

## Intrastack rotation in pyrene hexafluoroarsenate

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

2004 J. Phys.: Condens. Matter 16 9109

(<http://iopscience.iop.org/0953-8984/16/50/001>)

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

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 19:27

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

# Intrastack rotation in pyrene hexafluoroarsenate

S Matejcek and E Dormann

Physikalisches Institut, Universität Karlsruhe (TH), D-76128 Karlsruhe, Germany

Received 7 October 2004

Published 3 December 2004

Online at [stacks.iop.org/JPhysCM/16/9109](http://stacks.iop.org/JPhysCM/16/9109)

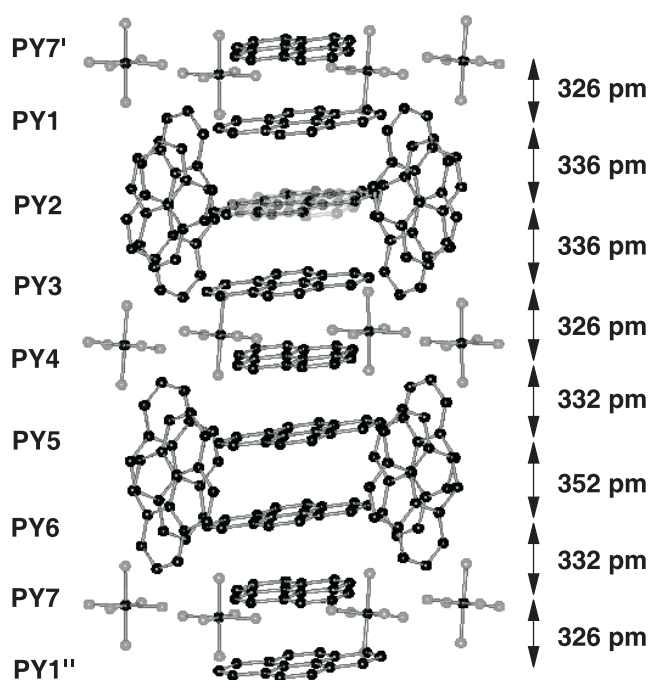
doi:10.1088/0953-8984/16/50/001

## Abstract

The specific heat of the quasi-one-dimensional organic conductor pyrene hexafluoroarsenate  $((\text{Py})_7(\text{Py})_4(\text{AsF}_6)_4 \cdot 4\text{CH}_2\text{Cl}_2)$  was measured between 10 and 250 K using the method of continuous heating. The contribution of the lattice to the specific heat was modelled using the Debye model and Einstein terms. The variation of the specific heat at the structural phase transition that is accompanied by  $60^\circ$  rotation of one of the stacked pyrene molecules could be reproduced well using a cooperation model including the formation of domains, and the surprisingly high transition entropy was explained qualitatively.

## 1. Introduction

Due to the many possibilities of combining arenes like naphthalene, fluoranthene, pyrene and perylene with the counterions  $\text{AsF}_6$ ,  $\text{SbF}_6$  or  $\text{PF}_6$ , a rich choice of quasi-one-dimensional conductors can be grown [1]. The crystal structure of the radical cation salts follows a uniform principle: the flat arene molecules form stacks and the counterions are located in channels between these stacks. The overlap of the  $\pi$ -orbitals of neighbouring arene radical cations and charge transfer from the arenes to the counterions give rise to a one-dimensional conduction band in the stacking direction. While most of the arenes show only one unique packing scheme [1], namely parallel for perylene, antiparallel for fluoranthene and  $90^\circ$  for naphthalene, pyrene ( $\text{C}_{16}\text{H}_{10}$ ) shows an unusual degree of freedom:  $(\text{Py})_7(\text{Py})_4(\text{AsF}_6)_4 \cdot 4\text{CH}_2\text{Cl}_2$  shows both parallel as well as  $60^\circ$  oriented molecules in its stacks (figure 1). Since for one of the seven stacked molecules both orientations are possible, the system crystallizes in two different modifications: I and II [2]. Modification I shows a first-order structural phase transition ( $T_C$ ) due to the reorientation of this molecule by  $60^\circ$  when the crystal is cooled and thus the intrastack distance is reduced. This transition is only partially reversible and shows a variation of  $T_C$  over a wide temperature range (150–200 K in the cooling mode and 215–240 K in the heating mode). In modification II the low temperature structure of modification I is already stable at room temperature, supposedly because the actual content of  $\text{CH}_2\text{Cl}_2$  molecules within the crystals is lower for modification II. The evaporation of the solvent may also be the reason for the non-negligible ageing of the crystals.



