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## Liquid Crystals

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### Raman spectroscopic investigations of the structure and phase transitions of liquid crystalline lead(II) alkanooates

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## Raman spectroscopic investigations of the structure and phase transitions of liquid crystalline lead(II) alkanooates

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Lead(II) alkanooates with even chain lengths from octanoate to octadecanoate have been investigated by Raman spectroscopy. In the low frequency region, transverse and longitudinal acoustical modes (TAM, LAM) have been assigned. It was shown that LAM-1 is the vibration of the double chain with the node of the vibration in the  $\text{Pb}^{2+}$  layer. A fully extended conformation of the chains in the low temperature phase was confirmed. The frequencies and intensities of the LAMs as compared with those of the alkanes and the fatty acids led to an estimate of the force constant and polarizability of the  $\text{Pb}^{2+}-\text{COO}^-$  bond relative to the C-C bond. The defects at the chain ends were investigated in the  $\nu(\text{CH}_3)$  and  $\nu(\text{CC})$  region. For the intermediate (CM) phase, both the  $\text{Pb}^{2+}$  layer distance reduction and the chain length independent enthalpy contributions can be attributed mainly to defects at the chain ends.

### 1. Introduction

Long chain lead(II) alkanooates show one or more mesophases between the solid and isotropic liquid [1-4]. The lead(II) alkanooates with all even chain lengths from octanoate to octadecanoate will be referred to here as **Pb-C<sub>8</sub>**, **Pb-C<sub>18</sub>**, etc. Previous X-ray powder diffraction [1-3],  $^{207}\text{Pb}$  NMR [4], Raman [1, 2] and infrared [2, 5] spectral studies have shown that the solid phase (C) consists of a lamellar structure built up from planes containing equivalent metal ions with the carboxylate chains arranged in an all-*trans*-conformation at right angles to these layers (see figure 1).

With increasing temperature, the carboxylates show a transition to a highly ordered phase (either crystalline or highly ordered smectic) denoted CM. The enthalpy of this transition ( $135 \text{ J g}^{-1} (\text{CH}_2)$ ) can be attributed mainly to a loosening of the chain packing, with only limited conformational disordering of the hydrocarbon chains [2]. The mean reduction in the  $\text{Pb}^{2+}$  layer distance is about  $1.9 \text{ \AA}$ , whilst the molecular cross-section increases by  $2.5 \text{ \AA}^2$  [2].

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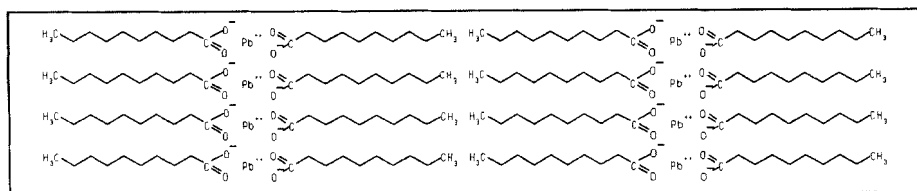


Figure 1. Low temperature solid phase (C) of lead(II) decanoate.

Further heating of the longer chain carboxylates (**Pb-C<sub>14</sub>** to **Pb-C<sub>18</sub>**) results directly in the melt transition, whereas the shorter ones show a smectic A (*L<sub>a</sub>*) mesophase (denoted M), characterized spectroscopically by considerable chain disorder and decreased lead-carboxylate interactions [2]. The lamellar spacing *d* is significantly reduced, with the variations of *d* with the chain length *n* being 0.7 Å/CH<sub>2</sub> (cf 1.25 Å/CH<sub>2</sub> in the phases C and CM). The molecular cross-section increase for lead(II) decanoate compared to the CM phase is about 7.5 Å<sup>2</sup> [2]. The enthalpy of the CM/M transition is 180 J g<sup>-1</sup> (CH<sub>2</sub>) [2]. In this study, our intention is to look for transverse and longitudinal acoustical modes (TAM, LAM) and to locate the conformational defects, especially those involved in the C→CM transition.

