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Adiabatic scanning calorimetric results for the 260 K orientational transition of C_{60}

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We have measured the temperature dependence of the enthalphy and the specific heat capacity near 260 K orientational order-disorder transition of three different C_{60} samples, using high-resolution adiabatic scanning calorimetry. Extremely slow heating and cooling runs (at rates of the order of 100 mK/h) show that even at these low scanning rates the results are rate dependent. This indicates that even at such low rates the material is not in a thermodynamic equilibrium state and behaves as a system with a very long internal relaxation time (order of 10 h) in completing the first-order transition, as found in some binary systems.

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I. INTRODUCTION

In recent years the order-disorder phase transition in solid C_{60} at about 260 K has been investigated by various experimental methods such as differential scanning calorimetry (DSC),[1] x-ray diffraction,[1] nuclear magnetic resonance,[2] neutron diffraction,[3] and dielectric spectroscopy.[4] The orientational phase transition (PT) affects physical quantities such as the thermal conductivity,[5] the attenuation of sound,[6] and the magnetic susceptibility.[7]

At room temperature solid C_{60} adopts a face-centered-cubic (fcc) structure.[1] The molecules which are orientationally disordered, rotate nearly freely and independent of each other.[1] Below ~260 K, the electrostatic interaction of the electron-poor and electron-rich regions of the neighboring molecules produces a freezing of the free molecular rotation.[3,8] In this state, the four molecules of the fcc conventional unit cell become orientationally nonequivalent and the C_{60} crystal undergoes a first-order transition to a simple-cubic (sc) structure.[1,3]

Our interest in this molecular crystal originated partially from our previous calorimetric and dielectric work on liquid crystals showing orientational order but no or low dimensional positional order while this new quasiplastic crystal exhibits three-dimensional positional but no orientational order at high temperature. But most of all we were intrigued by the double and multiple peak anomalies in the experimental results of the temperature dependence of the specific heat capacity, by the different values for the transition temperatures as well as by the different values for the transition enthalphy changes as reported in the literature.[9–21] In literature many of the anomalies are ascribed to the presence of higher fullerenes (C_{70}), intercallated oxygen, physical impurities (defects introduced by fast crystallization or sublimation rate), solvent molecules, etc.

In our opinion some of the unusual specific heat capacity behaviors might be experimental artifacts introduced by the applied method. Indeed, most of the reported $C_p(T)$ results have been obtained by differential scanning calorimetry (DSC), a method shown to be unable to discriminate between pretransitional heat-capacity increases and latent heats.[22,23] Since in DSC experiments a constant heating (cooling) rate ($\dot{T}$) is imposed on the sample, at a first-order phase transition one runs into basic difficulties because the latent heat of transition cannot be delivered (or extracted) instantaneously and the peak-temperature of $C_p(T)$ lags behind the real transition temperature. Rounding off and smearing out over a finite temperature interval follows. This is a major drawback of DSC instruments which operate in a constant $\dot{T}$ mode (for more detail see, e.g., Fig. 1 of Ref. 24). Even the recently developed modulated differential scanning calorimetric (MDSC) method, which combines the advantages of an ac method with the classical DSC technique cannot overcome the basic disadvantages mentioned above. In addition, the rather large heating (cooling) rates (0, 1 to 10 K/min) in DSC's present in many cases thermodynamic equilibrium problems as well. The basic DSC problem is not encountered in the adiabatic scanning calorimetric (ASC) method used here and also the problem of thermodynamic equilibrium is to a very large extent avoided because scanning rates of a few mK/min have been used.

The measurements reported in this paper have been carried out with a high-resolution adiabatic scanning calorimeter of the same type as used previously by one of us (J.T.) for measurements on the blue phases of cholesteryl nonanoate[25] and on other liquid crystal compounds.[23–27] Cooling and heating runs were performed on three different polycrystalline C_{60} samples of different purity obtained from two different companies [MER, Tucson (AZ) and Hoechst AG, Germany]. Samples were checked for solvent contents, higher fullerene impurities, epoxides, etc. by high pressure liquid chromatography (HPLC), thermogravimetric analysis (TGA), and mass spectroscopy (MS).

