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## Crystalline and magnetic ordering in the monoclinic phase of the layered perovskite PAMC

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**Abstract.** A single-crystal elastic neutron scattering experiment between 4.2 and 115 K has been performed on the low-temperature monoclinic  $\zeta$  phase of the layered perovskite bis(propylammonium)manganesetetrachloride (PAMC). The crystalline structure is commensurately modulated, with a modulation vector of  $\frac{1}{3}b^*$ , and below 39 K PAMC is an antiferromagnet with a small ferromagnetic component. The temperature dependence of the monoclinic angle  $\alpha$  depends on the mosaicity of the crystal which increases with the number of 'cooling cycles'. The satellite reflections do not have any contribution from the magnetic ordering, but their intensity has abrupt changes that coincide with changes in either the nuclear or the magnetic ordering parameter. Magnetoelastic effects seem to influence the ordering of the crystal.

### 1. Introduction

The layered perovskite  $(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{MnCl}_6$  (PAMC) is an example of an antiferromagnet that shows weak ferromagnetism. The small ferromagnetic moment is believed to originate in anisotropic exchange interactions of the form  $D \cdot (S_1 \times S_2)$ , where  $D$  is a constant vector and  $S_1$  and  $S_2$  are the spins of the two interacting atoms; this interaction is possible because the low crystal symmetry allows the magnetic moments in the pure antiferromagnet to tilt without change of symmetry (Groenendijk *et al* 1979, Achiwa *et al* 1990b). In addition PAMC exhibits a large sequence of structural phases. The structure consists of  $(\text{MnCl}_6)$  octahedra sandwiched between propylammonium chains—a crystalline model of lipid bilayers. The ammonium group hydrogens may bond to the  $\text{Cl}^-$  ions in the octahedra in four different positions (Depmeier 1986, Murali *et al* 1988). At high temperatures all four positions are equally possible (tetragonal symmetry), but upon cooling there is a gradual freezing of the bonds followed by a reorientation of the propylammonium groups, and the structure becomes orthorhombic and finally monoclinic. The structural phase sequence with phase transition temperatures and conventional or super-space groups as appropriate is as follows:  $\alpha$  phase  $I4/mmm$ , 441 K;  $\beta$  phase  $Abma$ , 388 K;  $\gamma$  phase  $N_{111}^{Abma}$ , 339 K;  $\delta$  phase  $Abma$ , 168 K;  $\epsilon$  phase  $P_{s11}^{Abma}$ , 112 K;  $\zeta$  phase  $P_{i s}^{P2_1/b}$ , 39 K; the magnetically ordered phase.

At the phase transition at 112 K the dynamical disorder of the propylammonium chains freezes, and the crystal structure goes from dynamical disordered orthorhombic symmetry to a monoclinic symmetry (Depmeier and Mason 1983, Steurer and Depmeier 1989). At the phase transition, multiple twinning occurs, which may be observed directly as a splitting of the Bragg reflections. Simultaneously with the monoclinic distortion the incommensurate

modulation of the  $\epsilon$  phase (modulation vector of  $(\frac{1}{3} + \delta)b_{\text{ortho}}^*$ ) locks in to a commensurate value and turns to be along  $\frac{1}{3}b_{\text{mono}}^* \simeq \frac{1}{3}(b_{\text{ortho}}^* + c_{\text{ortho}}^*)$ . At 39 K, PAMC orders magnetically into an antiferromagnetic structure where the magnetic moments mainly are perpendicular to the  $a$ - $b$ -plane, but there is a small ferromagnetic moment in the  $a$ -direction.

To understand the interactions between the crystal structure and the magnetic structure we have performed an elastic neutron scattering experiment in the low-temperature monoclinic  $\zeta$  phase of PAMC, where we have measured the temperature dependence of the monoclinic distortion and of the satellite intensities.

