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Raman study of the incommensurate layer crystal (CH₃CH₂CH₂NH₃)₂MnCl₄ (=PAMnC) from 10 to 300 K

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Abstract. The temperature dependent Raman spectra of the title compound confirm the presence of some rotational disorder of the NH₃ end groups below 112 K. The central carbon-carbon stretching mode around 865 cm⁻¹ is coupled to the order parameter of the incommensurate phase transition at 168 K. No other clear evidence of the incommensurate modulation appears in the Raman spectra between 112 and 168 K. In the *Abma* phase (above 168 K) a dynamic conformational gauche-trans equilibrium is observed. The corresponding enthalpy difference is estimated to be 18.4 ± 6.5 kJ mol⁻¹.

1. Introduction

(CH₃CH₂CH₂NH₃)₂MnCl₄ (abbreviated to PAMnC in the following text) belongs to a family of layer crystals (RNH₃)₂MCl₄ with R = methyl, ethyl, propyl, etc and M = Mn, Fe, Cd, Cu etc. These crystals undergo a variety of structural [1] and magnetic [2] phase transitions.

PAMnC presents a rich phase sequence with 5 structural phase transitions [3] (and references therein):

441 K 388 K 340 K 168 K 113 K

I4/mmm (α) ↔ *Abma* (β) ↔ *INC*(1) (γ) ↔ *Abma* (δ) ↔ *INC*(2) (ε) ↔ (ζ).

The γ and ε phases are incommensurately modulated. The non-standard space groups have been chosen to emphasize the group-subgroup relations between the different phases.

The ε-ζ phase transition is rather unique: the modulation vector $q = (\frac{1}{3} + \delta)b^*$ of the ε phase shows a strong decrease of δ when approaching $T_c = 112.5$ K. At this temperature, the modulation vector locks in at δ = 0, but additionally, it flips into the (b* - c*) direction.

This study was undertaken (completing our preliminary Raman studies [4]) to complement the available experimental data on PAMnC, especially in the low temperature ε and ζ phases. Another aim was to observe the possible manifestation of the incommensurate modulation in the Raman spectra of the ε phase.

In this paper we present polarized Raman spectra of PAMnC from 10 to 300 K in both the lattice mode region as well as in the internal mode region (up to 1700 cm⁻¹).

2. Crystal structure and low temperature phase transitions

The space group of the room temperature δ phase is *Abma* [5]. The structure consists of layers of corner-sharing MnCl_6 octahedra. These layers are connected vertically by the propylammonium groups: the NH_3 end groups form hydrogen bonds with the Cl atoms of the octahedra and the CH_3 groups of propylammonium moieties belonging to two different layers are linked by van der Waals interactions. The *Abma* phase is dynamically disordered: the propylammonium groups jump between two equiprobable sites related by the crystallographic mirror. Other crystals of this family (e.g. $(\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{MCl}_4$ with $\text{M} = \text{Mn}$ and Cd , abbreviated EAMnC and EACdC) present the same structure and disorder at room temperature [1].

The δ - ϵ phase transition is of second-order [3] (and references therein).

The crystal structure of the ϵ phase [6] shows that the dynamic disorder of the *Abma* phase is still present. Bounded projections of the $(3 + 1)$ -dimensional Fourier functions for the different atoms show (among other things) that the terminal CH_3 groups have a strong x -component modulation amplitude and a weak y -component one, while the axial Cl atom and the NH_3 groups have strong y -component modulation and a weak x -component one. Other investigations using NQR, NMR and elastic neutron diffraction [7] suggest that the origin of the incommensurate modulation is the competition between the hydrogen bonding of the NH_3 groups with the octahedra and the propylammonium chain packing by van der Waals interactions.

The ϵ - ζ transition is a first-order transition. Multiple and reversible twinning occurs below this transition [8].

The ζ phase is monoclinic with space group $P2_1/b11$ and $Z = 6$ [3, 7]. NMR measurements show that NH_3 rotational motions are still present down to 100 K, below this temperature the crystal is ordered on the timescale of this technique [7].

3. The experiment

Crystals were grown from aqueous solutions using stoichiometric amounts of the starting chlorides. These moderately hygroscopic crystals are chemically stable and can be kept for years when stored in a dessicator.

Raman measurements were performed with a laboratory assembled instrument interfaced with a personal computer for data acquisition. The measurements were done using the 488 and 514.5 nm lines of the argon laser with a typical power of 100 mW on the sample. Low temperature measurements were done with an Oxford Instruments helium flow cryostat equipped with a temperature controller. The temperatures quoted in the figures below are those read on this instrument. The sample temperature is about 3 K higher due to laser heating of the slightly absorbing crystals in the temperature domain of interest.