## 2. Experimental

The preparation, purification and characterization of the lead(II) carboxylates have been described elsewhere [1, 2]. Raman spectra of recrystallized samples in 2 mm capillaries were recorded on a Spex 1403 double monochromator equipped with a PMT (RCA) and a CCD camera (Photometrics, model CH260) as detector systems. Scattered light was collected at 90°, the spectral resolution being in most cases 2.5 cm<sup>-1</sup>. The output of the argon-ion laser (Coherent, model Innova 70-2) at 514.5 nm was adjusted to provide not more than 50 mW at the sample to prevent local heating. Temperature was regulated by a West 3800 controller with an accuracy of ± 1 K. For band fitting and integration we used the FIT program (Spectrum Square Associates) running under LabCalc (Galactic). Peak shapes chosen were a sum of gaussian and lorentzian (asymmetric lorentzian for fitting the Rayleigh Line); errors reported for intensities are calculated from the covariance matrix.

## 3. Results

### 3.1. Low frequency region

The low frequency Raman spectra (up to 500 cm<sup>-1</sup>) were recorded for solid even chain length lead(II) alkanoates **Pb-C<sub>8</sub>**—**Pb-C<sub>18</sub>**. In the low temperature crystalline phase, the chains are in an all-*trans*-conformation. Two chains are coupled with their carboxylate ends via Coulombic and covalent interactions to a Pb<sup>2+</sup> ion. This is similar to fatty acids and long chain alcohols, which have a dimeric coupling through hydrogen bonds. In those systems, the LAM-1 band is the accordion-like ground vibration of the double chain with the node of the vibration in the plane in between the chains [6, 7]. In the past, this caused some confusion when the frequencies of LAMs have been compared to that of alkanes with the same chain length [6]. It was of interest for us whether the results for these systems could be transferred to the lead(II) alkanoates.

Additionally, the TAMs have been investigated, both to get information about the crystalline structure and to check the possibility of transferring the results gained with

alkanes [8] to other systems. The TAMs include in-plane bending, out-of-plane bending and twisting modes. Since the atoms vibrate perpendicular to the chain axis, the frequencies of the TAMs are, in contrast to the LAMs, critically dependent on the lattice interactions. Because of our observation of band splitting in the  $\delta(\text{CH}_2)$  region, an orthorhombic sub-cell structure for the lead(II) carboxylates has been assumed. This is confirmed by the assignment of the TAMs, which are comparable to those of the orthorhombic *n*-alkanes [8].

Figures 2 and 3 show an overview of the spectra. The frequencies of the TAMs and LAMs are listed in tables 1 and 2. Both the frequencies of the LAMs and the TAMs match the dispersion relations deduced by Olf and Fanconi (table 3) [8]. The spectra of the *n*-alkanes  $\text{C}_{2n}\text{H}_{4n+2}$  [8,9 and references therein] and **Pb-C<sub>n</sub>** are comparable. Therefore, we calculated the phase relations of the double chain. The plots showing the frequencies as a function of the phase (figures 4 and 5) confirm this assignment. For the TAMs the deviations at smaller phase angles, i.e. smaller chain lengths can be explained by the pinning of the double chains in their middle because of the Pb-Pb interactions.