**Figure 1.** Crystal structure of  $(\text{Py})_7(\text{Py})_4(\text{AsF}_6)_4 \cdot 4\text{CH}_2\text{Cl}_2$ . The notation, the distances of the intrastack molecules and their orientations as well as the disorder of PY2 are shown.  $0^\circ$  packing is found for larger intermolecular distance and  $60^\circ$  packing for shorter separation. The solvent molecules are left off [2].

**Table 1.** Difference of the Peierls transition temperature  $T_P$ , the temperature of the structural phase transition  $T_C$  (non-existent in mod. II), and the ESR linewidth  $\Delta B_{1/2}$  (measured at 290 K and 9.45 GHz) between modifications I and II of  $(\text{Py})_7(\text{Py})_4(\text{AsF}_6)_4 \cdot 4\text{CH}_2\text{Cl}_2$ .

Modification	$T_P$ (K)	$T_C$ (K)	$\Delta B_{1/2}$ (mG)
I	73	150–200/215–240	36
II	105	—	54

It was suggested [2] that in mod. I crystals there exist domains with slightly different Peierls transition temperature  $T_P$ , caused by a differing degree of disorder as the reorientation of the stacked molecules mentioned above occurs in only 50%–70% of the unit cells. The differences important for this work between modifications I and II of  $(\text{Py})_7(\text{Py})_4(\text{AsF}_6)_4 \cdot 4\text{CH}_2\text{Cl}_2$  are listed in table 1.

Only a thermodynamic analysis can identify clearly the details of the structural phase transition, especially the number of motional degrees of freedom affected at  $T_C$ . Therefore in this contribution we present an analysis of the specific heat of this interesting radical cation salt.

## 2. Crystal growth and crystal structure

Shining black, needle-shaped pyrene hexafluoroarsenate crystals were grown by electrocrystallization techniques, with anodic oxidation of the pyrene molecules, as described before [3–6]. The crystals were stored in a freezer at  $T = -18^\circ\text{C}$  until used. In figure 1

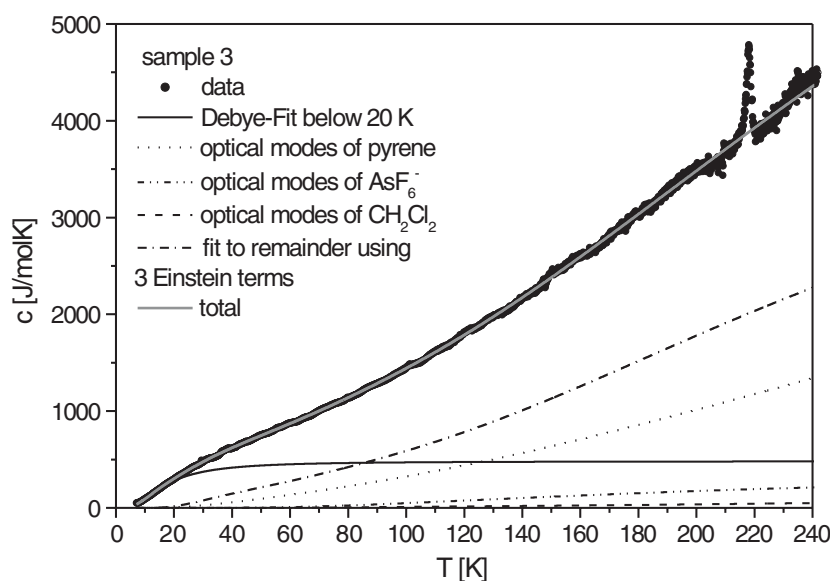
the crystal structure of  $(\text{Py})_7(\text{Py})_4(\text{AsF}_6)_4 \cdot 4\text{CH}_2\text{Cl}_2$  at  $T = 105 \text{ K}$  is shown. The marking and the distances of the seven stacked pyrene radical cations which build the repetition unit are explained. The stacks are separated by the counterions, four neutral pyrene molecules and the solvent molecules (not shown in figure 1). Four of the seven stack molecules define the  $0^\circ$  orientation, two are oriented at  $60^\circ$  and the PY2 position is disordered, with about 50%–70% [2] of the PY2 molecules oriented at  $60^\circ$  and the remaining ones at  $0^\circ$ .