## 2. Experimental details

The neutron experiment was done on a non-deuterated single crystal of approximate dimensions 2 mm (along  $c_{\text{ortho}}$ )  $\times$  15 mm (along  $b_{\text{ortho}}$ )  $\times$  10 mm (along  $a_{\text{ortho}}$ ). The spectrometer was the two-axis spectrometer TAS3 at Risø National Laboratory, Denmark, where a Ge monochromator (311) reflection selected neutrons of wavelength 1.291 Å. The crystal was mounted with the  $b$ - $c$ -plane horizontal in a  $^4\text{He}$  cryostat and could be cooled to 4.2 K. It is important to note that the present experiment was done on a so called virgin crystal, i.e. it had not been at temperatures below 300 K before starting the data collection. Therefore the data presented in this paper were collected in one go while cooling step by step from room temperature to 4.2 K. After each change of temperature, we waited 30 min before starting the data collection. During data collection, the temperature was stable within 0.02 K. The measurements of the monoclinic angle were done by  $\omega$  scans through the very strong (040) reflection (orthorhombic Miller indices) at each temperature. The measurements of the intensities of the satellite reflections were more elaborate. They had to be done very accurately, because the satellites move a little due to changes of the monoclinic angle and the cell dimensions. Therefore these measurements were done by scanning nets in reciprocal space through several satellites at each temperature. The net scanning of the satellites lasted about 15 h per temperature, and the corresponding satellite intensities were determined from fits to two-dimensional Gaussians. In addition, preliminary neutron experiments were done on similar non-virgin crystal, with either the  $b$ - $c$ - or the  $a$ - $c$ -plane in the horizontal scattering plane.

## 3. The supercell

The detailed diffraction pattern for the  $b$ - $c$ -plane is shown in figure 1. The reciprocal lattice of the primitive crystallographic unit cell of  $\zeta$  PAMC is drawn by solid lines ( $b^*$ ,  $c^*$ ) and by dashed lines for the twin component ( $b'^*$ ,  $c'^*$ ). It should be noted that throughout the paper we have adopted the term twin component to describe the crystal component having  $c'^* = -c^*$ . The crystal is twinned in the sense that it contains two monoclinic domains with oppositely directed  $c^*$ -axes as indicated in figure 1. The cell dimensions for the  $\zeta$ -phase were found to be

$$\text{neutrons (6K): } a = 7.44(1) \text{ \AA} \quad b = 7.10(1) \text{ \AA} \quad c = 13.14(1) \text{ \AA}.$$

The monoclinic angle,  $\alpha$ , for the orthorhombic case (no splitting of the reflections) is 105.68°. The splitting of the orthorhombic (040) reflection was measured carefully (see figure 4) and the value  $0.378(6)^\circ = 2 \times 0.189(3)^\circ$  was found at 6 K. This corresponds to a deviation of the monoclinic angle  $\Delta\alpha = 0.189(3)^\circ \sin^2 \alpha^* = 0.176(3)^\circ$  (see figure 1). The monoclinic angle was therefore measured at 6 K to be

$$\alpha = 105.68(1)^\circ - 0.176(3)^\circ = 105.50(1)^\circ.$$

A pseudo-orthorhombic unit cell can be constructed from this by letting  $a_{\text{ortho}} = a$ ,  $b_{\text{ortho}} = b$  and  $c_{\text{ortho}} = 2c + b$ ; the dimensions at 6 K then become  $a_{\text{ortho}} = a = 7.44 \text{ \AA}$ ,  $b_{\text{ortho}} = b = 7.10 \text{ \AA}$ ,  $c_{\text{ortho}} = 25.32 \text{ \AA}$  and  $\alpha = 90^\circ - 0.189^\circ \approx 90^\circ$ . The reciprocal lattice vectors for this cell,  $(b_{\text{ortho}}^*, c_{\text{ortho}}^*)$ , are drawn as dash-dot lines in figure 1.

