Magnetic and neutron diffraction studies on $(Co_{1-x}Mn_x)_2P$

1990 J. Phys.: Condens. Matter 2 3359

(http://iopscience.iop.org/0953-8984/2/14/020)

J. Phys.: Condens. Matter **2** (1990) 3359–3368. Printed in the UK

Magnetic and neutron diffraction studies on $(Co_{1-x}Mn_x)_2P$

P Radhakrishna†, H Fujii‡, P J Brown§, S Doniach‖, W Reichardt¶ and P Schweiss††

† Laboratoire Léon Brillouin, Laboratoire Commun, CEA–CNRS, CEN Saclay, 91191 Gif-sur-Yvette, France

‡ Hiroshima University, Hiroshima, Japan

§ Institut Laue–Langevin, BP 156 X, Grenoble, France

‖ SLAC, Stanford, USA

¶ Kernforschungszentrum, Karlsruhe, Postfach 3640, D7500 Karlsruhe, Federal Republic of Germany

†† KFK and Institut für Mineralogie und Kristallographie, University of Marburg, 3550 Marburg, Federal Republic of Germany

Received 31 July 1989, in final form 6 November 1989

Abstract. Magnetic and neutron diffraction studies on the series of mixed $(Co_{1-x}Mn_x)_2P$ phosphides are described. The magnetisation of CoMnP has been measured as a function of field at 4.2 K. The temperature dependence of the magnetisation along the *b* axis of the compounds with $x = 0.2$, 0.5, 0.63 and 0.65 has been measured. Single-crystal neutron diffraction data at room temperature were used to refine the structure of two compositions with $x = 0.5$ and 0.62. Polarised neutron measurements on CoMnP are interpreted in terms of antiferromagnetic-like domains associated with the orientation of the cobalt moments. The spin wave dispersion relations of CoMnP and $(Co_{1-x}Mn_x)_2P$, $x = 0.65$, have been determined at 300 K and in a low-temperature helical phase for the latter. A theoretical understanding of these results is possible in terms of the canting of cobalt moments due to a Dzyaloshinski–Moriya interaction.

1. Introduction

The mixed phosphides $(Co_{1-x}Mn_x)_2P$ display a wide range of crystallographic structures and associated magnetic properties which have been discussed in terms of an itinerant electron model. It is of interest to correlate these transformations with model Hamiltonians for d electrons occupying a narrow valence band [1]. Some of the relevant crystallographic and magnetic features of the series are summarised below [2, 3].

(i) From $x = 0$ to $x = 0.8$, the nuclear structure is orthorhombic, with the space group *Pnma*, and for $x > 0.8$, it is hexagonal.

(ii) At the two extremes, with $x = 0.0$ and $x = 1.0$, Co_2P is a Pauli paramagnet, while Mn_2P is an antiferromagnet with $T_N = 103$ K. Ferromagnetism occurs in the intermediate range, between $x = 0.06$ and 0.63. Between $x = 0.63$ and 0.73, a metamagnetic phase occurs, in which a magnetic spiral is formed, with its axis along the *c* direction. Above the metamagnetic temperature, ferromagnetism occurs, up to 380 K for $x = 0.65$. Beyond $x = 0.73$, a single antiferromagnetic phase is formed. These results, due to Okamoto *et al*, are summarised in a phase diagram (figure 1).

0953-8984/90/143359 + 10 $03.50

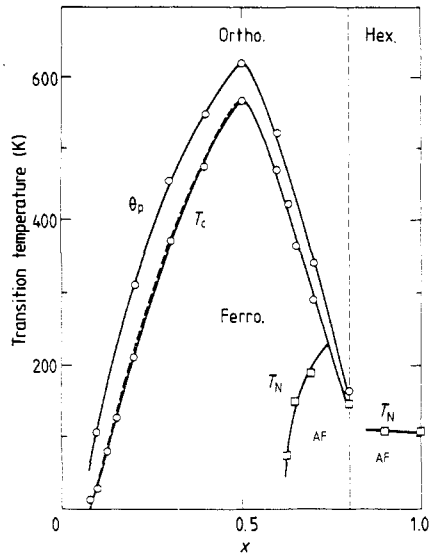

Figure 1. Magnetic phase diagram for $(Co_{1-x}Mn_x)_2P$.