PAMnC crystallizes in the shape of platelets with the c -axis normal to the platelet face. The polarization measurements were done using the following referential with respect to the room temperature crystal axes:

$$X' = a + b \quad Y' = a - b \quad Z = c.$$

figure 1(A) shows the orientation for the measurements of the (ZZ) component; this element corresponds in the *Abma* phase (above 168 K) to the (cc) tensor element of A_g symmetry. In figure 1(B), the incident polarization in the laboratory frame P_{iz} yields

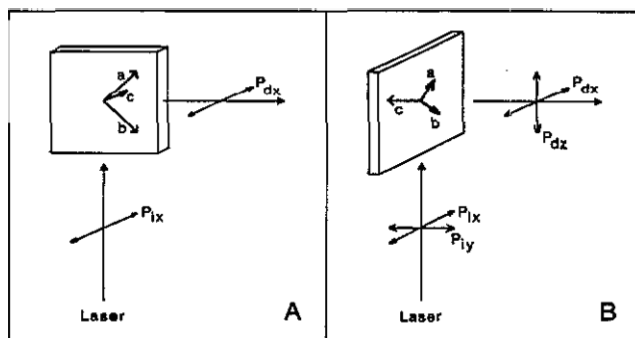


Figure 1. Geometry of the polarization experiments: laboratory referential (x, y, z), crystal referential (a, b, c), polarization referential (X', Y', Z'). The incident polarization is noted P_i , the detected polarization P_d . (A) Geometry for the measurement of the (ZZ) component. (B) Geometry for the measurement of the $(X'X') + (X'Y')$ and the $(ZX') + (ZY')$ component.

without analyser the elements $(X'X') + (X'Y')$; P_{iy} yields without analyser $(ZX') + (ZY')$.

4. Results and discussion

4.1. Low frequency Raman spectra

Figure 2 shows the low frequency spectra of PAMnC for different polarization geometries. The Raman spectra of other crystals of this family [4, 9–12] showed that the highest frequency vibration that is not an internal cation mode is the metal chloride stretching mode. In the case of PAMnC, this mode is observed at room temperature at 206 cm^{-1} [9]. The higher frequency bands arise from internal vibrations of the propylammonium groups.

The spectra at 15 K present more lines than the spectra of the monoclinic phase of $(\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{CdCl}_4$ (=EACdC) [4, 9]. For PAMnC in the ζ phase with $Z = 6$, factor group analysis predicts 39 modes of A_g symmetry and 39 modes of B_g symmetry at the zone centre. In each of the 3 polarization geometries shown in figure 2, there are about 23 to 30 bands observed below 220 cm^{-1} . This number of observed bands is compatible with the proposed size of the unit cell.

It is important to note that the low temperature spectra of PAMnC in the $(X'X') + (X'Y')$ polarization do not present the NH_3 torsional mode around 300 to 330 cm^{-1} as observed in the similar crystals EAMnC, EACdC and PACdC [9, 10]. Instead, one observes at 15 K two strong bands between 235 and 270 cm^{-1} in this polarization. They arise from the NH_3 torsional mode which interacts with the CH_3 torsional mode. A similar interaction had been observed in the low temperature Raman spectra of *N*-deuterated EACdC (unpublished results obtained by H Hagemann). A further argument in favour of this assignment are the infrared spectra of PAMnC at 90 K [13] which showed a weak NH_3 bending and torsional combination band around 1820 – 1850 cm^{-1} and which yielded an estimated NH_3 torsional mode frequency of 270 cm^{-1} . The present Raman observation confirms that the value of the fundamental frequency