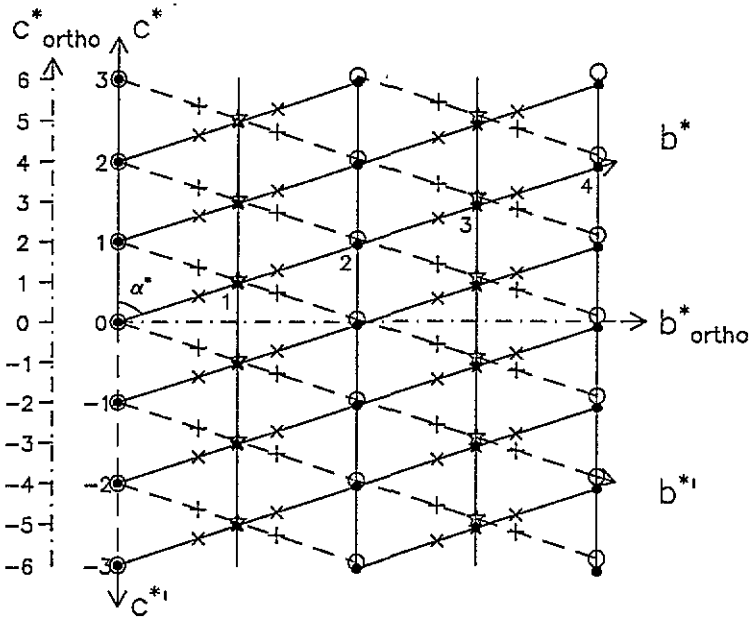


Figure 1. The diffraction pattern in the  $Ok_l$  plane, observed by neutron scattering. ● and ○ are nuclear reflections, filled and unfilled stars are magnetic reflections, and × and + are satellite reflections. The unprimed axes give the cell for one crystal orientation and the primed axes give the cell for the other crystal orientation.

The circles (● and ○) show the nuclear main reflections that split into two components parallel to the  $c^*$ -axis as a result of the twinning. For illustrative purposes the twinning effect is over emphasized. The filled and unfilled stars are magnetic reflections that appear at temperatures below 39 K. These reflections are also split because of twinning. The crosses (×) and pluses (+) are the satellite reflections that appear for a commensurate modulation vector of  $\frac{1}{3}b^* = \frac{1}{3}(b_{\text{ortho}}^* + c_{\text{ortho}}^*)$ . In this case reflections originating from twinning do not overlap; they appear on lines parallel to  $b^*$  and  $b^{*'}$ , respectively.

In the monoclinic cell each reflection may be given four indices,  $hklm$ , so that main reflections are indexed  $hkl0$  and satellite reflections  $hklm$ . A reflection  $(hkl1)$  is at the position  $hk + \frac{1}{3}l$  and a reflection  $(hkl\bar{1})$  is at the position  $hk - \frac{1}{3}l$ , when using conventional Miller indices. The selection rule for the nuclear reflections in the  $b$ - $c$ -plane is  $Oklm, k + m = 2n$ , indicating a  $b$ -glide perpendicular to  $a$  and a ' $t$ -glide' in the fourth dimension. A four-circle x-ray experiment (Harris *et al* 1994) gave the additional selection rule  $h000, h = 2n$ , and we obtain superspace group  $P_{\bar{1}}^{P2_1/b}$  for the crystal structure (see de Wolff *et al* 1981 and Yamamoto *et al* 1985). The average unit cell and crystal structure of  $\zeta$  PAMC are shown in figure 2.

Scans in reciprocal space parallel to the  $c^*$ -direction for  $k = 2\frac{2}{3}$  and  $k = 3\frac{1}{3}$  are shown in figures 3(a) and (b), respectively. The  $x$ -axis is indexed according to the pseudo-