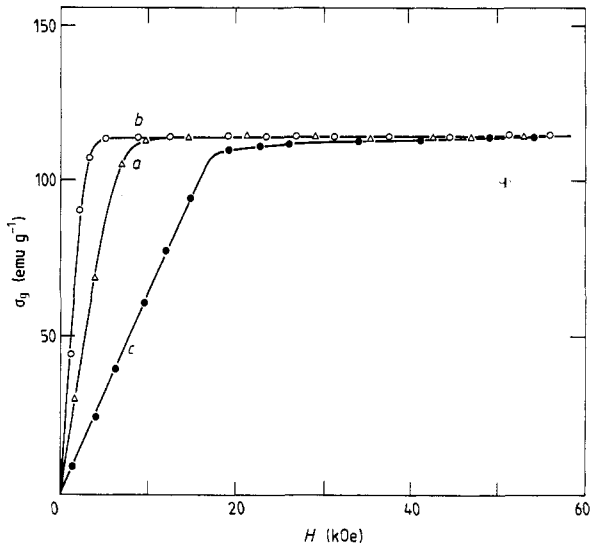

Figure 2. Magnetisation curves along the principal axes at 4.2 K for CoMnP.

We have studied the CoMnP compound and the composition with $x = 0.62$ in particular. Both compounds have an orthorhombic structure with space group P*nma*. The lattice parameters for CoMnP at room temperature are $a = 5.9371$ Å, $b = 3.4997$ Å, and $c = 6.7158$ Å. The Co, Mn and P are in the sites 4*c* at $(x\frac{1}{4}z)$ [4].

In continuation of the program of measuring the magnetic properties of these compounds we have measured the magnetisation curve of the composition $x = 0.5$ along the easy direction [010] at 4.2 K and the data are depicted in figure 2. The temperature dependence of the magnetisation of $(Co_{1-x}Mn_x)_2P$ single crystals with $x = 0.2$, 0.50, 0.63, 0.65 has been measured in two fields along the easy direction [010] and the results are shown in figure 3. The easy direction was along the *b* axis for all the compositions studied. For the compounds with $x = 0.2$ and 0.5, which are ferromagnetic, the presence of a single transition corresponding to the Curie point is clearly visible. The *M* versus *T*