Exposure to light as well as to air was avoided as much as possible. The measurements were carried out during several weeks with the sample exposed to a dynamic vacuum of better than 10^{-6} mm Hg.

One of the main findings of this work is that even at these very low scanning rates, the thermal hysteresis, the C_p peak value, the full width at half maximum (FWHM), as well as the phase transition temperature are still rate dependent.

II. EXPERIMENT

Here only a brief account of some basic aspects of the adiabatic scanning calorimetric measuring procedure will be given as far as needed for the proper understanding of the reported results. Full details on the construction of such a calorimeter and its possible modes of operation can be found elsewhere.[28]

The present calorimeter consists of three stages: a central stage containing the sample and two other shielding stages. All stages are thermally insulated from each other and are made of good heat-conducting materials to avoid temperature gradients. The measured (constant) power (P) is continuously applied to (or extracted from) the central stage containing the sample. The total specific heat capacity C_1 for stage 1, being the sum of that of the sample (C_s) plus that of the sample holder (C_h) is given by

$$C_1 = C_s + C_h = P_1 / \dot{T}_1 . \tag{1}$$

The specific heat capacity C_h of the sample holder can be obtained from calibration measurements and can thus always be separated from the specific heat capacity of the sample.

In Eq. (1) the total heating power P_1 to stage 1 is the sum of the power applied electrically to the heater of stage 1 and the heat leaks with the shielding stage 2. In order to arrive at the specific heat capacity C_s of the sample [see Eq. (1)], one has to measure P_1, $\dot{T}_1$, and C_h.

The rate $\dot{T}_1$ is found by numerical differentiation from a careful measurement of the temperature (T_1) versus time (t) evolution of stage 1. The temperature of this stage was measured every second by means of a calibrated thermistor [calibration carried out against a calibrated Pt100 (Tinsley Co.)] and stored in computer memory.

Keeping P_1 constant (not $\dot{T}_1$ as in a DSC measurement) has the advantage that the temperature versus time $[T(t)]$ result can be converted easily into an enthalpy versus temperature $[H(T)]$ curve. If a first-order PT occurs at a certain temperature T_{PT}, a step will occur in the $H(T)$ curve and the temperature T will stay constant for a certain time interval until the latent heat ΔH_L is supplied to cross the transition.

In this way, it is clear that we easily can distinguish between pretransitional increases and latent heats, and a value for the true latent heats in a first-order PT can be derived. The temperature dependence of the specific heat capacity $C_p(T)$ is obtained by differentiating the $H(T)$ curve with respect to temperature $[C_p = (\partial H / \partial T)_p]$.

We studied three C_{60} samples: samples $M1$ and $M2$ prepared by MER Corporation (Tucson, AZ) and sample $H1$ prepared by Hoechst AG (Frankfurt, Germany). Sample $M1$ obtained by sublimation has a purity of 99.5%, contained a solvent concentration (toluene) lower than 0.1% and was after sublimation heated for about 5 h at 570 K at a dynamic vacuum of better than 10^{-6} mm Hg. From electron diffraction experiments (at RUCA, Antwerp) it appears that the crystallinity of this powder was very good and that the amount of stacking faults was very low. The Hoechst sample $H1$ studied afterwards was a ‘‘super gold grade’’ powder (purity 99.9%). HPLC indicated that the concentration of solvents was very low (toluene: 0.089%; acetone: 0.051%; diethylether: 0.046%). Standard differential scanning calorimetry (DSC) between −70 and +30 °C at 5 K/min resulted in the appearance of one single peak at 259.98 K. Only a very small peak at 736 mu was seen by mass spectrometry (MS) which was assigned to $C_{60}O$ ($\leqslant 0.2\%$). Finally, a very pure sublimed sample from MER (sample $M2$) was measured. Analytical results from HPLC, MS and from thermogravimetric analysis (TGA) indicate that the purity is better than 99.95%.