### 3. Experimental details and results

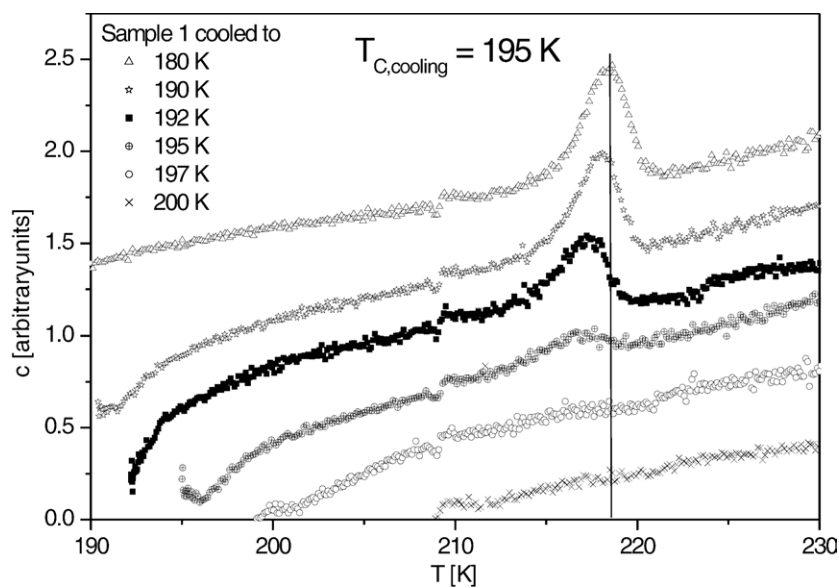
The specific heat of  $(\text{Py})_7(\text{Py})_4(\text{AsF}_6)_4 \cdot 4\text{CH}_2\text{Cl}_2$  (mod. I) was measured with a standard  $^4\text{He}$  bath cryostat using the method of continuous heating [5]. The heating rate was varied between 0.6 and  $1.5 \text{ K min}^{-1}$ . Sample 1 contained 6.3 mg, sample 2 4.6 mg and sample 3 9.9 mg of the crystals. The samples were thermally contacted with 2, 0.93 and 3.3 mg Apiezon-N grease respectively. For the measurement of the specific heat the crystals had to be selected by ESR analysis, because both modifications I and II, which have comparable appearance, are found in one growth run and can only be distinguished by their ESR linewidth [2] (see table 1). This time-consuming procedure causes, however, an unavoidable ageing of the crystals. In addition to the fact that an average specific heat of many crystals is measured this may be the reason why the wide variation of the transition temperatures, that was reported for individual single crystals of mod. I [2], was not found in the specific heat measurements. Sample 1 contained one-year-old crystals, while the crystals of samples 2 and 3 were freshly grown. Unfortunately the crystal growth is very subtle and the new crystals were of lower quality than those of sample 1, which clearly were stable single crystals of mod. I (as was verified by ESR analysis directly before the measurement). As the ESR analysis revealed, samples 2 and 3 contained polycrystals where crystals of mod. I and mod. II as well as decomposed crystals could not clearly be separated, so these measurements could only be used for the modelling of the lattice contribution and for the examination of the dependence of  $T_C$  on the heating rate and the number of temperature cycles but not for a reliable quantitative analysis of the transition peak area.