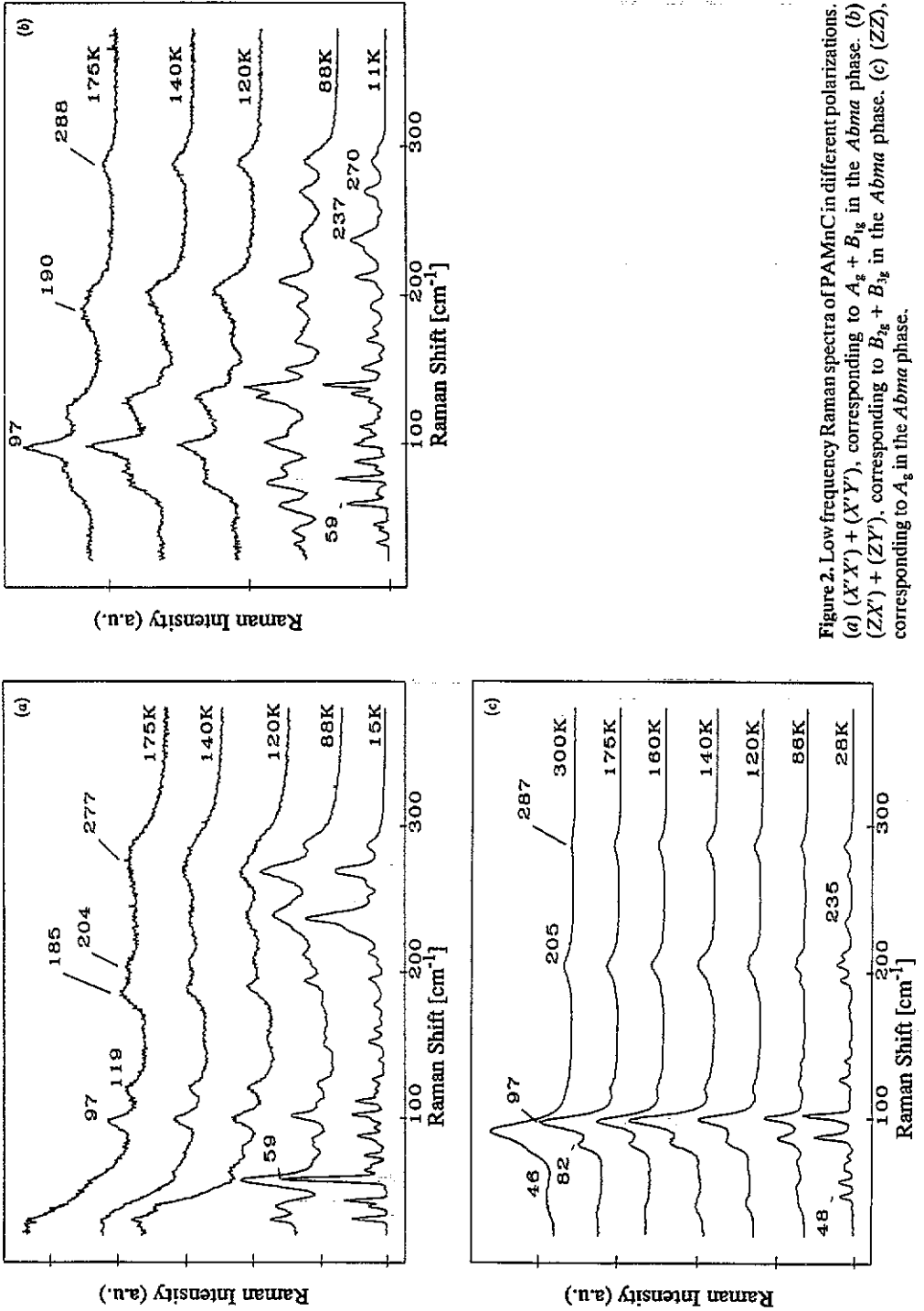


Figure 2. Low frequency Raman spectra of PAMnC in different polarizations. (a) $(X'X') + (X'Y')$, corresponding to $A_g + B_{1g}$ in the $Abma$ phase. (b) $(ZX') + (ZY')$, corresponding to $B_{2g} + B_{3g}$ in the $Abma$ phase. (c) (ZZ) , corresponding to A_g in the $Abma$ phase.

of the NH_3 torsional mode in PAMnC is about 270 cm^{-1} or below, i.e. that the hydrogen bond strength in PAMnC is weaker than in the other crystals of this family.

The band around 285 cm^{-1} (clearly seen in the (ZZ) polarization) appears equally in the cadmium analog PACdC [9, 10] as well as in the spectra of the *n*-propylammonium halides (Cl, Br, I) [4]. This internal propylammonium vibration is assigned by analogy with the spectrum of *n*-butane [14, 15] and the following arguments to a (CCCN) deformation mode.

The five lowest frequency cation vibrations correspond to three torsional modes and two skeletal deformation modes. The torsional modes are expected below 285 cm^{-1} for the propylammonium group in PAMnC: the NH_3 and CH_3 torsions were identified above, and are located between 270 and 235 cm^{-1} . The torsion around the central carbon-carbon bond is expected at even lower frequencies (122 cm^{-1}) for *n*-butane [15]. The *ab initio* calculation for different conformers of the *n*-propylammonium group [16] yielded results similar to those for butane: this supports the proposal that the potentials for the torsion around the central carbon-carbon bond of butane and *n*-propylammonium are comparable.

The spectra at 88 K (figure 2) show significant broadening of several bands. The half-width at half-maximum (HWHM) of the bands at 235 and 268 cm^{-1} (CH_3 and NH_3 torsional modes) in the (ZZ) polarization increases from 4.3 and 3.3 cm^{-1} at 28 K to 7.2 and 8.2 cm^{-1} , respectively, at 85 K. These bands present the strongest broadening observed. Other bands broaden less from 28 to 88 K: e.g. the Mn-Cl stretching mode at 206 cm^{-1} broadens from 2.5 to 4.3 cm^{-1} (HWHM), and the CCCN deformation mode at 285 cm^{-1} broadens only very slightly from 4.7 to 5.3 cm^{-1} . Additionally, the spectra in the $(X'X') + (X'Y')$ polarization show clearly the appearance of Rayleigh wings, whereas those in the $(ZX') + (ZY')$ polarization develop this feature to a much less extent. In accordance with earlier findings [7], these facts tend to show that NH_3 group dynamics is important in this temperature range. Around 100 K, the band positions agree with those reported by Adams and Stevens [17].

The ϵ - ζ phase transition manifests itself by the following spectral changes:

(i) There are sudden changes within 3 K in the spectra, in accordance with the first-order nature of this transition.

(ii) Several lines disappear with increasing temperature (e.g. at 58 cm^{-1} in all polarizations). The disappearance of the bands at 235 and 268 cm^{-1} in the $(ZX') + (ZY')$ polarization probably illustrates the factor group change from monoclinic to orthorhombic symmetry, by analogy with the behavior of the NH_3 torsional mode in EACdC around 112 K [4, 18].

