beta_1 = 0.22(1)$ , with a crossover to  $\beta_2 = 0.31(2)$  at  $\epsilon \sim 0.02$  (Koyama *et al* 1987). Recently, Bramwell and Holdsworth (1993) have shown how  $\beta$  values in the region of 0.23 can arise from a [2d] model.

Table 1. Critical exponents ( $\beta_1, \beta_2$ ) and crossover temperature  $\epsilon_{X0}$  in Mn phosphate and phosphonate hydrates.

	$\beta_1$	$\beta_2$	$\epsilon_{X0}$	Interlayer spacing (Å)
$\text{KMnPO}_4 \cdot \text{H}_2\text{O}$	0.23(2)	0.4(3)	0.09(1)	8.33
$\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$	0.21(3)	0.40(7)	0.07(1)	8.81
$\text{MnC}_2\text{H}_5\text{PO}_3 \cdot \text{H}_2\text{O}$	0.21(2)	0.73(2)	0.085(2)	10.24
$\text{MnC}_3\text{H}_7\text{PO}_3 \cdot \text{H}_2\text{O}$	0.18(1)	0.42(6)	0.015(2)	11.71
$\text{MnC}_4\text{H}_9\text{PO}_3 \cdot \text{H}_2\text{O}$	0.18(1)	0.4(2)	0.010(5)	14.72

The higher temperature  $\beta_2$  values in the Mn alkylphosphonates are much less well defined than  $\beta_1$  because they are based on fewer data points. Still, it is clear that  $\beta_2$  is much bigger than  $\beta_1$ . The  $M^I\text{Mn}^{\text{II}}\text{PO}_4 \cdot \text{H}_2\text{O}$  compounds ( $M^I = \text{NH}_4, \text{ND}_4, \text{K}$ ) all have  $\beta_2 \sim 0.4$  (Carling *et al* 1993), equal to that in  $\text{MnC}_3\text{H}_7\text{PO}_3 \cdot \text{H}_2\text{O}$ . In the  $\text{C}_2\text{H}_5$  derivative,  $\beta_2$  is much larger, and though there are only two data points it appears that in the  $\text{C}_4\text{H}_9$  compound it is comparable in magnitude. Whilst the measured  $\beta_2$  are larger than predicted for any of the [3d] models it seems safe to say that the crossover is a consequence of an evolution from [2d] to [3d] behaviour.

The reduced temperatures  $\epsilon_{X0}$  at which the crossovers occur also vary significantly from one compound to another within the Mn phosphate (phosphonate) hydrate series.

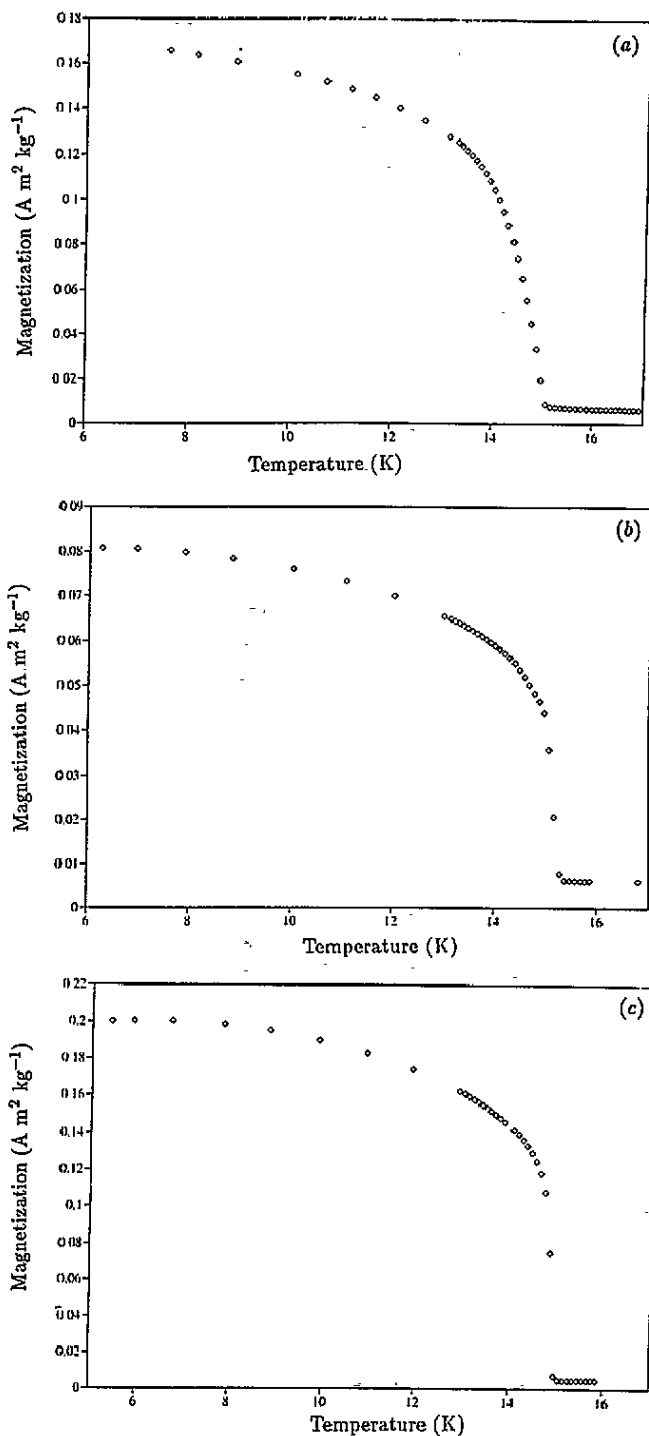


Figure 1. Temperature dependence of magnetization in  $\text{MnC}_n\text{H}_{2n+1}\text{PO}_3 \cdot \text{H}_2\text{O}$ :  $n = 2$ (a); 3(b); 4(c).