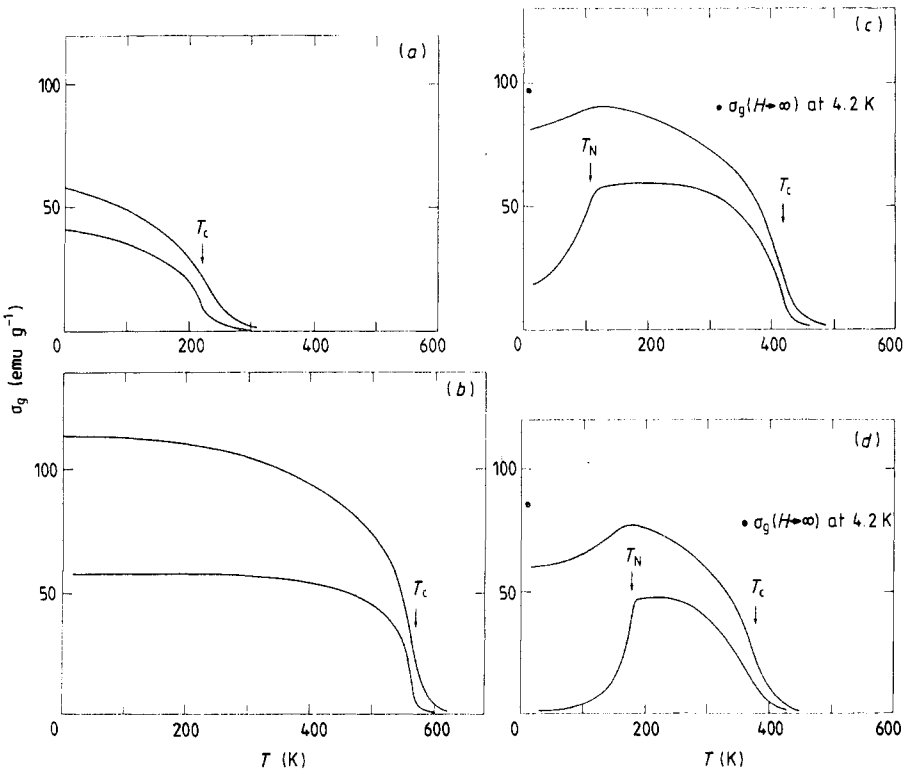

Figure 3. Temperature dependence of the magnetisation of $(Co_{1-x}Mn_x)_2P$, $x = 0.2$, 0.5, 0.63, 0.65 ((*a*), (*b*), (*c*) and (*d*) respectively) along the *b* axis for two applied fields $H =$ 8 kOe: upper curve; $H = 1.8$ kOe: lower curve.

curves for $x = 0.63$ and 0.65 show a discontinuity in the slope associated with the appearance of a ferromagnetic to antiferromagnetic spiral transition at T_N in addition to the Curie point. In these cases, the magnetisation does not saturate at 8 kOe in the spiral phase. Higher fields would be necessary in order to determine the variation of saturation magnetisation with temperature.

2. Magnetic structure

The x-ray crystallographic study of CoMnP is due to Fruchart *et al* [4]. The magnetic structure of CoMnP has been studied by Fruchart *et al* [5] by neutron powder diffraction diagrams at 640 K, above T_c (563 K) and below it, at 77 K. The moments on the atoms at the different sites have been evaluated from the intensities in the powder diagrams.

We have undertaken a single-crystal study of the magnetic and nuclear structure of the $x = 0.5$ and $x = 0.62$ compounds of this series in order to refine the values of the moments and to determine their orientations. The four-circle diffractometer situated on the beam hole at the reactor Orphée was used. Measurements of the integrated intensities were performed on crystals of dimensions of a few mm. Two wavelengths were used and each reflection was subjected to a preliminary inspection. The collected data were then treated by a refinement program based on the Cambridge Crystallographic routines. At a wavelength of 0.83 Å, 2535 reflections were collected for the

Table 1. Structure of $(Co_{1-x}Mn_x)_2P$, $x = 0.5$. (*a*) Atomic parameters from 530 independent reflections at $\lambda = 0.8307$ Å: $R = 3.73\%$. (*b*) Magnetic structure, from 42 independent reflections, $R = 8.63\%$.

(*a*)	*x*	*y*	*z*
Co	0.8575 ± 3	0.25	0.0643 ± 3
Mn	0.9721 ± 1	0.25	0.6688 ± 1
P	0.2326 ± 1	0.25	0.1259 ± 1
(*b*)	Moment in μ_B	θ (deg)†	φ (deg)†
Co site	0.7 ± 0.05	90 ± 1	21.02 ± 1
Mn site	3.04 ± 0.05	90 ± 1	90 ± 1

† θ and φ refer to spherical coordinates, as in (r, θ, φ).