(iii) The strong and broad Rayleigh wing as well as a broad band around 270 cm^{-1} that appear above 112 K in the $(X'X) + (X'Y')$ polarization are very similar to those observed and discussed for all crystals of this family in the *Abma* phase [9-12]. These features are characteristic of the disorder of the entire organic group (jumps between the two mirror plane related sites). This observation shows that the disorder of the organic group in the incommensurate ϵ phase is similar to the disorder in the δ phase.

Almost no spectral changes are observed between 120 and 175 K in the three polarizations shown in figure 2, illustrating the second-order nature of the δ - ϵ transition. In the (ZZ) polarization, the three components of the Mn-Cl stretching mode are still distinguishable at 120 K; they collapse into a single line at 175 K. However, the important overlap of these bands does not allow one to monitor the convergence of these bands without significant error margins. Similarly, there are other weak bands in the other

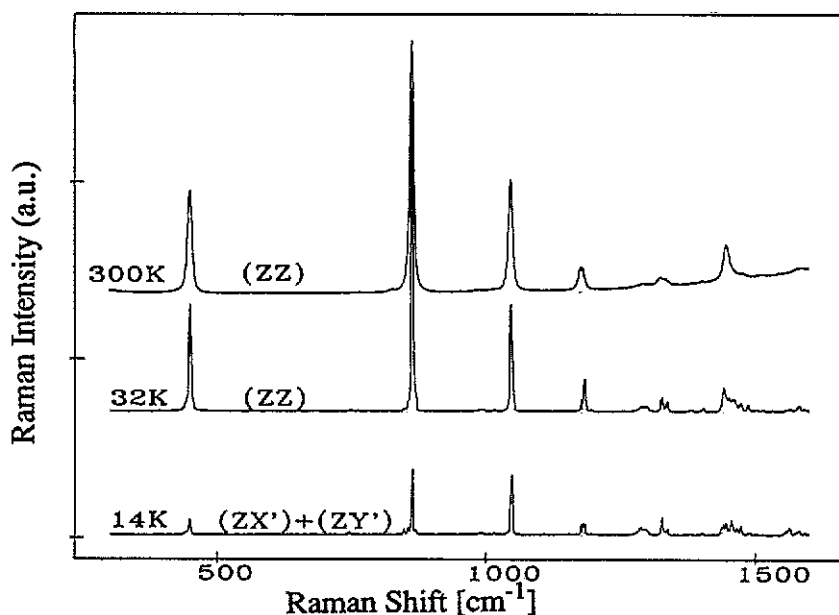


Figure 3. High frequency Raman spectra of PAMnC.

polarizations that disappear at 175 K and that cannot be analyzed because of their intrinsically low signal-to-noise ratio. No amplitudon or phason is observed in the low frequency Raman spectra in the incommensurate ϵ phase.

Adams and Stevens [17] have obtained polarized FIR spectra of PAMnC at the following temperatures: 50, 100, 190 and 295 K. Significant changes are observed between 50 and 100 K as well as between 100 and 195 K. Between 50 and 100 K, the bands at the lower and higher frequency side (about 70 and 210 cm^{-1} at 50 K) move towards the other bands (to about 75 and 190 cm^{-1} at 100 K). Recall that there is no phase transition between 50 and 100 K.

Between 100 and 190 K, the FIR bands converge even further, in agreement with the reduction of the unit-cell size across the phase transitions at 112.5 and 168 K.

4.2. High frequency Raman spectra

Figure 3 shows survey Raman spectra from 300 to 1600 cm^{-1} . The values of the room temperature Raman shifts for the $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+$ species are collected in table 1. The assignments proposed in this table have been obtained by comparison with force field calculations for the isoelectronic butane [14, 15] and our previous studies of alkylammonium halides [4, 16, 19, 20]. It is important to note that the calculations for butane suggest that the 865 cm^{-1} band has mainly central carbon-carbon stretching character, while the 1050 cm^{-1} band corresponds rather to the terminal carbon-carbon stretch. Both modes, however, present important couplings (up to 40% of the potential energy distribution) with other modes [14, 15]. It is characteristic for the (ZZ) polarized spectra of this family of crystals to present very strong bands for the skeletal stretching and deformation modes (see figure 3).

Table 1. Raman shifts (in cm^{-1}) of the internal propylammonium modes in PAMnC at room temperature. Abbreviations used to describe relative intensities: sh = shoulder, vvw = very very weak, vw = very weak, w = weak, m = medium, ms = medium strong, s = strong, vs = very strong, vvs = very very strong.

(ZZ)	(ZX') + (ZY')	(X'X') + (X'Y')	Assignment
287vw			CCCN def. (trans)
	349vwv		CCCN def. (gauche)
450s	450ms	451w	CCCN def. (trans)
	736vw		
	751vw	756vwv	CH ₂ rocking
825vw	829vw	828vw	CCCN stretch (gauche)
862vvs	862vs	865s	CCCN stretch (trans)
954vwv	952vwv		CCCN stretch (gauche)
990vw	988vw	993w	NH ₃ rocking
1021vwv		1022w	CCCN stretch (gauche)
1047vs	1046vs	1048ms	CCCN stretch (trans)
1178ms	1177m	1180ms	CH ₃ and CH ₂ twisting
1291w	1290ms		CH ₂ twisting
1324m			
1332m	1333s	1336m	CH ₂ twisting
	1383vw		
1401vw	1400vw		CH ₃ sym. deformation
1447ms			
1458sh	1458s	1453vs	CH ₃ def. or CH ₂ scissoring
1475w	1487sh	1481m	CH ₂ scissoring
1512vw			
1582w	1573m	1580m	NH ₃ deformation

The temperature dependent spectra (figure 4) of the bands around 450 (CCCN bending), 865 (central CC stretching) and 1050 cm^{-1} (terminal CC stretching) reveal two or more components in the ζ phase. The detailed investigation as a function of temperature of these bands revealed critical behavior present in all three regions shown, but illustrated most clearly in figure 4(b).

