Thermodynamic study of alkyl-cyclohexanes in liquid, glassy, and crystalline states

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The specific heat of some alkyl-cyclohexanes in their liquid, supercooled liquid, crystalline, and (for the first time) glassy states has been measured by quasiadiabatic calorimetry. Thermodynamic properties as well as the glass forming ability have been studied as a function of systematic changes of the molecular structure. Only one stable crystalline phase is observed experimentally for ethylcyclohexane, propylcyclohexane, and butylcyclohexane. In the case of methylcyclohexane, experimental evidence is provided of a crystal-to-crystal transition at temperatures just below the melting. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2238863]

I. INTRODUCTION

Glasses and glass transition related phenomena represent an open challenge in condensed matter physics and materials science.[1] In principle, a liquid cooled below its melting temperature T_m should undergo a first-order phase transition and become a crystal. This simple rule has nevertheless many exceptions. In fact, even at moderate cooling rates, crystallization is avoided in some substances, which can be easily studied in their supercooled state.[2–5] On further cooling, crystallization can occur at a temperature $T_{x,c} < T_m$. However, the so-called "good glass formers" do not crystallize[6] and finally reach a highly viscous state, the glassy state, in which they exhibit solidlike behavior.[7,8] The glass transition temperature T_g is marked by a change of slope in the temperature dependence of extensive thermodynamic properties such as volume and enthalpy.[9] At T_g a sudden decrease of the specific heat C_p indicates that many degrees of freedom are frozen-in going from the supercooled liquid to the glass.[10] Considering the inverse path, at increasing temperatures, these degrees of freedom are released when heating the glass through the glass transition temperature: an endothermic process accompanies the transition from the glass to the supercooled liquid. As the temperature is further increased above T_g, the sample might crystallize. This crystallization, which

starts at a temperature $T_{x,h}$, where $T_{x,h} < T_{x,c} < T_m$, might lead to a crystalline phase different from that obtained on cooling the high-temperature stable liquid.

As outlined above, even if a liquid can be cooled down to the glassy state avoiding crystallization, a transition to a crystalline state might happen on the reverse route going from the glass towards the liquid. Clearly this aspect has a great relevance in some different fields such as, cryopreservation,[11] biology, food science,[12] or design and production of tools subjected to large temperature excursions (industrial and aerospace applications).[13] In fact, unwanted crystallization could imply a severe change of the macroscopic properties (mechanical, dielectric, and optical), or an irreversible loss of functionality, in the case of living biologic matter.

The thermodynamic behavior of glass forming liquids can be more complex, including the presence of orientationally disordered crystalline phases such as plastic crystals or *glassy crystals.*[14] Even in the case of liquids with a simple molecular structure, such as ethanol, detailed studies performed by adiabatic calorimetry have clearly indicated the existence of different solid phases, only reachable following suitable thermal paths in the phase diagram.[15–17] These findings strongly suggest that any investigation of the dynamic behavior of a glass forming material from the liquid to the glassy state should be conveniently based on a detailed knowledge of its thermodynamic properties. In the present work we have studied thermodynamic properties, glass for-

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mation, and crystallization in a series of alkylcyclohexanes varying the length of the alkyl side chain, from methylcyclohexane to butylcyclohexane. Reasons of a special interest for this series of cyclohexane derivatives are (a) the existence of a premelting crystalline structure in methylcyclohexane, different from the low-temperature stable crystal, as recently suggested on the basis of Raman scattering experiments[18,19] (b) the unusual dynamical features of ethylcyclohexane, recently pointed out by mechanical[20] and dielectric spectroscopies.[21] On this basis we have performed calorimetric experiments on the series of alkylcyclohexanes using both the adiabatic and the continuous method. We have obtained detailed information on the phase diagram and measured the specific heat in the glassy phase, not available from previous literature. We have found evidence of a premelting transition into a second crystalline phase for methylcyclohexane, in agreement with the previous Raman scattering results.[18] Finally the results on these alkylcyclohexanes have been analyzed aiming to understand how systematic changes of the molecular structure can influence different thermodynamic aspects of the glass transition, as well as the glass forming ability.

II. EXPERIMENT

A. Materials

High purity samples of methylcyclohexane (MCH), ethylcyclohexane (ECH), *n*-propylcyclohexane (PCH), and *n*-butylcyclohexane (BCH) commercially available were used without further purification. They were transferred from the sealed bottles to the measurement cell using glass syringes with stainless steel needles.