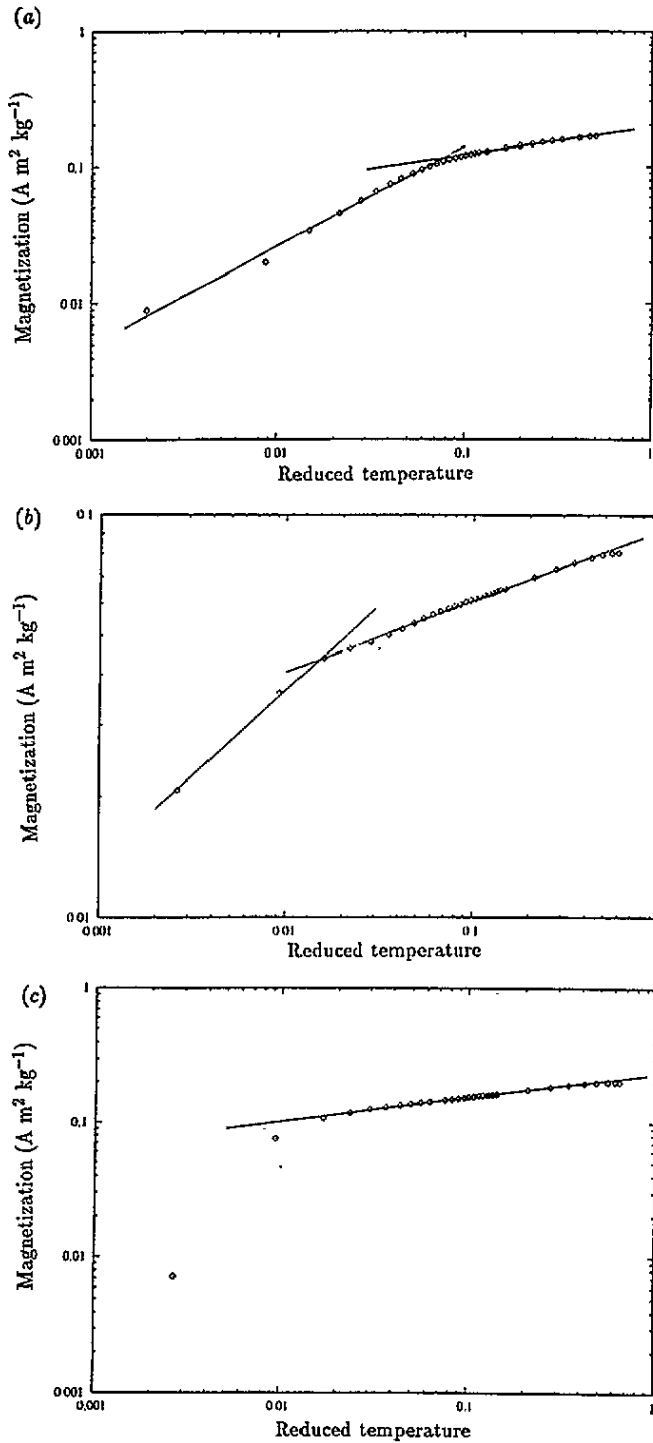


Figure 2. Exponential variation of magnetization with reduced temperature in  $\text{MnC}_n\text{H}_{2n+1}\text{PO}_3 \cdot \text{H}_2\text{O}$ :  $n = 2$ (a); 3(b); 4(c).

Among the  $M^I$  compounds  $\epsilon_{X0}$  is a little larger in  $KMnPO_4 \cdot H_2O$  (0.09(1)) than in the  $NH_4$  compound (0.07(1)), no doubt to be correlated with the smaller interlayer separation in the former. In the alkyl phosphonates too,  $\epsilon_{X0}$  decreases as the interlayer separation increases, corresponding to a decrease in the ratio of in-plane to out-of-plane exchange constants.

We believe we have presented the results of the first systematic study of the critical exponents and crossover temperatures for a series of two-dimensional weak ferromagnets. The correlations of  $\epsilon_{X0}$  with interlayer separation is clear, while the values of the two exponents  $\beta_1$  and  $\beta_2$  do not correspond to the predictions of any of the classical models. On the other hand  $\beta_1$  is close to the value 0.23 systematically invoked by the calculations of Bramwell and Holdsworth (1993).

We thank SERC for a studentship to SGC (21st Century Materials Initiative).

## References

- Bellitto C and Day P 1992 *J. Mater. Chem.* **2** 265  
Bramwell S T and Holdsworth P C W 1993 *J. Phys.: Condens. Matter* **5** L53  
Carling S G, Day P and Visser D 1993 *J. Solid State Chem.* **106** 111  
—— 1992 *Solid State Commun.* **88** 135  
—— *Inorg. Chem.* submitted  
Clarke S J, Harrison A, Mason T E, McIntyre G J and Visser D 1992 *J. Phys.: Condens. Matter* **4** L71  
de Jongh L J 1976 *Physica B* **82** 247  
de Jongh L F and Miedema A R 1974 *Adv. Phys.* **23** 1  
Ikeda H and Hirakawa K 1972 *J. Phys. Soc. Japan* **33** 393  
Koyama K, Nobumasa H and Matura M 1987 *J. Phys. Soc. Japan* **56** 1553  
Koyama K, Terata N and Matura M 1987 *J. Phys. Soc. Japan* **56** 1553