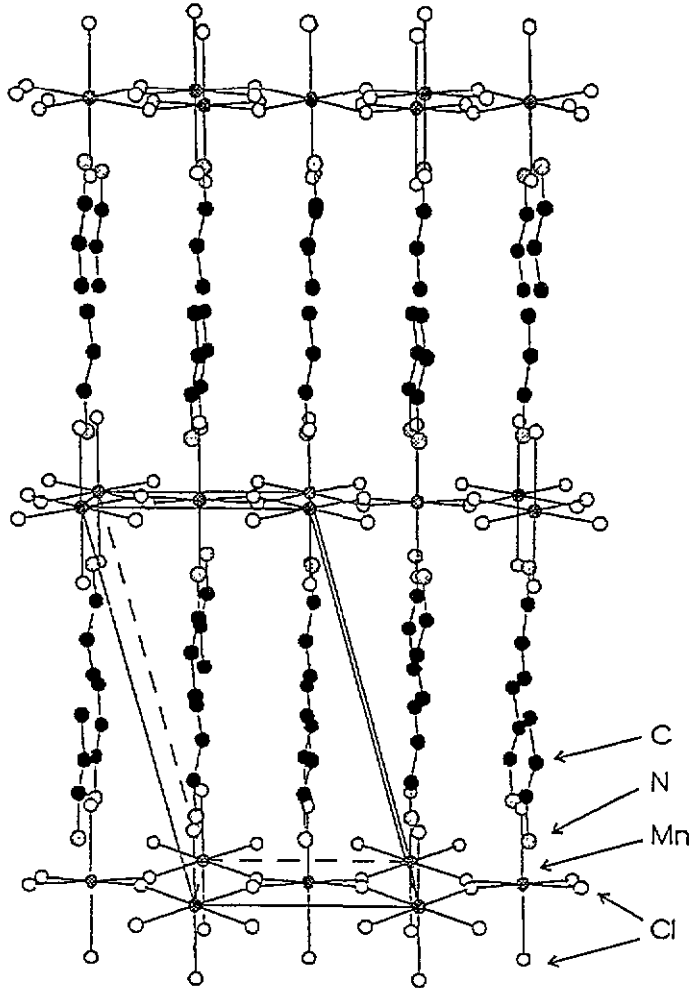
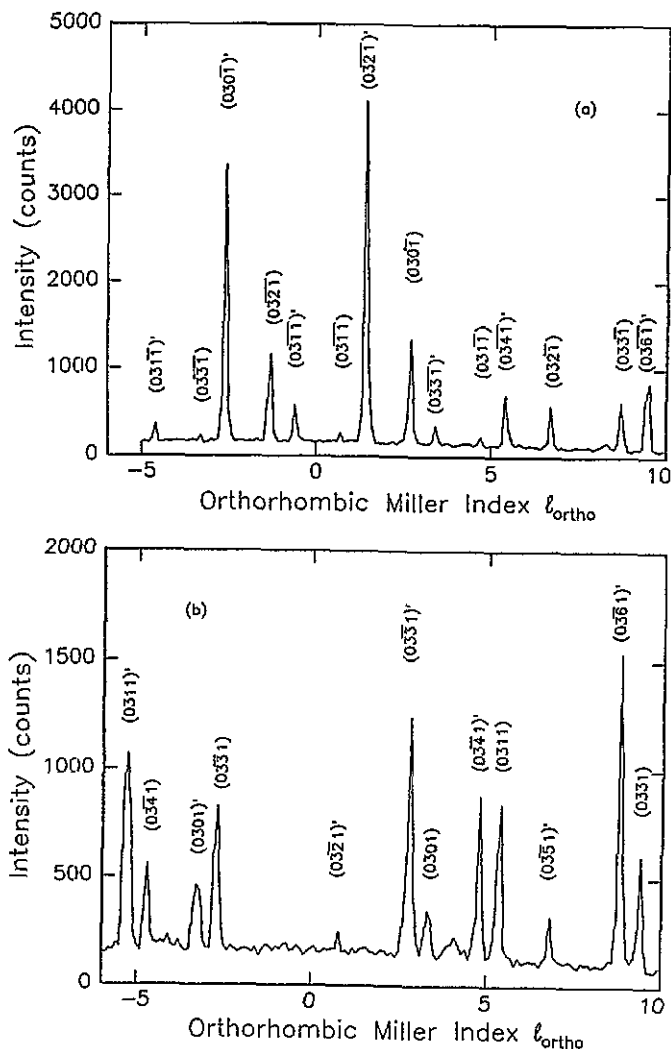


Figure 2. A perspective view of the average crystal structure of  $\zeta$  PAMC (Harris *et al* 1994) found at 8 K. The monoclinic cell is indicated. The modulation is in the  $b$ -direction.

orthorhombic  $c_{\text{ortho}}^*$ -axis ( $l_{\text{ortho}}$ ). For every observed reflection, the indices for the monoclinic cell are given, with the primed and unprimed indexing coming from the two separate twin individuals. Clearly, the distance between the satellites is larger along the  $k = 2\frac{2}{3}$  scan (figure 3(a)) than along the  $k = 3\frac{1}{3}$  (figure 3(b)). This effect is due to the twinning and is emphasized in figure 1.