B. Experimental setup

Specific-heat measurements have been performed using a calorimetric cell made of a copper cylindrical container (13 mm diameter, 25 mm height) with very thin walls (<0.5 mm) and with an indium-sealed copper cover. This design, which is very similar to the sample holder used for ultrasonic measurements, has been chosen in order to enable a direct comparison between the results of the two investigations. A check for mass losses was performed after exposing the cell to dynamic vacuum from a diffusion pump. A second check on the total mass of the measurement cell full of liquid was performed at the end of each measurement run. The cell was suspended from the inner flange of the cryostat by nylon threads. An electrical heater as well as a standard silicon diode operating at 10 μA were attached to the upper and lower ends, respectively, of the copper sample holder. Experiments were run in a ^{4}He cryostat, with two separate vacuum chambers of copper, so that a second heater and a second silicon diode allowed controlling the temperature of the internal sample chamber. Helium was used as exchange gas when a high cooling rate was required. Calorimetric measurements were conducted in a high-vacuum environment ($\sim 10^{-7}$ mbar).

C. Calorimetric measurements

Specific-heat measurements have been performed using two different methods: the standard adiabatic or Nernst method (by controlling the temperature of the internal sample chamber) and also a quasiadiabatic, continuous method.[22,23] In both cases, we always measure the heat capacity on heating. Results obtained with the two methods were in good agreement, supporting the assumption that the moderate cooling and heating rates employed allowed a reasonable thermal equilibrium in the sample. Comparison among different experimental runs, methods, data from the literature (see below), and expected systematic errors leads us to estimate an accuracy for the absolute heat-capacity data better than 4% in the temperature range between 77 and 200 K.

In an ideal, adiabatic system the power applied to the cell P_{heat} is proportional to the temperature increase via

$$C_p\left(\frac{dT}{dt}\right) = P_{\text{heat}} = V_h I_h, \tag{1}$$

where V_h and I_h are, respectively, the voltage applied to the heating resistive element and the electric current flowing through it. Hence the heat capacity is directly obtained by applying heat pulses $\Delta Q = V_h I_h \Delta t$ and measuring the produced increase of temperature ΔT: $C_p = \Delta Q / \Delta T$.

When the calorimetric cell is in contact to the thermal reservoir at 77 K through an effective thermal link (mainly arising from blackbody thermal radiation plus conduction through the electrical wiring), it is also subjected to a cooling power P_{cool}, so that

$$C_p\left(\frac{dT}{dt}\right) = P_{\text{heat}} + P_{\text{cool}} = V_h I_h + C_p \dot{\tau}. \tag{2}$$

In this equation $\dot{\tau} \equiv \dot{\tau}(T)$ is the (negative) thermal drift in K/s observed during a spontaneous cooling, which can be measured as a function of temperature at $I_h = 0$, with the reservoir fixed at $T = 77$ K. Therefore, the heat capacity of the cell is

$$C_p = \frac{V_h I_h}{[(dT/dt) - \dot{\tau}]}. \tag{3}$$

This thermal drift $\dot{\tau}(T)$ was observed to be fully reproducible for each studied phase, even at different starting temperatures, and it only depends on temperature. When cooling a liquid sample, the thermal drift was typically around -1.1×10^{-3} K/s ($=-0.07$ K/min) at 100 K or around 3×10^{-3} K/s ($=-0.2$ K/min) at 150 K [see, for example, curve 1 of Fig. 1]. For heat-capacity measurements, we have typically used (see Fig. 2) heating rates of approximately $+1$ K/min.