In figure 2 the specific heat of  $(\text{Py})_7(\text{Py})_4(\text{AsF}_6)_4 \cdot 4\text{CH}_2\text{Cl}_2$  (mod. I) is shown. The structural phase transition is clearly seen as a pronounced peak at about 218 K. For all measurements,  $T_C$  in the heating mode varied in the narrow temperature range between 218 and 220 K. The hysteretic behaviour of the structural phase transition was further studied by measurements using different heating rates. For a first-order transition one would expect a rising  $T_C$  with higher heating rates. However, only sample 2 which contained the least aged mod. I crystals showed a dependence of  $T_C$  on the heating rate with  $T_C = 219.2 \text{ K}$  at  $0.7 \text{ K min}^{-1}$ ,  $T_C = 219.6 \text{ K}$  at  $1.2 \text{ K min}^{-1}$  and  $T_C = 219.8 \text{ K}$  at  $1.5 \text{ K min}^{-1}$ . The fact that  $T_C$  in the heating mode decreases with the increasing number of cooling/heating cycles, which was reported for individual single crystals, could be affirmed for sample 2 with  $T_C = 219.6 \text{ K}$  after two and  $T_C = 218.5 \text{ K}$  after eight cooling/heating cycles (for both measurements a heating rate of  $1.2 \text{ K min}^{-1}$  was used). For all samples the partial irreversibility of the transition could be proven, leading to a reduction of the peak height by about 25% between the first and all following measurements.

Although the experimental setup allows only measurements in the heating mode, the hysteresis could indirectly be determined by heating continuously after the sample was cooled carefully from high temperatures to various temperatures above and below the value of  $T_C$  which was found in the ESR measurements and the microwave conductivity when the sample was cooled. This is demonstrated in figure 3. For all samples this method yielded  $T_C \approx 195 \text{ K}$  in the cooling mode.



**Figure 2.** Specific heat of  $(\text{Py})_7(\text{Py})_4(\text{AsF}_6)_4 \cdot 4\text{CH}_2\text{Cl}_2$  (mod. I), sample 3, and the different contributions to the specific heat of the lattice. For the Debye model formula  $C_D(T) = 9nR\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x dx}{(e^x - 1)^2}$  with  $\Theta_D = \frac{\hbar\omega_D}{k_B}$  was used, while the Einstein terms had the form  $C_i(T) = R\left(\frac{\Theta_{E,i}}{T}\right)^2 \frac{e^{\Theta_{E,i}/T}}{(e^{\Theta_{E,i}/T} - 1)^2}$  with  $\Theta_{E,i} = \frac{\hbar\omega_i}{k_B}$ . For details see the text.



**Figure 3.** Measurements determining the hysteresis of sample 1. The sample was successively cooled to the varying temperatures indicated in the figure legend and then the specific heat was measured in the heating mode. The small anomaly at  $T \approx 209$  K is of experimental origin.

Not surprisingly, the Peierls transition could not be detected in the specific heat. For arene radical cation salts in general it is difficult to see the Peierls transition in the specific heat as most of the transition entropy is distributed over a wide temperature range due to the thermodynamic

fluctuations that precede the three-dimensional manifestation of the lattice distortion [4]. It is even more difficult for pyrene hexafluoroarsenate because even an individual single crystal seems to consist of domains with a distribution of slightly different transition temperatures that leads to the smearing of the transition anomalies observed in the microwave conductivity for individual crystals.

## 4. Discussion

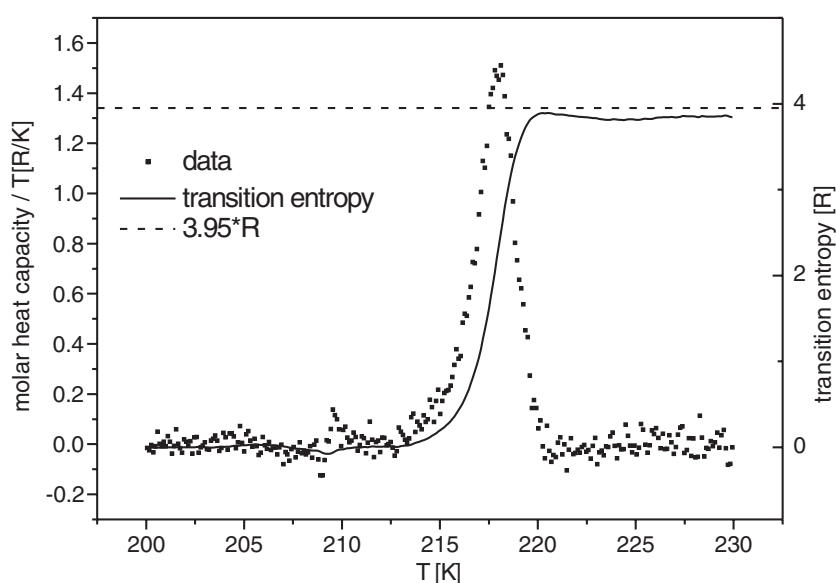
### 4.1. Contribution of the lattice to the specific heat