composition with $x = 0.5$. For the other composition, 2711 reflections were measured at 0.8307 Å and 3503 reflections at 0.5247 Å. All these measurements were made at 300 K, below 563 K, and at 400 K, respectively corresponding to the Curie temperatures. The nuclear structures of $(Co_{1-x}Mn_x)_2P$ for $x = 0.5$ and the $x = 0.62$ composition were refined using all the reflections with $\sin\theta/\lambda$ above 0.5, to reduce magnetic contributions. In the second case, the occupancy of the manganese site was set to 1, and the results of the refinement converged to occupancies of 0.76 and 0.234 for cobalt and manganese on the second site, corresponding to a composition of $(Co_{0.38}Mn_{0.62})_2P$. The positional parameters and the temperature and scale factors were thus determined. The data was fitted in each case to two different wavelengths. The inclusion of corrections for extinction did not improve the agreement significantly. After fixing the parameters and the scale factor, the magnitudes of the magnetic moments on the manganese and cobalt sites and their orientations were refined using all the reflections with $\sin\theta/\lambda$ below 0.5. In the calculation, an averaging procedure was performed for the intensities over equal domain populations. The positional parameters and the results of the magnetic refinements are listed in tables 1 and 2. For $x = 0.5$ (figure 4), the magnetic moments of the manganese of 3.04(5) μ_B lie along the Y axis. The cobalt moments of 0.70(5) μ_B are inclined at an angle of 21(1) degrees to the X axis. The magnetic model has lost the centre of symmetry, as well as the mirror plane and the glide plane. The structure is primitive, denoted by P. The components of the cobalt moment are coupled antiferromagnetically in the X direction and ferromagnetically in the Y direction. The refinement for the magnetic structure with $x = 0.62$ was attempted using the same model as for the sample with $x = 0.5$. No convergence was obtained. However, a model in which the centre of symmetry and the *a* glide plane were retained gave a satisfactory convergence. The manganese moments of 1.72 μ_B were along the Y axis. The moments on the cobalt of 0.5 μ_B were now completely along the X axis and ferromagnetically coupled. This compound goes over into a screw antiferromagnetic phase below 160 K. A band structure calculation on the compounds Fe_2P, Co_2P and CoMnP due to Fujii *et al* [6] is in overall agreement with experiment. From the calculation of the density of states, the authors find that it is possible to explain the occurrence of ferromagnetism in $(Co_{1-x}Mn_x)_2P$ up to $x = 0.63$, and antiferromagnetism, thereafter, till $x = 0.8$. The calculated magnetic moments of 0.06, 3.113 and -0.05 μ_B for cobalt, manganese, and phosphorous respectively, are, however, in disagreement with our conclusions.

The first polarised neutron measurements on CoMnP are due to one of the authors [7]. The results were interpreted in terms of a completely collinear model. The material

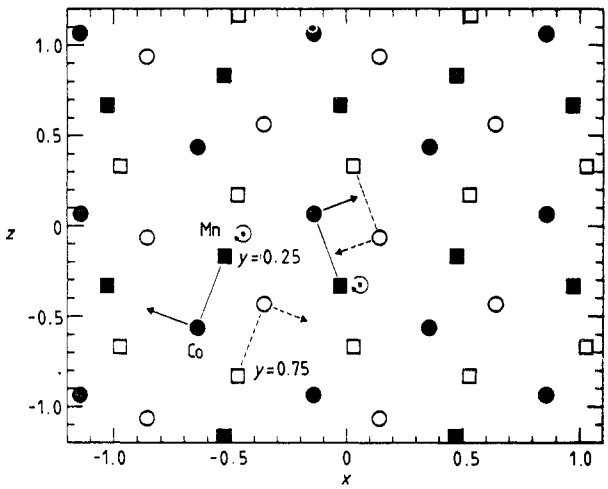

Figure 4. Magnetic structure of CoMnP. The directions of the magnetic moments on the cobalt atoms are indicated. The cobalt atoms are also at $Y = 0.25$ and 0.75.

Table 2. Structure of $(Co_{1-x}Mn_x)_2P$, $x = 0.62$. (*a*) Atomic parameters from 531 independent reflections at $\lambda = 0.8307$ Å: $R = 3.7\%$. (*b*) Magnetic structure, from 68 independent reflections, at 0.524 Å, $R = 12.37\%$ and 70 independent reflections at 0.8307 Å, $R = 13.76\%$.