Using the band pairs at 443–451, 864–870 and 1048–1051 cm^{-1} , we have plotted the relation:

$$\ln[(\Delta\nu_a - \Delta\nu_b)_T / (\Delta\nu_a - \Delta\nu_b)_{T=5K}] = A \ln[(T_c - T)/T_c] + B$$

where $T_c = 112$ K. Figure 5 shows that the slope $A = 0.095 \pm 0.03$ applies for all three bands within experimental error. However, it is important to stress that the split components do not result in a single band, as is expected for a first-order phase transition at 112 K (see figure 4).

The band around 865 cm^{-1} (figure 4) exhibits interesting behavior in the ε phase. At 112 K, the high frequency shoulder becomes much stronger than at lower temperatures. Increasing the temperature from 112 to 160 K, the intensity of the lower frequency component decreases continuously; at 185 K, a single symmetrical line remains.

Using the band pair at 864–870 cm^{-1} , we have plotted the relation (figure 6):

$$\ln[(\Delta\nu_a - \Delta\nu_b)_T / (\Delta\nu_a - \Delta\nu_b)_{T=5K}] = A \ln[(T_i - T)/T_i] + B$$

where $T_i = 168$ K. The resulting slope is found to be $A = 0.45 \pm 0.05$. The plot shown

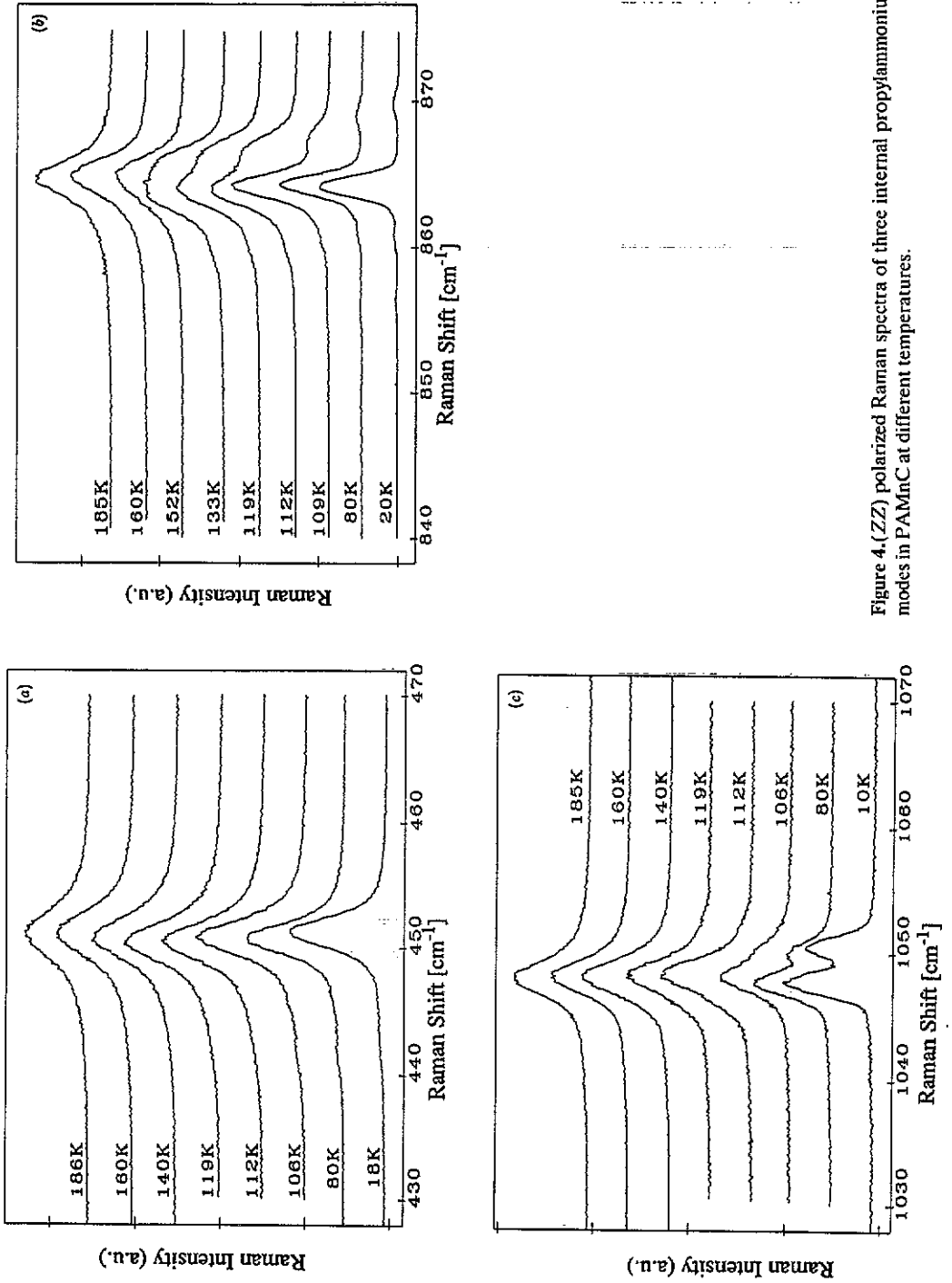


Figure 4. (ZZ) polarized Raman spectra of three internal propylammonium modes in PAMnCl at different temperatures.

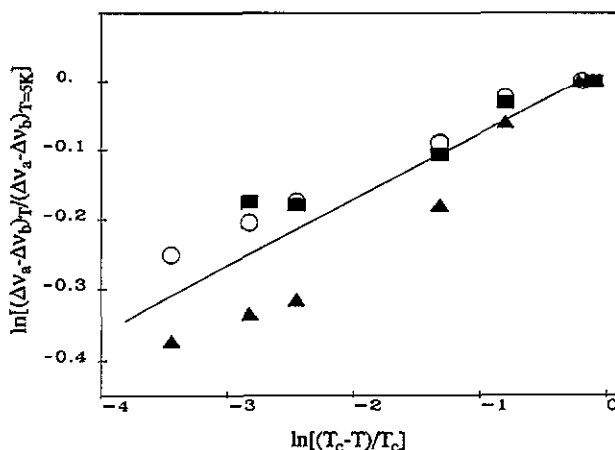


Figure 5. In-ln plot (see text) of the line splitting versus $(T_c - T)/T_c$ for the three bands shown in figure 4. The position of the bands quoted below are those measured at 10 K. \circ band pair at 443–451 cm^{-1} ; \blacktriangle : band pair at 864–870 cm^{-1} ; \blacksquare : band pair at 1048–1051 cm^{-1} .

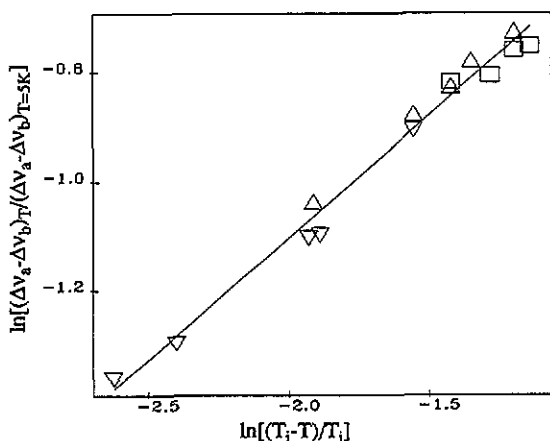


Figure 6. In-ln plot (see text) of the line splitting versus $(T_i - T)/T_i$ for the 865 cm^{-1} band. The symbols distinguish measurements with 3 different crystals and different thermal history.