The contribution of the lattice to the specific heat was modelled using a combination of the Debye model and Einstein terms (see the caption of figure 2). The Debye model is only valid for acoustical phonons, so only the data in the temperature range below 20 K were used for the fit. The fit yields a Debye temperature  $\Theta_D \approx 70$  K and  $n = 19.3$  oscillators for the unit cell, which is in good agreement with the 19 molecules per unit cell. The resulting curve is shown as a solid line in figure 2.

Einstein's approximation of constant phonon frequencies can be used for the optical phonon modes. If the frequencies are known (from Raman and infrared spectroscopy) the contribution of the optical phonon modes to the specific heat can be determined as an addition of terms (one for each frequency  $\omega_i$ ) of the form shown in the caption of figure 2. In this way the contribution of the optical modes of pyrene using the Raman and infrared frequencies published in [7–9], of  $\text{CH}_2\text{Cl}_2$  using the data of [10, 11] and of the  $\text{AsF}_6^-$  anion using the data of [12] to the specific heat was determined. The results are also shown in figure 2 and were, together with the Debye fit, subtracted from the measured data. The remaining part of the lattice contribution is caused by the remaining optical phonon modes of  $(\text{Py})_7(\text{Py})_4(\text{AsF}_6)_4 \cdot 4\text{CH}_2\text{Cl}_2$ . Since these frequencies are not known, this part of the specific heat was fitted for convenience using three Einstein frequencies which are required even under Einstein's simplified assumption that molecules of the same kind have the same frequency due to the cations, the anions and the solvent molecules (however, the results of the fit can only approximate the real optical modes of the compound). This fit is also shown in figure 2 as well as the sum of all these contributions, which describes the measured data well except for the anomalies close to  $T_C$ .

### 4.2. Transition entropy

Subtraction of the lattice contribution from the data and integration of the molar heat capacity divided by  $T$  over  $T$  yields the surprisingly high transition entropy of  $\Delta S \approx 3.9R$  shown in figure 4. In perylene radical cation salts with parallel packing of the perylene molecules, a much smaller entropy variation of  $0.39R \ln 2$  and  $0.45R \ln 2$  was observed for perylene hexafluorophosphate and perylene hexafluoroarsenate, respectively, at a second-order structural phase transition which is caused by a uniform reorientation of the stacks by small angles [4]. For a transition where one of two possible molecule orientations is frozen out, one would expect an entropy of  $\Delta S = R \ln 2 = 0.693R$ , so the high transition entropy clearly indicates that the rearrangement within the unit cells caused by the transition is more complicated. We have already mentioned above that the molecules prefer the  $60^\circ$  orientation for smaller intrastack intermolecular distances, which gives us a qualitative argument for a rough estimate of the transition entropy taking into account the molecular vibrations of the involved molecules. As the reorientation is accompanied by the reduction of the distance between at least two molecules, the atomic motional degrees of freedom in the stacking direction of those  $\text{C}_{16}\text{H}_{10}$  molecules are restricted, and if  $2 \times 26 = 52$  atomic degrees of freedom are thus