(*a*)	*x*	*y*	*z*
Co	0.8574 ± 3	0.25	0.0664 ± 1
Mn	0.9720 ± 1	0.25	0.6693 ± 1
P	0.2311 ± 1	0.25	0.1259 ± 1
(*b*)	Moment in μ_B	θ (deg)	φ (deg)
Co site	0.51 ± 0.03	90 ± 1	0 ± 1
Mn site	1.40 ± 0.05	90 ± 1	90 ± 1

is not, however, a simple collinear ferromagnet. The non-collinear components can, under certain circumstances, contribute to the cross-section of polarised neutrons, which indicated the interest of a further study. The diffractometer used for this purpose is situated at the beam hole on the hot source at the reactor Orphée. The flipping ratios of several reflections of the type (*h*0*l*) were measured at room temperature in a field of about 10 kOe. Measurements at three wavelengths of 0.54 Å, 0.76 Å, and 0.8 Å were used to correct for extinction. The efficiency of flipping was unity, since a cryogenic flipper was used. Small systematic differences were observed in the values for equivalent reflections of the type (*h*0*l*). The crystal was then inverted in the field and the measurements were repeated. The flipping ratios were observed to depend on the orientation in the field in a systematic manner. For instance, the flipping ratios observed for the (101) and the ($\bar{1}$01) directions were 0.0488(5) and 0.0646(5) and were inverted when the field was along the *b* axis. We conclude that non-negligible *Z* components occur in the moments on the cobalt.

3. Magnetic excitations

Magnon dispersion curves were measured for CoMnP and for a compound with $x = 0.65$ at room temperature and in zero magnetic field. The monochromators and analysers

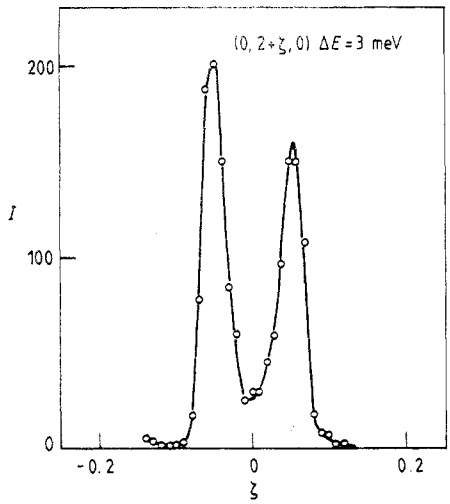

Figure 5. Neutron groups in an inelastic scan of the dispersion relation in CoMnP (T = 300 K).

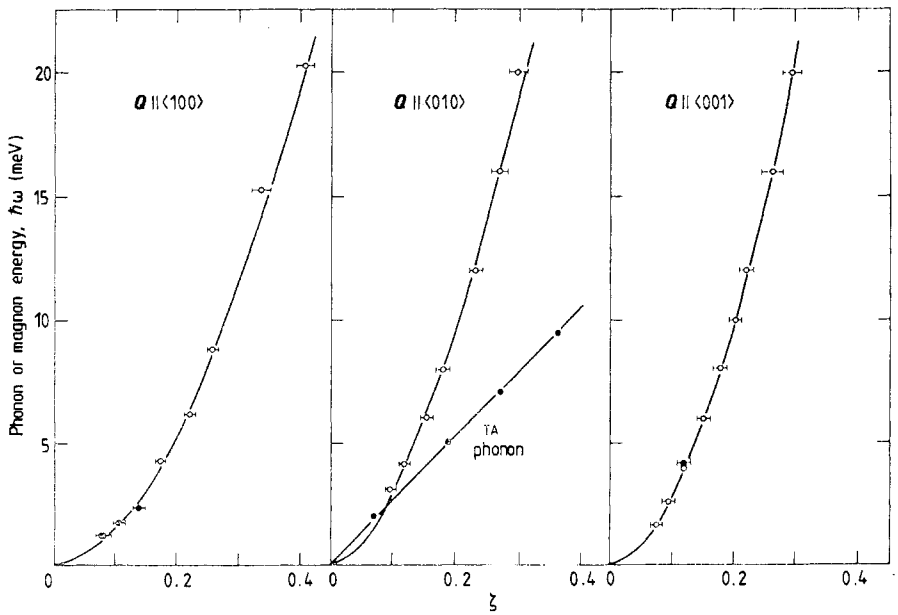

Figure 6. Dispersion relations in CoMnP at 300 K.