Band splitting of the longitudinal modes is caused by interaction with other vibrations (for example, LAM-1 interacts in some cases with TAM-1 and TAM-2). Minoni *et al.*, presented a coupled oscillator model for the interpretation of LAMs of dimerized chain molecules [7]. Considering the frequencies and intensity ratios of the LAMs, it is possible to estimate the force constant and the polarizability of the coupling bond relative to the C-C bonds within the chains. The frequencies  $\nu_k$  and integrated

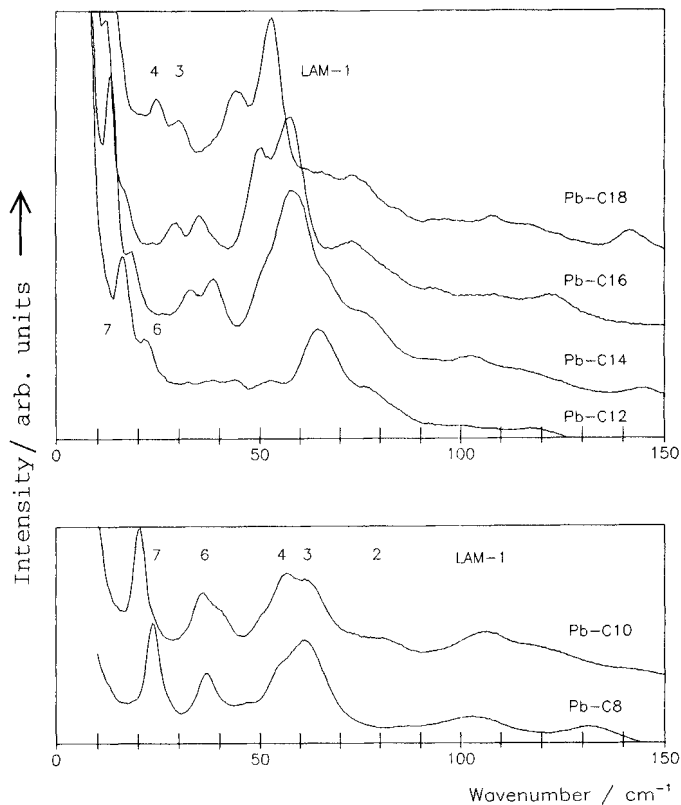


Figure 2. TAM band series (2-7) and LAM-1 of the lead(II) alkanoates.

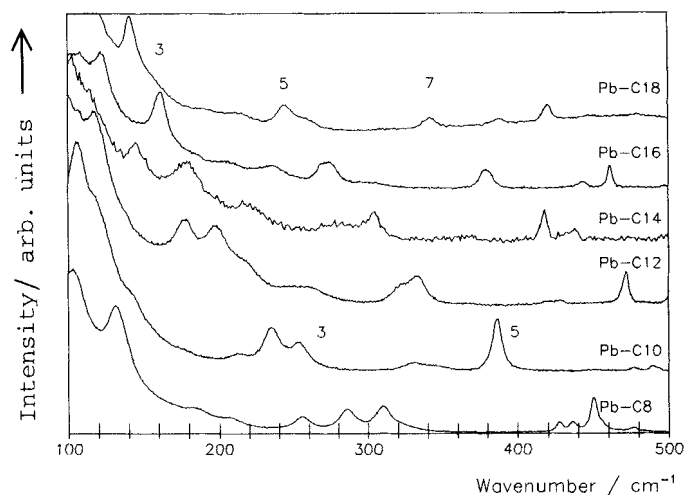


Figure 3. LAM-3/5/7 of the lead(II) alkananoates.

Table 1. Wavenumbers of the TAM band series.

Sample Pb-C <sub>n</sub>	$\nu/\text{cm}^{-1}$						
	TAM-1	TAM-2	TAM-3	TAM-4	TAM-5	TAM-6	TAM-7
<b>8</b>		85.1	60.9	54.0	44.1	36.2	22.9
<b>10</b>		78.8	62.0	55.5	39.1	34.1	19.3
<b>12</b>	99.8	51.4	35.9	31.0	21.8	15.6	
<b>14</b>	102.7		38.7	32.6	23.3	18.2	13.0
<b>16</b>	105.1		34.9	27.9			13.0
<b>18</b>	108.6		29.8	23.2	(20)		

Table 2. Wavenumbers of the LAM band series.