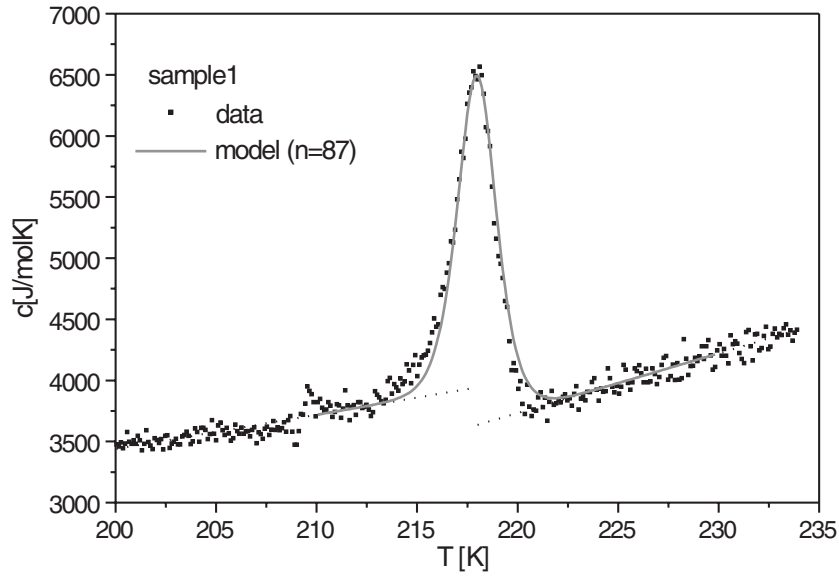


**Figure 4.** Transition related molar heat capacity of sample 1, divided by  $T$  (left axis), and the transition entropy (right axis, solid curve).

reduced, this leads to a transition entropy of  $\Delta S = R \ln 52 = 3.95R$  shown in figure 4. This estimate, however, is based on the assumption that all PY2 molecules are reorientated, while the crystal structure and ESR analysis suggest that only about 50%–70% of the PY2 molecules are rearranged [2, 6]. For this reason we have to conclude that the reorganization involves at least two intrastack molecules and the above estimate gives only a lower limit for the transition entropy.

#### 4.3. Cooperation model

In order to describe the thermodynamics of the structural phase transition, a cooperation model described in [13] (there called low-spin–high-spin transition) was used. Starting with the Gibbs free energy variation  $\Delta G$  accompanying the transformation of  $N$  molecules in the high temperature (HT) phase into the low temperature (LT) phase, the transition temperature where the amount of HT molecules is equal to that of the LT molecules is  $T_C = \Delta H / \Delta S = 216$  K, in fairly good agreement with the experiment.  $\Delta H = 7000$  J mol<sup>-1</sup> and  $\Delta S = 32.4$  J mol<sup>-1</sup> K<sup>-1</sup> were determined from the measurement. To account for intermolecular cooperativity we first tried out a version of the model including an interaction term of the form  $\Gamma = \gamma x(1-x)$  [13, 14], because this leads to a hysteretic transition.  $\gamma$  is an empirical interaction parameter and  $x$  is the HT molar fraction. However, the measured hysteresis could not be reproduced by the choice of only one value for  $\gamma$ , and the resulting shape of the transition peak did not reproduce the measurement well, even when it was folded by a Gaussian distribution [5] to take account of the averaging over many crystals. As mentioned above, recent ESR studies [6] suggest that the crystal is divided into domains with different Peierls transition temperatures, a fact that also explains the smearing of the transition anomalies related to the Peierls transition found in microwave conductivity data [2]. So a version of the model [13, 15] where the formation of domains with 0° or 60° oriented PY2 molecules is introduced seemed most plausible to describe the measured data. Taking into account the mixing entropy due to the different possibilities to



**Figure 5.** Specific heat of sample 1. The solid curve shows the result of the cooperation model including domains of size  $n = 87$  described in the text. The dotted lines mark the extrapolation of  $c_{LT}$  and  $c_{HT}$  to  $T_C$ .

arrange  $M$  domains containing  $n = N/M$  molecules within the crystal, the specific heat is

$$c_P = c_{LT} + \frac{c_{HT} - c_{LT}}{1 + A} + \frac{n\Delta H^2 A}{RT^2(1 + A)^2} \quad (1)$$

where  $A$  is

$$A = \exp\left[\frac{n\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_C}\right)\right]. \quad (2)$$

Extrapolating the specific heat below and above the phase transition to the transition temperature  $T_C$  yields the number  $n$  directly from the measured data, so no parameter is left to fit:

$$n = \frac{4RT_C^2}{\Delta H^2} \left[ c_P(T_C) - \frac{c_{LT}(T_C) + c_{HT}(T_C)}{2} \right]. \quad (3)$$

For the experimental data of sample 1 after one cooling and heating cycle a domain size  $n = 87$  was determined, which was used to calculate the specific heat using formula (1). The resulting curve reproduces the measured data very well, as is shown in figure 5.