The selection rule found for the magnetic reflections is  $0k10, k = 2n + 1$ . Generally the selection rule for the magnetic reflections were found to be  $hk10, h + k = 2n + 1$ , indicating antiferromagnetic ordering where the magnetic moment on every atom is antiferromagnetically coupled to the nearest neighbours in the  $a$ - $b$ -plane. This means that the magnetic moment on the Mn atom in the position  $(0,0,0)$  is directed opposite to the moment at the position  $(\frac{1}{2}, \frac{1}{2}, 0)$ . Susceptibility measurements (Groenendijk *et al* 1979, Achiwa *et al* 1990) show that the magnetic moments are mainly parallel to the  $c_{\text{ortho}}$ -axis, but that there is a weak ferromagnetic moment parallel to the  $a$ -axis. The tilt of the magnetic moments towards the  $a$ -axis has been determined to be  $0.05^\circ$  (Groenendijk *et al* 1979).



**Figure 3.** Scans parallel to the  $c^*$ -direction for  $k = 2\frac{2}{3}$  (a) and  $k = 3\frac{1}{3}$  (b). The intensity is plotted against the pseudo-orthorhombic Miller index  $l_{ortho}$  (see figure 1). The indices indicated above the reflections correspond to reflections from the primed and unprimed monoclinic lattices in figure 1.

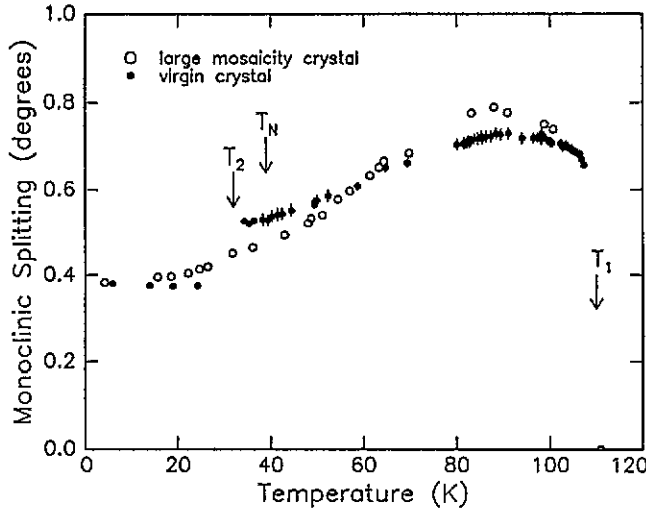
#### 4. Monoclinic angle

When the crystal transforms from the orthorhombic  $\epsilon$  phase to the monoclinic  $\zeta$  phase multiple twinning in the  $b$ - $c$ -plane occurs. The positive  $a$ - and  $b$ -axes of one twin individual coincide with negative  $a'$ - and  $b'$ -axes of the other twin individual and as  $c$ - and  $c'$  are not parallel, the Bragg peaks split parallel to the  $c^*$  direction.

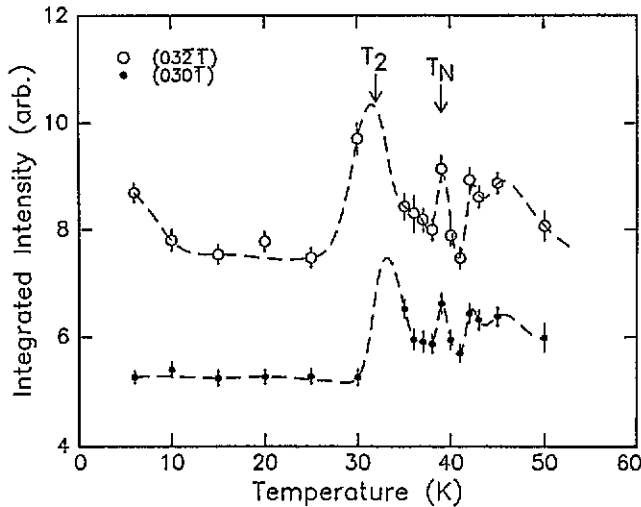
The splitting of the reflections is very small (between  $0.35^\circ$  and  $0.8^\circ$ ); it does, however, offer a way to measure the deviation from the orthorhombic symmetry directly, which is related to the order parameter of the crystal structure in the  $\zeta$  phase.