were of pyrolytic graphite, reflection (002), and a graphite filter was used to eliminate energies higher than 13.7 meV in the incoming or outgoing beams. The horizontal collimations were usually 40 min throughout. The dispersion curves for CoMnP were measured in the (ζ00), (0ζ0) and the (00ζ) directions. The results are summarised in figures 5 and 6 and in table 3. Studies on the dispersion curves in $(Co_{0.35}Mn_{0.65})_2P$ were carried out at room temperature and at 15 K. At the lower temperature, a spiral structure is formed with a period of about 50 Å, propagating along the c axis. The evolution of the characteristic satellites as a function of temperature in zero field is shown in figure 7. Inelastic scans were made along the (ζ00) and (00ζ) directions. The results are shown in figures 8 and 9. The dispersion was steeper than at room temperature and corresponded to the relation $\hbar\omega$ (meV) = 94.52 ζ^2.

Table 3. Spin wave dispersion of CoMnP: $\hbar\omega$ (meV) = $Dq^2(1 - \beta q^2) + C$.

	D (meV Å^2)	β (Å^2)	C (meV)
$\boldsymbol{Q}\parallel$ [100]	139	0.75	~0
$\boldsymbol{Q}\parallel$ [010]	260	1.90	~0
$\boldsymbol{Q}\parallel$ [001]	266	1.30	~0

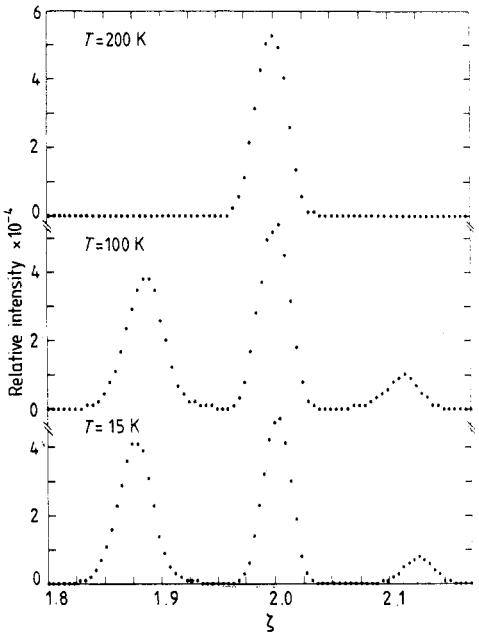

Figure 7. Appearance of satellites around the Bragg reflection (002) of $(Co_{0.35}Mn_{0.65})_2P$.

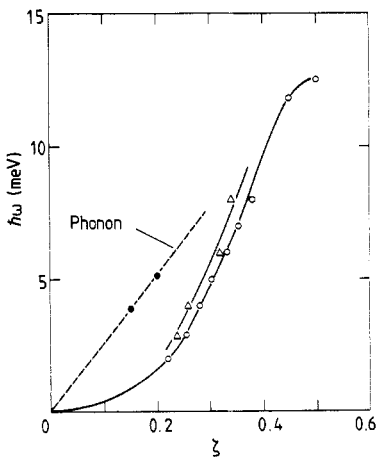

Figure 8. Dispersion relations in $(Co_{0.35}Mn_{0.65})_2P$ in the $(2 + \zeta, 0, 0)$ direction ○: 296 K; △: 230 K.