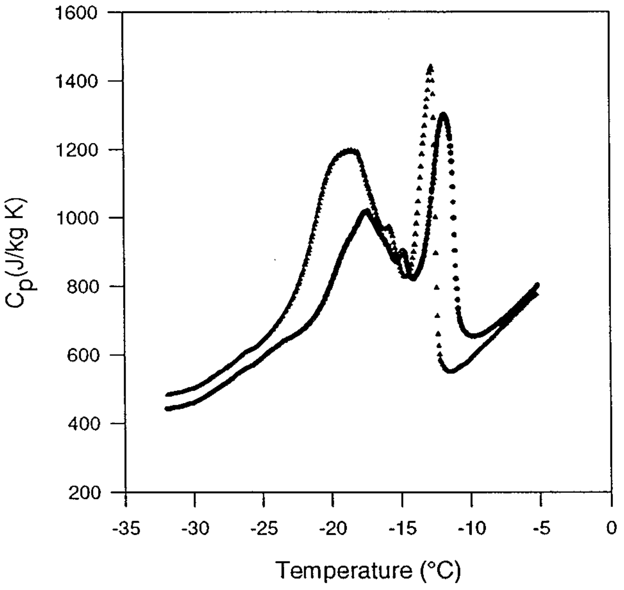

FIG. 1. Specific heat capacity $C_p(T)$ of sample $M1$ (MER: 99.5+% C_{60}): ● data measured on heating; ▲ data measured on cooling. The main peak (from heating run data) occurs at 261.4 K (−12.8 °C), second peak at 255.6 K (−17.6 °C), and small peak in between at 258.3 K (−14.9 °C). Mean scanning rate: 100 mK/h. Thermal hysteresis ≈1 K.

III. RESULTS AND DISCUSSION

Figure 1 shows ASC results (at scanning rates of ≈100 mK/h) from 1 g of MER powder (sample $M1$). We observe in the measured temperature range three features in the specific heat capacity heating curve: (i) a sharp peak at 261.4 K (−12.8 °C), (ii) a relatively broad peak at 255.6 K (−17.6 °C), and (iii) a very small peak in between at 258.3 K (−14.9 °C). All these features are retained in the cooling curve with a shift of about 1 K towards the low temperature side. Several runs have been done using different heating power (P) values and the results have been found to be largely independent of the heating and cooling rates. It has to be noted that the features in the cooling curve are slightly sharper and that the specific heat capacity values are considerably different from those of the heating curve below 264 K. It is interesting to note that the temperature (261.4 K) at which the sharpest peak occurs, corresponds to the highest temperature reported for the orientational ordering transition in a C_{60} single crystal.[14,15] Another interesting feature is that this peak is very sharp and thus the thermal hysteresis is well resolved. It has been discussed in the literature that samples with higher impurity amount have a much lower transition temperature and show a broader peak.[2,20,22]

We have also calculated the enthalpy increments for the two prominent peaks from the experimental $T(t)$ curve, using the relation (2) for the enthalpy change. The enthalpy increment associated with the peak in the temperature range 259 to 264 K is estimated to be ≅2,8 kJ/kg. A similar analy-