Sample Pb-C <sub>n</sub>	$\nu/\text{cm}^{-1}$			
	LAM-1	LAM-3	LAM-5	LAM-7
<b>8</b>	102.3/132.3	255.2/285.0/309.7	426.9/435.7/449.8	
<b>10</b>	104.7/121.4/140.0	210.7/234.0/252.9	385.6	
<b>12</b>	64.1	198.0	320.7/332.7	471.1
<b>14</b>	57.6/75.4	178.5	303.5	417.2
<b>16</b>	49.1/57.0	160.5	272.3	378.7
<b>18</b>	43.2/52.2	142.5	243.9	341.2

Table 3. Dispersion relations of the TAM band series [8].

TAM	2	3	4	5	6	7
Phase	$\frac{n-4}{n-1}$	$\frac{n-6}{n-2}$	$\frac{n-1}{n+1}$	$\frac{n-2}{n+1}$	$\frac{n}{n+1}$	$\frac{n-1}{n+1}$
$\pi$	$\frac{n-4}{n-1}$	$\frac{n-6}{n-2}$	$\frac{n-1}{n+1}$	$\frac{n-2}{n+1}$	$\frac{n}{n+1}$	$\frac{n-1}{n+1}$

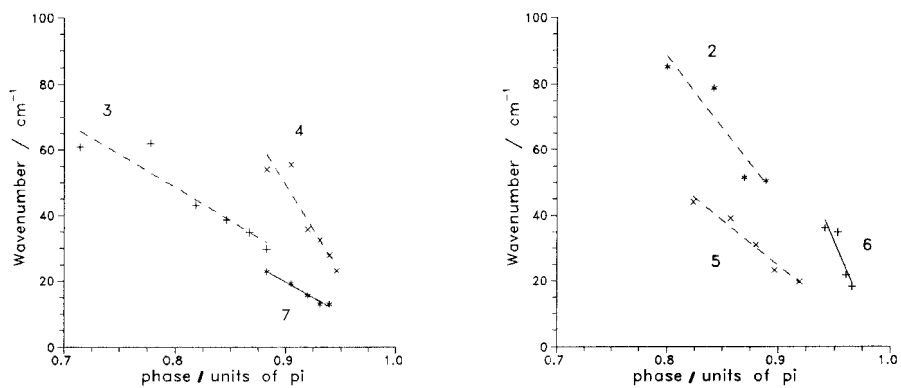


Figure 4. TAM progression frequencies versus phase (calculated for the double chain  $2n$ ).