By measuring the splitting of the orthorhombic  $(0400)$  reflection into the two monoclinic  $(04\bar{2}0)$  and  $(0420)$  reflections between 4.2 K and 112 K we were able to find

the angular deviation from the orthorhombic symmetry. The result of these measurements on a virgin crystal is shown in figure 4 (filled circles). After a small increase of the angle, it does not remain constant as expected, but decreases upon cooling. The rate of decrease flattens somewhat around 50 K, but at  $T_2 \approx 32$  K the angle decreases abruptly to a constant value.



**Figure 4.** The angular splitting found by omega scans of the orthorhombic (0400) reflection into the two (0420) and (0420)' reflections of the monoclinic system. •, measurements on a virgin crystal. ○, measurements on a crystal with large mosaicity (after Achiwa *et al* 1990a).



**Figure 5.** The temperature dependence of the integrated intensities of two satellite reflections, measured on cooling of a virgin crystal. The dashed curves are guides to the eye.

After several thermal cycles through the orthorhombic–monoclinic transition at 112 K the mosaicity of the crystal increases. Measurements on such a crystal are also shown in figure 4 (unfilled circles), and it is seen that the abrupt decrease at 30 K smears out.

The overall behaviour of the monoclinic splitting with temperature is relatively independent of the mosaicity, and may be induced by the onset of the magnetic order. However, the size of the jump in the angle around 30 K as well as the maximum value of the angle at around 85 K depends crucially on the mosaicity and we therefore suggest that there is internal strain in the crystal that disappears as the mosaicity increases.

The maximum value appears at around 85 K. This is just below the temperature where the hydrogen atoms in the  $\text{NH}_3$  groups no longer exchange by jumpwise rotation around their threefold molecular axis (Muralt *et al* 1988). It is also around that temperature where the birefringence studies of Brunskill and Depmeier (1982) show a broad minimum for PAMC.

## 5. Satellites

The satellite reflections may gain intensity from the magnetic ordering by two different mechanisms. One possibility is a contribution from a positional modulation of the Mn atoms and another is a contribution from a rotational modulation of the tilted magnetic moments, originating from an interaction between the magnetic moments and the tetrahedra (as seen in figure 2 the Mn atoms are seated in the middle of the tetrahedra). One could imagine the magnetic moments following the movements of the tetrahedra in the modulational wave.

Therefore, we investigated the integrated intensities of some nuclear satellites as a function of temperature between 50 K and 4.2 K. To make sure that we measured real changes of the total satellite intensity and not intensity changes induced by changes of the unit cell parameters, this was done by scanning in nets in reciprocal space around the satellites at each temperature (see section 2).

The somewhat surprising results are shown in figure 5 for the satellites  $(03\bar{2}\bar{1})$  and  $(030\bar{1})$ . The two reflections show similar behaviours, and definitely no systematic increase in intensity below 39 K is seen. Instead the intensity varies between 50 K and 30 K and is then stable below 30 K. There is a sharp peak around 32 K ( $T_2$ ), a smaller one at 39 K ( $T_N$ ) and a broad increment between 50 and 42 K. On an absolute scale these increments are small, but they are statistically significant.

We do not have any explanation for the broad increment for temperatures between 41 K and 50 K. It does not depend on the mosaicity, and was also observed in crystals with larger mosaicity, where the measurements, however, were less accurate. The peak at 39 K is presumably induced by the magnetic order. When cooling the virgin sample through  $T_N$  we did not expect the intensity to decrease again at lower temperatures. Because the sample could not be thermally cycled the increased intensity is only observed at one temperature, which indicates that the peak in intensity near  $T_N$  must be quite narrow and may be due to fluctuations in the crystal structure. The second peak at 32 K coincides with the jump in monoclinic angle (see figure 4). Therefore one could expect this peak to disappear as the mosaicity increases. This is in agreement with the fact that we have not observed this peak in crystals with larger mosaicity.

## 6. Discussion

The monoclinic splitting has an unexpected temperature dependence; on lowering the temperature, it increases slightly, then it decreases, and finally it locks in to a fixed value at a temperature just below the temperature of the magnetic phase transition,  $T_N$ . This may be an indication of coupling between the magnetic ordering and the monoclinic distortion, the origin of which we will discuss below.