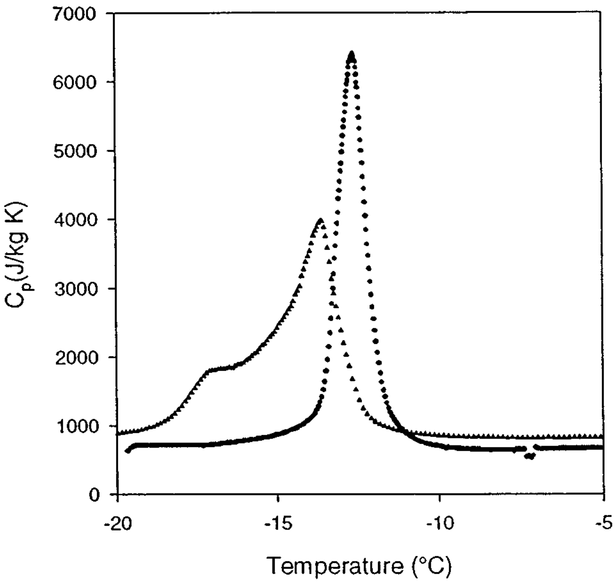

FIG. 2. Specific heat capacity $C_p(T)$ of sample $H1$ (Hoechst AG: 99.9+% C_{60}): ● heating run data; ▲ cooling run data. There is no sign of a peak at 255.6 K in the heating run and only a shoulder on the low T side at about 3.5 K below T_{PT} in the cooling run. Thermal hysteresis ≈1 K.

sis has been carried out for the peak at lower temperature considering the temperature range 249.5 to 259.1 K (which also includes the small peak) and avoiding the pretransitional increase associated with the highest peak. This calculation results in an enthalpy increment of ≈5,6 kJ/kg. It is interesting to note that the sum of these enthalpies (≈8,4 kJ/kg) compares well with the enthalpy increment for the orientational transition, without considering the precursor effect, as obtained by a DSC study of a single crystal.[15] Although this result suggests the possibility of stepwise orientational transitions occurring close to each other in C_{60}, we have no proof for this idea. On the other hand, we find in literature no evidence for the second peak at 255.6 K.

Figure 2 shows a typical result obtained on the Hoechst sample $H1$. This sample of higher purity (99.9%) than the $M1$ sample exhibits in its temperature dependence of the specific heat capacity the following characteristics: recorded under the same ASC conditions as above (for the $M1$ sample) we found no pronounced extra peak anymore at 255.6 K. Nevertheless, in the cooling runs a weak shoulder on the low T side is found at about 3.5 K below the main peak temperature.

An important observation was the scanning rate dependence of the $C_p(T)$ data even at these very low scanning rates: the lower the scanning rate the more the ordening transition temperature shifts to lower (higher) temperatures for the heating (cooling) runs. Moreover, the lower the scanning rate, the sharper the excess $C_p(T)$ peak [the full width at half maximum (FWHM) decreases and the $C_p(T)$ maximum increases]. We want to underline that in an ASC measurement we directly measure the temperature dependence of the enthalpy [$H(T)$] (without any shift) and that we define the transition temperature as the temperature of the system where $H(T)$ has his largest slope within the two phases region. Therefore the C_p-peak temperature coincides with the transition temperature. This is in contrast to the result obtained from a DSC measurement where rate dependent shifts are introduced.