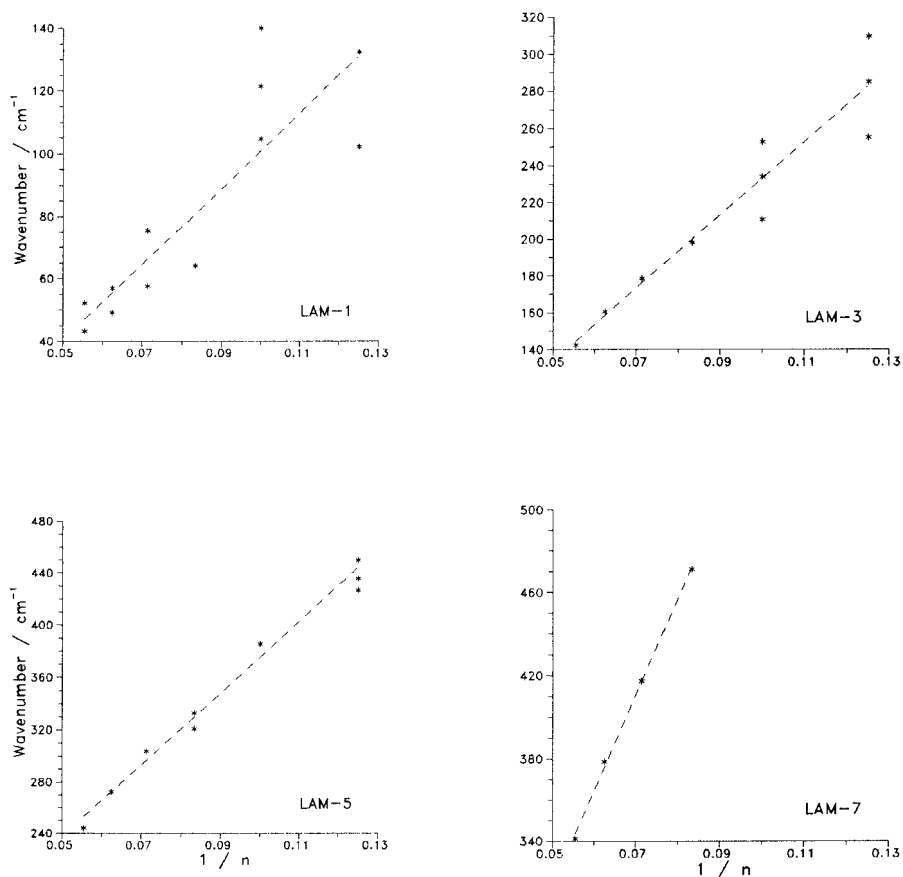


Figure 5. LAM progression frequencies versus inverse chain length  $n$  (proportional to phase).

intensities  $I_k$  of the LAMs were determined by band fitting ( $k$  denotes the mode of the LAM). Eliminating the temperature factor  $f_T(v_k)$ , the scattering activities which do not depend on temperature,  $S_k$ , were calculated.

$$I_k = S_k f_T(v_k), \quad f_T(v_k) = \frac{1}{1 - \exp(-hv_k/kT)}$$

With these data a force constant ratio of about 0.085 for the coupling bond ( $-\text{COO}^- \text{Pb}^{2+} - \text{OOC}-$ ) relative to the C–C bond is calculated. The polarizabilities of the coupling and of the C–C bond are approximately of the same size. Because the node of the LAMS is located in the Pb layer, the coupling bond can be considered as a series connection of two bonds. In a first approximation, the polarizabilities are additive, whereas for the calculation of the overall force constant the reciprocal values of the single force constants must be added. So the force constant ratio of the  $-\text{COO}^- \text{Pb}^{2+}$  bond is 0.17, whereas its polarizability is about half as large as that of the C–C bond.

At a first glance, the force constant seems to be rather low for a predominantly ionic interaction, whereas the X-ray diffraction [10] and the infrared spectral studies [5] suggest a marked covalent character for the Pb–O bond in lead(II) alkananoates. Attempts were made to study the low frequency Raman spectra in the other phases of the lead(II) alkananoates. Unfortunately, at the C→CM phase transition, the lines broaden and are smeared into the Rayleigh line.

### 3.2. $\rho(\text{CH}_3)$ region

In order to examine conformational disorder, the  $\rho(\text{CH}_3)$  frequency region ( $830\text{--}900\text{ cm}^{-1}$ ) was studied. In this spectral region, bands appear which are associated with specific localized modes at the end of an aliphatic chain and involve primarily methyl rocking and CC stretching coordinates [11]. Kim *et al.*, calculated the dependence of the frequencies on the conformation at the chain end (for  $tt-$ ,  $gt-$ ,  $gg-$ ,  $tg-$ ,  $ttg-$ ,  $gtg-$ , where the dash denotes an all-*trans*-conformation of the remaining part of the chain) [11]. Because the intensity factors are known, it is possible to calculate quantitatively the chain end conformations. We investigated the temperature dependence of all the available lead(II) carboxylates in this frequency region. Figure 6 shows typical spectra with all observed defect bands. In figure 7 the concentration of the chain end