in figure 6 collects measurements with three different crystals: the first was cooled to 60 K and subsequently heated up to 120 K, the second cooled to 140 K and carefully cooled to 115 K but not below the phase transition temperature, and the third crystal was cooled to 130 K and then heated to 160 K. The value of A can be compared with determinations of the critical exponent of the incommensurate ϵ phase by NQR ($\beta = 0.37 \pm 0.03$), quadrupole perturbed D-NMR ($\beta = 0.38 \pm 0.04$) and elastic neutron diffraction ($\beta = 0.43 \pm 0.03$) [7]. The value obtained from the Raman line splittings is approximately equal to the value of the order parameter. This suggests that the coupling with the order parameter η is of the type $\eta Q^* Q$ for this mode.

The band at 1050 cm^{-1} does not present an absolutely symmetrical lineshape in the ϵ phase. Attempts to resolve individual components with smaller slit widths (down to 40 microns) were unsuccessful. Estimates from the observed total linewidth or from line

fittings show that the splitting (if present) is of the order of 0.5cm^{-1} , while the HWHM for the individual band is about $1\text{--}1.5\text{cm}^{-1}$.

Other continuous spectral changes in this temperature range (112–160 K) are also observed between 1400 and 1600cm^{-1} (figure 7); this is illustrated very clearly by the NH_3 deformation mode in the $(ZX') + (ZY')$ polarization around 1573cm^{-1} where the high frequency shoulder disappears with increasing temperature. Interestingly, it appears that a log–log plot similar to those mentioned above yields a very different slope, namely 0.19 ± 0.05 . This observation is possibly related to the fact that the hydrogen bonding of the NH_3 group is one of the two competing interactions which are at the origin of the incommensurate modulation [7].

Different types of coupling with the order parameter have also been observed by NQR measurements [7] for the axial and equatorial Cl atoms in PAMnC in this phase.