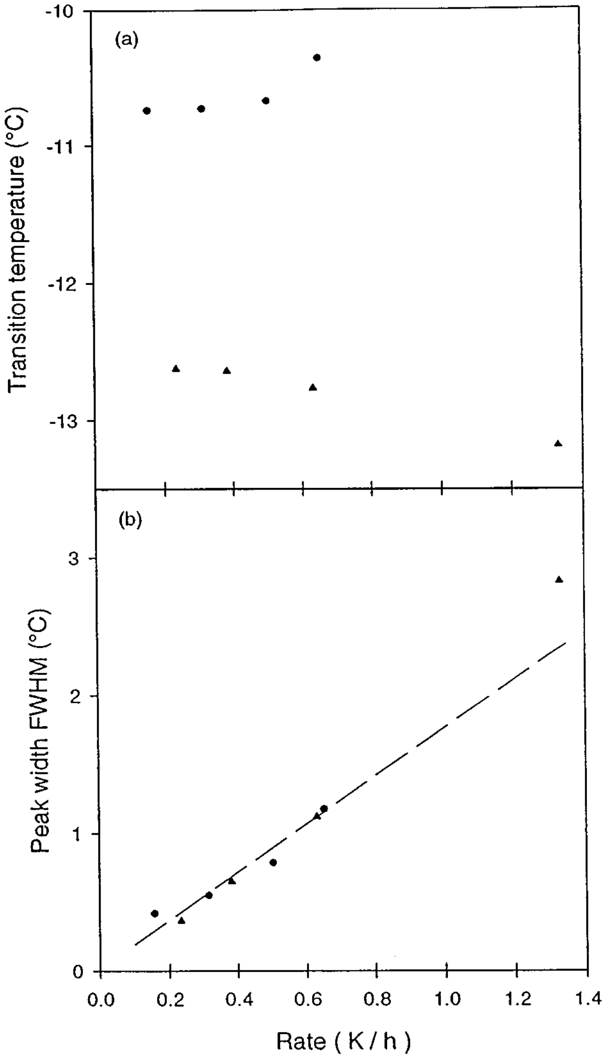

FIG. 3. MER sublimed C_{60}, sample $M2$ (purity 99.95+%): ● heating runs; ▲ cooling runs. (a) Phase transition temperature versus scanning rate (far away from the transition. (b) Peak width (FWHM) versus scanning rate.

In order to get more precise information about this phenomenon and its relations to sample purity, we started studying the more pure MER sample $M2$ (99.95% C_{60}). Heating and cooling scan data obtained on sample $M2$ are given in Fig. 3. Figures 3(a) and 3(b) represent respectively the scanning rate dependence (realized by using different heating and cooling powers) of the ordening transition temperature and of the full width at half maximum of the excess specific heat capacity. From Fig. 3(a) it is clear that scanning rates of about 100 mK/h yield T_{PT} results considerably different from those obtained at a rate of 1 K/h. Therefore one may question the results obtained by standard DSC where heating (cooling) rates of 5 or 10 K/min are normally used. The same data show that at the lowest scanning rate the value of the ordening temperature associated with a heating run is 262.4 K (−10.8 °C) and 260.6 K (−12.6 °C) for a cooling run. The thermal hysteresis at the lowest scanning rate is about 1.8 K.