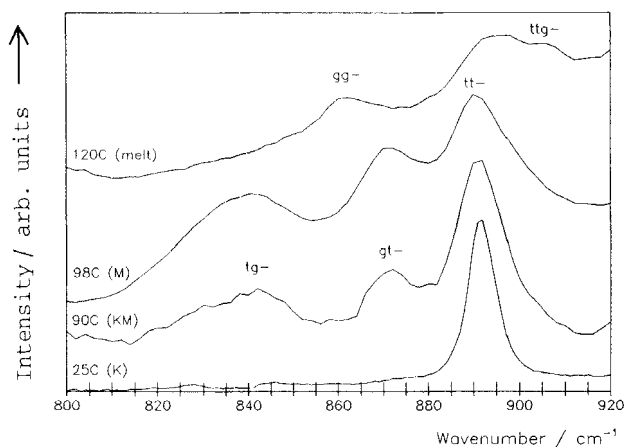


Figure 6.  $\rho(\text{CH}_3)$  bands of  $\text{Pn-C}_{10}$ . The defect bands; temperatures and phases are indicated.

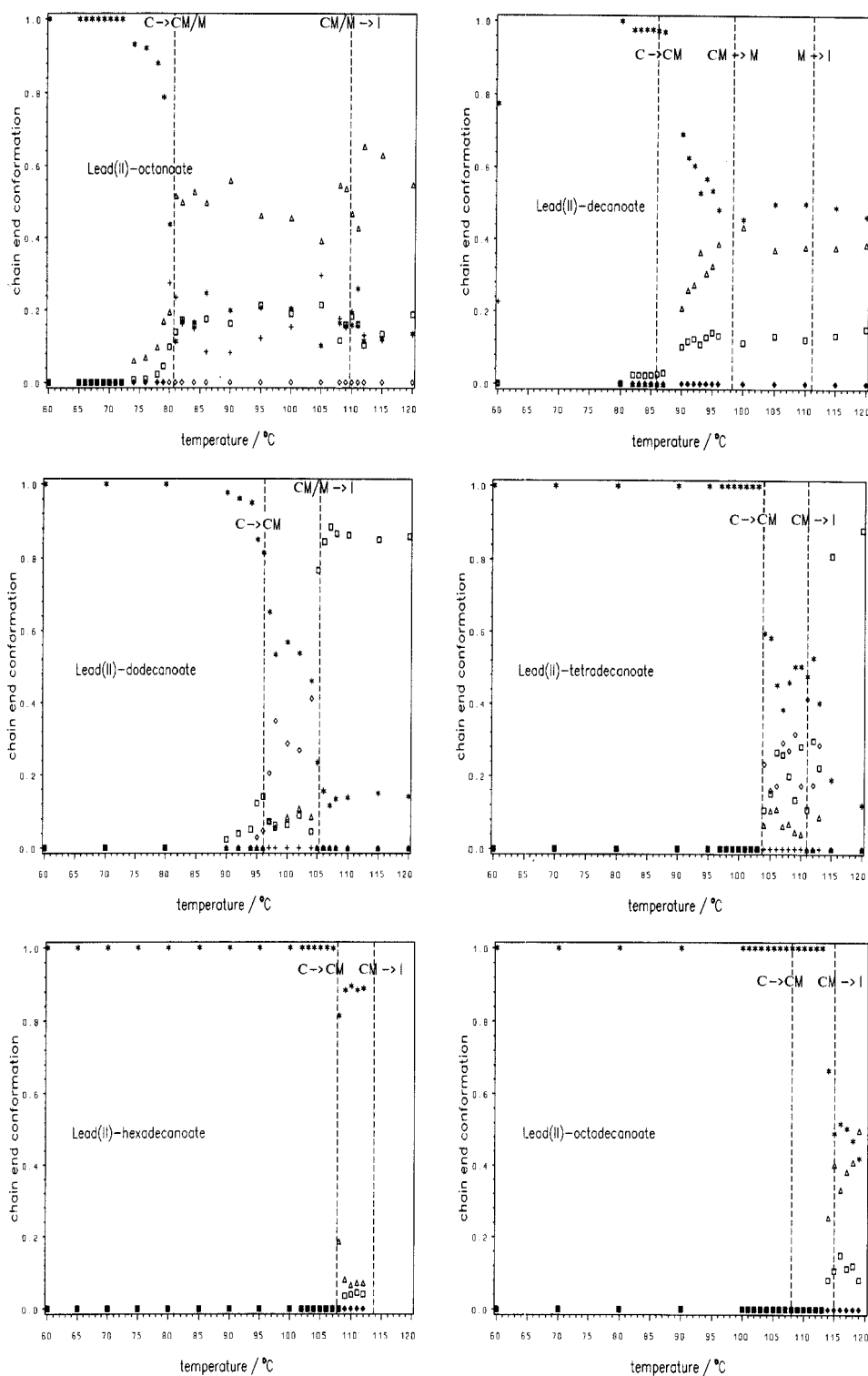


Figure 7. Concentration of the chain end conformations for the even-membered homologous lead(II) alkanooates (Δ) t-g; (◇) g-g; (□) g-t; (\*) t-t; (+) t-t-g.



conformations is plotted as a function of temperature for all even chain length lead(II) alkanoates studied. The broken vertical dashes indicate the phase transitions [3]. In the crystalline low temperature phase, the chains are in the fully extended all-*trans*-conformation. At the onset of the C→CM transitions, defect specific bands arise. These bands can be assigned mainly to tg- and gt- defects, together with some ttg- ( $n=8$ ) and gg- ( $n=12, 14$ ) conformations. The small slope of the baseline [12] indicates that these defects are predominantly at the chain ends. This is consistent with results of  $^{13}\text{C}$  NMR investigations [13] which show a high mobility of the methyl group.

Raising the temperature (M and I phases) the end defect concentration grows slightly, but most of the defects are now within the chain. This cannot be monitored directly in the spectral region investigated, but an indication is obtained from the larger slope of the baseline [12]. Further,  $^{13}\text{C}$  NMR spectral studies on the M and I phases of lead(II) decanoate show that disordering occurs along the chain, and is not localized [13].