The small ferromagnetic moment is generally believed to originate in anisotropic exchange interactions of the form  $D \cdot (S_1 \times S_2)$  (Moriya 1960). From the crystal symmetry (the  $2_1$ -axis along  $a$ ),  $D$  is confined to the  $b$ - $c$ -plane. The magnetic moments in the antiferromagnet may then tilt without change of symmetry, and because no additional reflections will appear, the tilt cannot be observed in a diffraction experiment. In a Cartesian coordinate system with the  $x$ -axis along  $a$ , the  $y$ -axis along  $b$  and the  $z$ -axis along  $c^*$  two interacting moments will have the coordinates

$$S_1 = \begin{pmatrix} s_f \\ 0 \\ s_a \end{pmatrix} \quad S_2 = \begin{pmatrix} s_f \\ 0 \\ -s_a \end{pmatrix}$$

which are antiferromagnetic ( $s_a$ ) in the  $z$ -direction and ferromagnetic in the  $x$ -direction ( $s_f$ ).  $D$  is determined by the crystal symmetry, and for the very small changes in this crystal system ( $\simeq 0.4^\circ$  as seen in figure 4) we may assume that the orientation of  $D$  with respect to the unit cell will be constant. In the  $a, b, c$  coordinate system,  $D$  will be expressed as  $(0, D_b, D_c)$ , which transformed to the  $x, y, z$  coordinate system is

$$D = \begin{pmatrix} 0 \\ D_b + D_c \cos \alpha \\ D_c \sin \alpha \end{pmatrix}.$$

$D \cdot (S_1 \times S_2) = 2s_a s_f (D_b + D_c \cos \alpha)$ , or in other words, there is a coupling between the anisotropic exchange and the monoclinic distortion.

From figure 4 it is obvious that the monoclinic distortion not only is temperature dependent, but also depends on the mosaicity in the crystal. The mosaicity is connected to the internal strain in the crystal, which will decrease with decreasing mosaicity. It is apparent that there is a lock-in transition at  $T_2 \simeq 32$  K; for a virgin crystal this transition is abrupt, like a first-order transition; for a crystal that has gone through several thermal cycles and therefore has a larger mosaicity and less internal strain it is smooth, like a second-order transition.

If we assume that the intensities of the satellites are very sensitive to small changes in the crystal structure, their somewhat strange temperature behaviour can be connected to the arguments given above.

- At 39 K the crystal undergoes a second-order magnetic phase transition, and there is an associated small peak in the intensities of the satellites.

- At 32 K the monoclinic angle jumps to a constant value, and there is a corresponding peak in the intensity of the satellites.

The fact that the monoclinic distortion appears simultaneously with lock-in and rotation of the modulation vector indicates that there is also an interaction between the monoclinic distortion and the modulation.

## 7. Conclusion

After accurately measuring the intensities of the satellite reflections, we may say that the magnetic order does not give any notable contribution to the satellite intensities. The positional modulation of the Mn atoms is too small to contribute significantly, and the tilted magnetic moments do not have a rotational modulation coming from an interaction with the octahedra structure; the tilt is confined to the  $b$ -direction.

It has become clear that the dynamics of PAMC and of similar compounds depend strongly on the history of the crystal. This is seen as a mosaicity dependence of the monoclinicity

from the two different datasets shown in figure 4. With increasing mosaicity the curve becomes smoother, probably because of a decrease of the internal strain in the crystal with increasing mosaicity. It could be due to magnetoelastic effects. This dependence of the thermal history makes it difficult to do quantitative measurements on PAMC, because it is necessary to do all the measurements simultaneously, to ensure compatibility. A similar effect has been observed by Ikeda *et al* (1992), on the compound PaCuC. For a virgin sample they see an abrupt change in monoclinic angle at 168 K. This abrupt change has completely disappeared after one cooling cycle, where the change is smooth.

The behaviour of the monoclinic angle with temperature and mosaicity must have its origin in competing interactions in the crystal. We suggest that these competing interactions are the strain in the crystal, the weak ferromagnetic interactions, and the modulation waves. These three phenomena all interact with the monoclinic distortion, and therefore they become correlated.

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