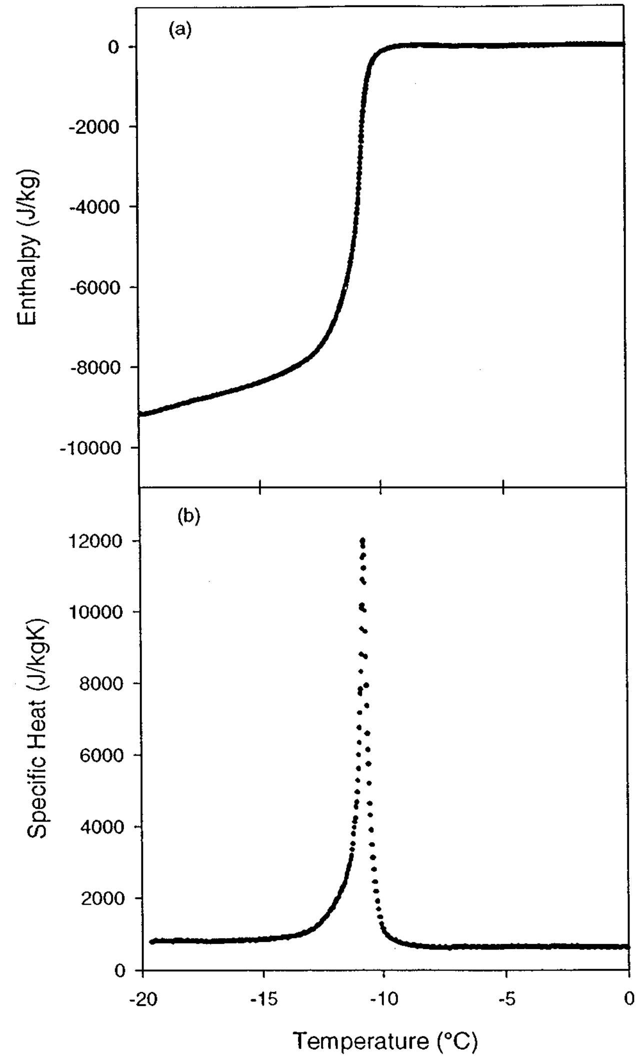

FIG. 4. MER sublimed C_{60}, sample $M2$ (purity: 99.95+%): temperature dependence of the enthalphy $H(T)$ (a) and of the specific heat capacity $C_p(T)$ (b) recorded during a heating run at the smallest heat input (133 μW) (lowest rate). T_{PT}=262.4 K (−10.8 °C).

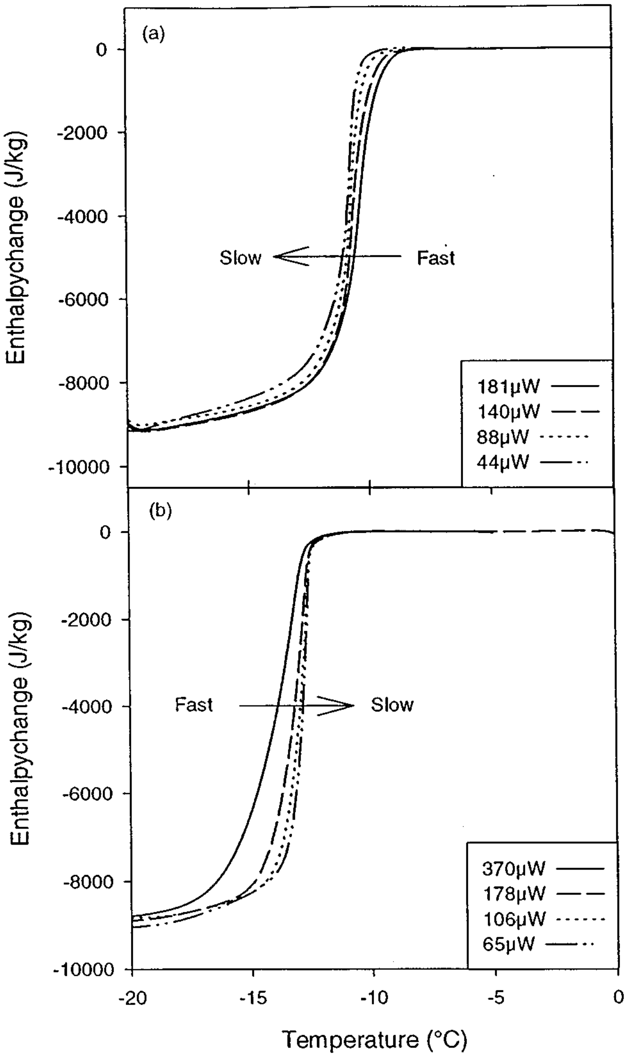

FIG. 5. MER sublimed C_{60} sample $M2$ (purity: 99.95+%): temperature dependence of the enthalphy $H(T)$ near the phase transition for 4 different power inputs (different scanning rates). (a) $H(T)$ curves from heating runs. (b) $H(T)$ curves from cooling runs.

This rather high value can be attributed to supercooling of the sample since this effect increases with sample purity.[29] Results of the change of the FWHM of the C_p peak at the ordening temperature, as given in Fig. 3(b), clearly show the quality of our results. They indicate that in the limit of extremely low scanning rates the FWHM becomes extremely small again referring to the high purity of the sample $M2$.