### 3.3. $\nu(\text{CC})$ region

A band group in a slightly higher frequency region ( $920\text{--}950\text{ cm}^{-1}$ ) was also investigated. These bands are assigned to the C–C– stretching vibration at the carboxylate end ( $\nu(\text{CC})_{\text{COO}}$ ) [14]. As already noted in [2], the frequency of this vibration is  $926\text{ cm}^{-1}$  for the longer chain samples (**Pb-C<sub>16</sub>** and **Pb-C<sub>18</sub>**) and for the recrystallized samples of **Pb-C<sub>10</sub>**, **Pb-C<sub>12</sub>** and **Pb-C<sub>14</sub>**. For the premelted samples and **Pb-C<sub>8</sub>**, the frequency is  $942\text{ cm}^{-1}$ . In both cases we discovered a shoulder at  $931\text{ cm}^{-1}$  and  $949\text{ cm}^{-1}$ . In both cases we discovered a shoulder at  $931\text{ cm}^{-1}$  and  $949\text{ cm}^{-1}$ , respectively. The intensity ratio is about 0.24. This supports the interpretation of  $^{13}\text{C}$  NMR data [13] on the splitting of the bands attributed to the three carbon atoms closest to the metal, that there are either two different environments of the carboxylate groups (for example, different oxygen–lead distances) or slight conformational changes (different C–C angles at the carboxylate end). In the CM phase, this band group broadens with its maximum at about  $937\text{ cm}^{-1}$ . In the M phase one cannot distinguish single lines any longer, while the peak frequency is about  $944\text{ cm}^{-1}$ . This confirms the idea that the conformational disorder within the chain is so large that the two components seen in the crystalline phase are smeared.