At 20 K, 5 components are observed for the NH_3 bending mode around 1575cm^{-1} : this number of factor group split components remains compatible with a unit-cell size of $Z = 6$. The width of these bands between 1550 and 1600cm^{-1} is larger than the width of the CH_2 bending modes around 1450cm^{-1} and confirms the local dynamics of the NH_3 group below 112 K.

The room temperature Raman spectra (figure 8) present several weak bands assigned to gauche conformers (see table 1). These bands disappear upon cooling to 170 K and reappear upon heating. Preliminary measurements of the intensity ratio of the bands at 826 and 865cm^{-1} at different temperatures from 200 to 300 K yield an enthalpy difference of $18.4 \pm 6.5\text{kJ mol}^{-1}$ ($=4.4 \pm 1.5\text{kcal mol}^{-1}$) between gauche and trans conformers in the δ phase. This enthalpy difference is rather large when compared with the calculated 4–31G *ab initio* value [16] for an individual gaseous propylammonium group (1.09kJ mol^{-1}) and shows that there is only limited space available in the crystal for gauche conformers. Using the value of 18.4kJ mol^{-1} , the ratio of gauche over trans conformer concentration is about 0.13% at 300 K.

5. Conclusions

The Raman spectra of PAMnC between 10 and 300 K yield (in agreement with other experiments [3, 7]) the following conclusions.

5.1. ζ phase

The low and high frequency Raman spectra between 10 and 40 K show an ordered crystal. The total number of observed bands supports the proposed unit cell size of $Z = 6$. No spectral changes were observed around the (antiferromagnetic) magnetic phase transition at $T_N = 39.2\text{K}$.

Upon heating progressively to 100 K, several features (line broadening, appearance of Rayleigh wings) indicate the onset of some rotational disorder of the NH_3 end groups. Using the relation [21]:

$$V_0 = \omega_t^2/4n^2A$$

which estimates (harmonic approximation) the potential barrier V_0 associated with small amplitude torsional vibrations for a sinusoidal potential function, we obtain $V_0 \approx 13.8\text{kJ mol}^{-1}$ (3.3kcal mol^{-1}) for a threefold barrier and $V_0 \approx 3.3\text{kJ mol}^{-1}$ (0.8kcal mol^{-1}) for a sixfold barrier. We have used for this estimation $\omega_t = 270\text{cm}^{-1}$;

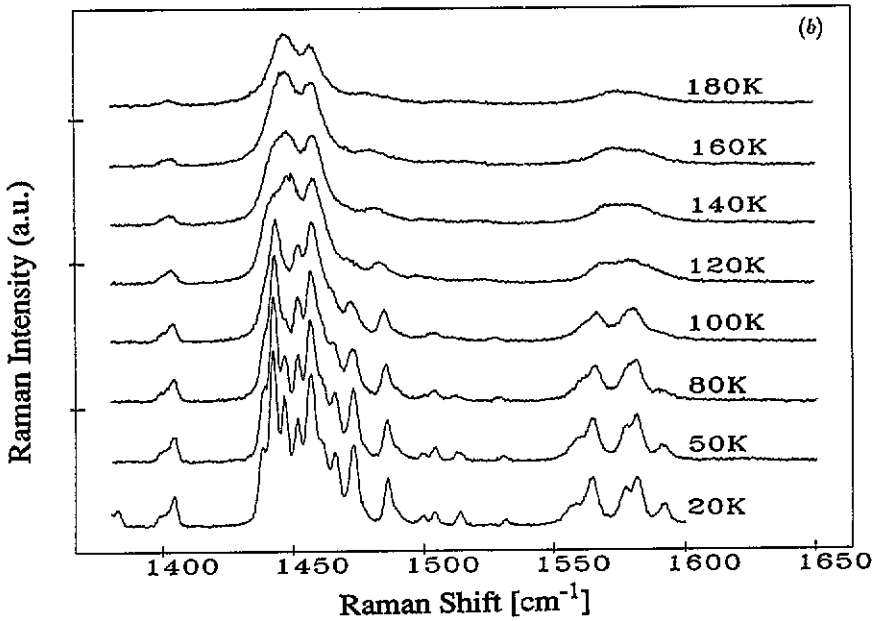
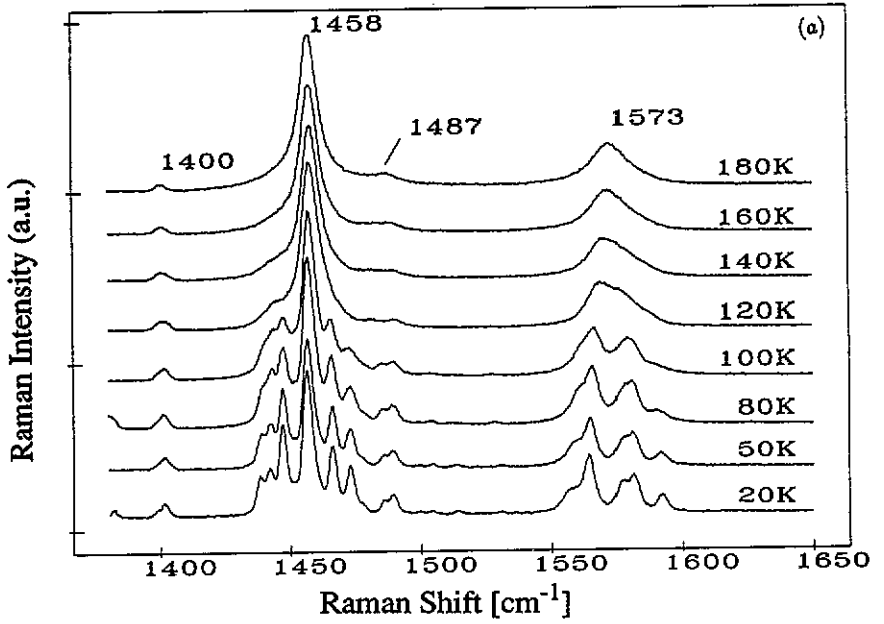