From the enthalpy $H(T)$ [recorded at the smallest input power (133 μW)] and the excess specific heat capacity $C_p(T)$ [see Figs. 4(a) and 4(b)] corresponding to the orientational transformation (after substraction of the linear background) we clearly see that the fcc/sc transformation is a first-order transformation. For the orientational transformation occurring at 262.4 K (−10.73 °C) during the heating run [Fig. 4(a)], the associated $C_p(T)$ peak is remarkably sharp and attains a value of 12 360 J/kg K [Fig. 4(b)]. For the slowest cooling run (not shown) we obtained an even larger peak value of 16 730 J/kg K at a transition temperature of 260.6 K (−12.56 °C). In both the heating and cooling $C_p(T)$ peaks a similar asymmetric shape with a low temperature side precursor is observed [see Fig. 4(b) for the heating run]. This was also recently found by Fischer *et al.*[30] in C_{60} powder using modulated differential scanning calorimetry at a scanning rate of 0.05 K/min. The corresponding enthalpy change including pretransitional effects (heat of transition) gives a value of about 9000 J/kg (6500 J/mol). This value is considerably smaller than a recently reported ''near-to-standard'' single crystal value of 12.500 J/kg (9000 J/mol) obtained by integrating a regular DSC scan at 10 K/min.[15] Up to now the transition temperature value T_{PT}=262.4 K is the highest one ever reported for C_{60}.

The systematic shift of the enthalpy curve $H(T)$ as a function of the input power (which determines the start scanning rate) for cooling as well as for heating runs [Figs. 5(a) and 5(b)] reveals that even at these extremely low scanning rates a thermodynamic nonequilibrium situation exists. This phenomenon is typical for the coexistence of two phases due to slow internal equilibration. In this case we believe one has to do with a very dilute system built up from physically different domains due to the presence of impurities (chemical and/or physical) within the C_{60} system. This binarylike mixture is also responsible for the broadening of the enthalphy change at the first-order transition temperature [see Fig. 4(a)]. It is well-known that imperfections in solids generally decrease the free energy of formation of a nucleus and thus favor the nucleation process, but the transformation rate to the new phase depends not only on the kinetics of nucleation but also on the growth of the nuclei as well as on the diffusion kinetics of the different domains.[31] The propagation process involving material transfer into the interior of the new phase by diffusion can be a very slow process. As an example of such a slow ordening process we refer for instance to a DB7OCN+8OCB liquid crystal mixture[32] were the rate at which Sm-A_d-type order transforms into Sm-A_2-type order with a time constant of 12 h. Taking into account the fact that in our slowest heating run the transformation in sample $M2$ was completed in about 30 h, it can be deduced that the internal relaxation time τ should be about 18 h (13 h) assuming the internal equilibrium was reached for about 80% (90%). The relaxation times indicate that the impurities are not frozen in or trapped in the C_{60} system, but have still a relative mobility.

Although we have observed about the same rate dependence in our Hoechst sample $H1$, it is at this moment not clear why rate dependence has not been found in the less pure sample $M1$, where most probably impurities are responsible for the observed double peak in the $C_p(T)$ curve.

IV. SUMMARY AND CONCLUSION

The present adiabatic scanning calorimetric measurements of three sublimed C_{60} samples of different origin and purity reveal that the structure of the $C_p(T)$ curve at the high-temperature phase transition is strongly impurity concentration dependent. It is is clear from these measurements that very small amounts of impurities (of the order of 0.01%) drastically influence the thermodynamic equilibrium of the system and thus the value of the physical quantities derived at specific measuring rates at the phase transition temperature. Moreover, it is evident that adiabatic scanning calorimetry gives direct information about the enthalpy changes at the phase transition, about the correct phase transition temperature, and about the structure of the $H(T)$ and the $C_p(T)$ curve. The T_{PT} derived from the slowest heating run is 262.4 K, higher than the values reported in the literature. The corresponding heat of transition is about 9000 J/kg (6500 J/mol), a value considerably smaller than recently reported for single crystals.

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