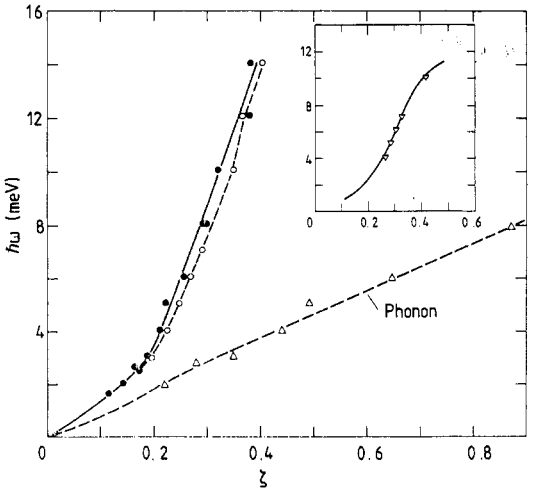

Figure 9. Dispersion relations in $(Co_{0.35}Mn_{0.65})_2P$ in the $(2 + \zeta, 0, 0)$ direction. ●: $(2 + \zeta, 0, +0.13)$ at 15 K; ○: $(2 + \zeta, 0, 0)$ at 140 K. In the inset, dispersion relations in the $(0, 0, 2 + \zeta)$ direction ▽: at 300 K.

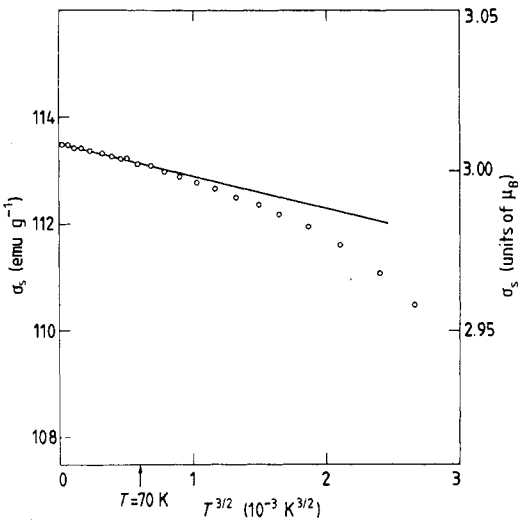

Figure 10. Temperature dependence of the spontaneous magnetisation (σ_s) of CoMnP along the b axis. $M_s = M_0(1 - CT^{3/2})$, $C = 5.1 \times 10^{-6}$, $D_{cal} = 251$ meV Å^2.

4. Discussion

The saturation magnetisation of CoMnP along the b axis follows the $T^{3/2}$ law expected at low temperatures, below 80 K, as shown in figure 10. The value of the stiffness coefficient D, estimated from this variation is 250 meV Å^2. This value is in reasonable agreement with $D_{obs} = 260$ meV Å^2 along the b axis obtained from the data. At much higher temperatures, however, one would expect that some mode–mode coupling should be taken into account in explaining the magnetisation–temperature curves. A conical or a ferromagnetic spiral along the c axis would produce a pattern of satellites similar to that observed for $(Co_{0.35}Mn_{0.65})_2P$, except that a magnetic contribution would occur at the nuclear positions. The expression for the spin dispersion relations in the helical structure have been given by Baryaktar and Maleev [8].

These compounds form a limited number of magnetic domains for different rearrangements of the spins. The compound with $x = 0.5$ forms four domains as a result of the operation of each of the missing symmetry elements. They are represented in figure 11. The centre of symmetry causes only an inversion of the spins. There are thus two domains in which the ferromagnetic component is switched. The loss of symmetry in the magnetic structure will cause reflections of the form (hkl) and $(h\bar{k}l)$ to be different. In a magnetic field along the Y direction all the spins tend to cant towards it to a degree determined by the type of domain. In the polarised neutron experiments, we have observed differences in the flipping ratios of the $(h0l)$ and the $(h0\bar{l})$ reflections which would appear to indicate a small non-negligible Z component. This component makes a small contribution to the predominantly nuclear reflections and its estimation from integrated intensity measurements is therefore difficult.