## 4. Discussion

The reported investigations confirm the view that in the C phase the chains are in an all-*trans* fully extended conformation. The C→CM transition can be characterized as a loosening of the chain packing (accompanied by a decrease in the van der Waals interaction) with conformational disordering only at the chain ends. A *gauche* defect at the chain end (gt- or tg-) reduces the length of the chain axis by about  $1.3\text{ \AA}$ . Under the assumption that the increase in the molecular cross section allows a better longitudinal packing of the chains, the observed reduction in the lamellar spacing can be attributed to the defects at the chain ends. Evaluating the chain end defect conformations, we calculated their enthalpy contribution to the C→CM transition, assuming a *gauche* defect enthalpy of  $2.94\text{ kJ mol}^{-1}$  [15]. The mean enthalpy contribution for **Pb-C<sub>10</sub>**...**Pb-C<sub>16</sub>** is  $3.2\text{ kJ mol}^{-1}$ . Taking into account the scatter of the measurements this value is rather close to the chain length independent transition enthalpy which was calculated as an extrapolation to zero methylene groups ( $2.7\text{ kJ mol}^{-1}$  [2]).

This resembles the rotator phase of the crystalline *n*-alkanes. Maroncelli *et al.*, localized the defects within the chains by an infrared CD<sub>2</sub>-substitution technique [16].

They showed that the highest *gauche* concentration is at the chain ends and that the concentrations at interior sites decrease exponentially towards the middle of the chain. The difference between the two systems is that the rotator phase of *n*-alkanes is linked with disorder in the longitudinal positioning, whereas the CM phase of the lead(II) alkanooates is induced by a lateral expansion. Besides, as noted elsewhere [2], the enthalpy change for the C→CM transition is too large for it to be just formation of a rotator phase.

In the M phase the situation is more complicated. There still exists a bilayer structure, but with a considerably decreased lamellar spacing and increased molecular cross section. The aliphatic chains are completely in their melt conformation. However, it is difficult to decide how the defects are packed into the lamellar structure. With the Raman spectroscopic investigation, it is only possible to detect the defects at the chain ends (adjacent to the carboxylate and methyl groups). At both ends there is conformational disorder, but it is not possible in this spectral region to determine the defect distribution within the chains.

A tilting of the chains, as proposed by Ellis and Vries [17], would lead to too large a cross section (cf. discussion in [2]).

A further possible arrangement of these defects is as kink-blocks (cf. similar structures: Lagaly bilayers, kink-block phase in polyethylene [18]). These are composed of *gtg*- sequences. However, the rather small chain length reduction observed with these kinks (about 1.3 Å) can hardly explain the observed shortening with the lead(II) alkanooates.

A conformation of which the molecular parameters are rather close to the experimental ones in the M phase is the all-*gauche* helix. The conformational data have been determined by semiempirical atomistic calculations for  $T=0$  K [19]. For the evaluation of the crystal data, a two shell approximation was used. The helix axis length is 0.938 Å/CH<sub>2</sub> (cf. the experimental value 0.7 Å). The molecular cross section per chain calculated for 0 K is 24.7 Å<sup>2</sup>. An extrapolation to 400 K [20, 21] yields a cross sectional area of 27 Å<sup>2</sup>. This is rather close to the experimental value of 29 Å<sup>2</sup>, especially if one takes into account the fact that the carboxylate head groups coupled to the Pb<sup>2+</sup> ion layer force a greater lateral distance between the chains than would be observed in a purely aliphatic hydrocarbon lattice. The energy of the all-*gauche* helix relative to the all-*trans*-conformation is 133 J g<sup>-1</sup> (CH<sub>2</sub>). This must be compared to the higher experimental value of 180 J g<sup>-1</sup> (CH<sub>2</sub>). The difference, however, can be explained by the smaller theoretical cross sectional area, and, hence, by the stronger lateral interaction. The all-*gauche* conformation is not possible for the whole chain, because the observed defect concentration is not high enough. However, it is highly feasible that a part of the chain is in the all-*gauche* helix conformation.

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