Figure 7. Raman spectra of PAMnC between 1380 and 1650 cm^{-1} at different temperatures. (a) $(ZX') + (ZY')$; (b) (ZZ) .

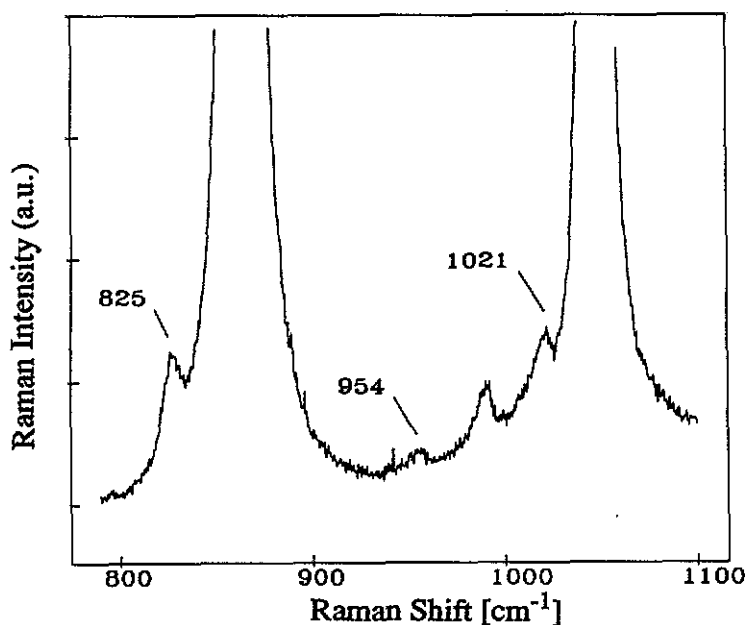


Figure 8. Room temperature Raman spectrum of PAMnC showing the presence of gauche conformers (bands at 825, 954 and 1021 cm^{-1}).

the rotational constant A was obtained via the data of Sourisseau and Lucazeau [22] for the layer crystal $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{MnCl}_4$. These relatively low values of the potential barrier justify the presence of NH_3 rotational disorder around 100 K in PAMnC.

The temperature dependant Raman spectra reveal critical behaviour (illustrated for three internal cation modes), but the band pairs studied do not collapse into single lines at the first-order transition at 112.5 K.

It is interesting to note that the FIR spectra of PAMnC [17] at 50 and 100 K are also somewhat reminiscent of critical behaviour.

5.2. ε phase

The ζ - ε phase transition is a first-order transition. In the ε phase, the disorder of the entire organic groups is similar to that in the δ phase (jumps between mirror-plane related sites).

No direct evidence of the incommensurate modulation of the ε phase is detected in the Raman spectra; the strong scattering at low Raman shifts (related to the disorder) probably prevents the observation of very low frequency Raman signals related to the modulation.

The temperature dependence of the splitting of the CCCN stretching mode at 865 cm^{-1} indicates a coupling with the order parameter. However, the important overlap of the split band pair results in a rather large experimental error for the determination of the critical exponent. Qualitatively, if one considers the presence of competing interactions at both ends of the propylammonium molecule (hydrogen bonding of the ammonium group and van der Waals interactions of the methyl group) the coupling of this central carbon-carbon stretching mode with the order parameter is not illogical. In

the diammonium crystals $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\text{MCl}_4$ with $M = \text{Cd}$ and Mn , the terminal ammonium group are oriented in different directions and in the high temperature phases twisted conformations are observed [23]. In the Raman spectra, these conformational changes are clearly seen in both skeletal stretching ($800\text{--}900\text{ cm}^{-1}$) and bending ($400\text{--}450\text{ cm}^{-1}$) regions. This observation confirms the sensitivity of these skeletal motions to torsional constraints.

The $\epsilon\text{--}\delta$ phase transition is a second order transition; the low frequency spectra change only very slightly between 120 and 175 K.

5.3. δ phase

The low frequency Raman spectra in this phase are very similar to the spectra of other crystals of this family (e.g. EACdC) in the *Abma* phase [9]. The high frequency Raman spectra from 200 to 300 K show that dynamic conformational disorder is present additionally in PAMnC. Due to the steric hindrance, the population of gauche isomers remains relatively low: at 300 K, the gauche population is estimated to be about 0.13%. It will certainly be of interest to monitor the conformational equilibrium at higher temperatures through the reentrant incommensurate γ -phase and in the β -phase. This subject will be studied in the near future.

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