The observed magnetic structure for the $x = 0.5$ composition (figures 4 and 11) may be interpreted as a simple consequence of a Dzyaloshinski–Moriya-type interaction

$$H_{DM} = \sum_i \boldsymbol{e}_{Mn\text{-}Co} \cdot \boldsymbol{S}_{i,Mn} \times \boldsymbol{S}_{i,Co}$$

where each Mn in the structure has associated with it the closest Co in the structure (see figure 4). $\boldsymbol{e}_{Mn\text{-}Co}$ is a unit vector joining these two atoms. Because of the inherent two-fold screw axis symmetry along the $(\frac{1}{2}Y\frac{1}{2})$ direction of the CoMnP structure in which for

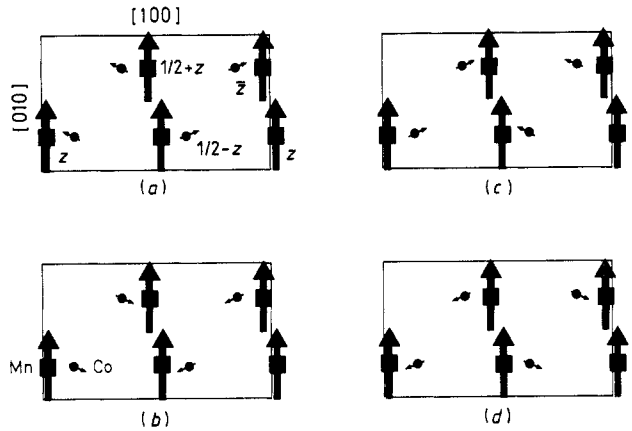

Figure 11. Magnetic domains in CoMnP. The lengths of the arrows are proportional to the magnetic moments.

each X–Z layer of atoms successive columns of atoms in the Z direction are rotated by 180°, H_{DM} naturally leads to an internal field on the Co which alternates in sign along the X direction thus providing a mechanism for the apparently antiferromagnetic arrangement of Co spins that is observed. In fact, H_{DM} would predict an alternating Z component as well as X component, which may be consistent with observed differences in flipping ratios mentioned above. The effect of H_{DM} is entirely consistent with the observed inversion of the Co antiferromagnetic arrangement on reversal of the applied field along the Y axis. This would not be expected to occur if H_{DM} were zero and the Co arrangement were due to a genuine Néel antiferromagnetism, since in this case the Néel system would be degenerate against a translation from one spin sublattice to the other. (An additional antiferromagnetic coupling between Co moments is not excluded, however.) The important point is that the cobalt arrangement must be driven by H_{DM}, so any Néel degeneracy is broken by the resulting internal staggered field. The observed ferromagnetic canting of the Co moments towards the Y axis (figure 10) is not explained by H_{DM} and indicates the presence of an additional weak *ferromagnetic* coupling between the Co and the Mn moments.

Acknowledgments

We wish to thank Mme P Charpin of the Service de Chimie Moléculaire, IRDI, CEN-Saclay, for her valuable help. R Dufour gave one of the authors (RK) invaluable technical support during the construction of the polarised neutron spectrometer at Orphée.

References

[1] Goodenough J B 1964 *J. Appl. Phys.* **35** 1083
[2] Okamoto T, Fujii H, Hihara T, Eguchi K and Hokabe T 1981 *J. Phys. Soc. Japan* **50** 3882
[3] Fruchart R, Roger A and Sénateur J P 1969 *J. Appl. Phys.* **40** 1250
[4] Fruchart D, Bacmann M and Chaudouet P 1980 *Acta Crystallogr.* B **36** 2759
[5] Fruchart D, Martin-Farrugia C, Rouault A and Sénateur J P 1980 *Phys. Status Solidi* a **57** 675

[6] Fujii S, Ishida S and Asano S 1988 *J. Phys. F: Met. Phys.* **18** 971
[7] Fujii H, Komura S, Takeda T, Hokabe T and Okamoto T 1979 *J. Magn. Magn. Mater.* **14** 181
[8] Baryaktar J G and Maleev S V 1963 *Fiz. Tverd. Tela* **5** 1175 (Engl. Transl. 1963 *Sov. Phys.–Solid State* **5** 858)