An apparent limitation of the model is that hysteresis can only occur if the sizes of the domains while cooling the sample are different from those in the heating mode, but since the transition is only partially reversible this assumption seems reasonable. As no data for the first cooling run could be measured, the domain size for the first cooling run with the transition taking place at  $T_C = 195$  K could only be estimated to  $n = 70$  using the values for  $\Delta H$  and  $\Delta S$  of the first heating run. This result confirms, however, the tendency of increasing  $n$  with increasing number of cooling and heating cycles. The same analysis was also done for sample 1 after 12 temperature cycles, yielding a domain size of  $n = 95$ , again corroborating the assumption of increasing domain sizes the more often the transition is gone through.



## 5. Conclusion

Recently we presented a pyrene radical cation salt with at least partially reversible rotation by  $60^\circ$  of one of the seven stacked pyrene molecules at  $T_C \approx 195$  K [2]. With the above analysis of the specific heat of  $(\text{Py})_7(\text{Py})_4(\text{AsF}_6)_4 \cdot 4\text{CH}_2\text{Cl}_2$  (mod. I) the results of these studies by local methods could be confirmed and completed. The good agreement between experimental data and the domain model (and the failure of another version of that model not considering domains) gives us a strong argument that our picture of the reorientation taking place in domains rather than statistically is the adequate description of the transition. We argue that, by cooling, the intermolecular distances are reduced within the stacks, increasing the probability for a molecule at the PY2 site to reorientate. This reduces the pressure on the neighbouring PY2 sites in the same stack, but increases the probability for PY2 molecules on the neighbouring stacks to also reorientate, so the domains containing reorientated PY2 molecules are formed perpendicular to the stacks rather than along the stacks.

A surprisingly high transition entropy was found and qualitatively explained, showing that a simple two-state model is not an appropriate description for the transition related with the reorientation of a pyrene molecule by an angle as high as  $60^\circ$  in the complex crystal structure shown in figure 1. Furthermore, we showed that our experimental technique allows reliable measurements of the specific heat even when only 5–10 mg of delicate crystals are available.

## Acknowledgments

We thank I Odenwald for crystal growth. This work was financially supported by the Deutsche Forschungsgemeinschaft within the Sonderforschungsbereich 195 (Universität Karlsruhe (TH)).

## References

- [1] Enkelmann V 1988 *Adv. Chem. Ser.* **217** 177
- [2] Pongs B, Wokrina T, Matejcek S, Buschhaus C and Dormann E 2002 *Eur. Phys. J. B* **28** 289
- [3] Enkelmann V, Morra B S, Kröhnke Ch and Wegner G 1982 *Chem. Phys.* **66** 303
- [4] Wolter A, Fasol U, Jäppelt R and Dormann E 1996 *Phys. Rev. B* **54** 12272
- [5] Matejcek S 2004 Phasenübergänge in pyren-arsenhexafluorid und dichlor(2,5-dithiahexan)-Kupfer(II) *PhD Thesis* (Göttingen: Cuvillier Verlag)
- [6] Pongs B 2001 Elektronenspinresonanz an pyrenradikalkationensalzen *PhD Thesis* (Aachen: Shaker Verlag)
- [7] Bauschlicher C W, Langhoff S R, Sandford S A and Hudgins D M 1997 *J. Phys. Chem. A* **101** 2414
- [8] Vala M, Szczepanski J, Pauzat F, Parisel O, Talbi D and Ellinger Y 1994 *J. Phys. Chem.* **98** 9187
- [9] Langhoff S R 1996 *J. Phys. Chem.* **100** 2819
- [10] Escribano R, Orza J M, Montero S and Domingo C 1979 *Mol. Phys.* **37** 361
- [11] Schrader B and Meier W 1974 *Raman/IR Atlas Organischer Verbindungen* vol 1 (Weinheim: Chemie)
- [12] Emara A A A and Schrobilgen G J 1992 *Inorg. Chem.* **31** 1323
- [13] Kahn O 1993 *Molecular Magnetism* (Weinheim: VCH Verlagsgesellschaft mbH)
- [14] Slichter C P and Drickamer H G 1972 *J. Chem. Phys.* **56** 2142
- [15] Sorai M and Seki S 1974 *J. Phys. Chem. Solids* **35** 555