In order to obtain the specific heat of the substance, the contributions due to the calorimetric cell must be subtracted. To this purpose measurements were performed on a empty cell using the same conditions and components than in the usual measurements. The different parts were, however, connected so that high vacuum could be obtained also inside the cell, still maintaining a reasonably good thermal contact. The measurement on a given empty cell was used for all similar
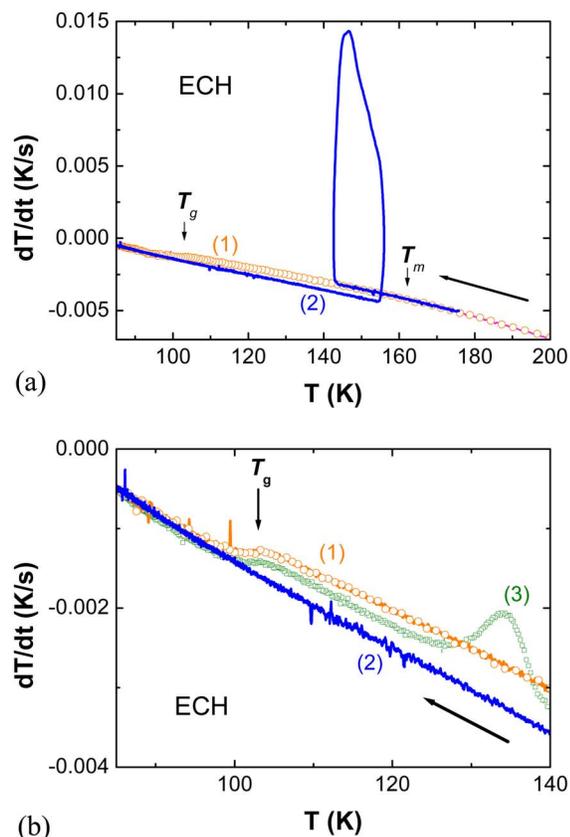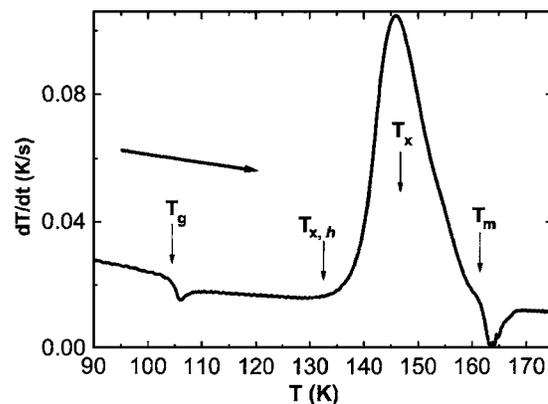
FIG. 2. Heating rate of a copper calorimetric cell containing ethylcyclohexane subjected to constant external heating power. From the left to the right: the glassy sample is heated from the initial temperature of 90 K. The endothermic feature starting at 105 K corresponds to the transition from the glass to the supercooled liquid. At $T_{x,h} = 132$ K is observed the onset of a big exothermic feature, the crystallization. On further heating, the crystal melts at $T_m = 161.5$ K.

FIG. 1. (a) Temperature variation of the copper calorimetric cell (13.90 g) completely filled with ethylcyclohexane (2.40 g) during different cooling runs. The open circles (curve 1) correspond to a slow cooling process ($dT/dt \approx -0.2$ K/min) which leads the sample to the glassy state at 105 K. The continuous line (curve 2), also corresponding to a cooling process, shows a crystallization whose onset is $T_{x,c} = 141$ K. A detailed view of the time-dependent temperature rate is provided in (b), in which is more evident the exothermic feature of curve 1 associated with the glass transition. Curve 3 (open squares) corresponds to a cooling process during which an exothermic peak is observed just below 140 K, then the system proceeds towards the glass transition, forming a glass.

copper cells employed, taking into account the (small) difference in mass of copper, which is the dominant contribution and whose specific heat is known.

III. RESULTS

A. Ethylcyclohexane

Experiments performed on ethylcyclohexane with the calorimetric continuous method have shown that, when slowly cooling the liquid from room temperature ($dT/dt \approx -0.2$ K/min), the substance rarely crystallizes and it undergoes the glass transition at about 105 K. The time-dependent temperature rate of a calorimetric cell filled with ethylcyclohexane in the case of slow cooling and formation of glass is shown in Fig. 1 (curve 1). In some occasions when cooling the liquid at comparably low cooling rates, mostly after melting the solid, crystallization occurs. In Fig. 1, curve 2 corresponds to a crystallization event. On the basis of an average of experimental data on different events, this kind of crystallization at cooling exhibits a typical onset crystallization temperature of $T_{x,c} = 141$ K and an enthalpy of

$\Delta H_{x,c} = 67.8 \pm 2.2$ J/g $= 7.6 \pm 0.2$ kJ/mol. The difference between the thermal behavior of a crystal and that of a supercooled liquid forming a glass is shown in detail in Fig. 1(b). In the same figure an unusual feature is shown: a small exothermic process, arising just below 140 K, is observed occasionally on cooling the liquid. At temperatures lower than the exothermic feature, the system behaves as supercooled liquid and finally undergoes the glass transition at T_g. The exothermic peak mentioned above could represent a frustrated crystallization or partial crystallization. The system loses one portion of the degrees of freedom which contribute to the specific heat, but it is still in the supercooled state because the glass transition is observed on further cooling. The relevant temperature range for this process is too close to the onset of crystallization, so that probably in many cases it cannot be observed because the crystallization occurs. However, we still have not definitive explanation and further experimental work is needed to confirm or disregard these occasionally observed phenomena and their possible origins. The behavior recorded on heating the glass by a continuous heating power is shown in Fig. 2. Firstly the glass transforms in a supercooled liquid across the glass transition, then the supercooled liquid crystallizes (crystallization has been observed during all the experiments), with a typical onset crystallization temperature of $T_{x,h} = 132$ K and an enthalpy of $\Delta H_{x,h} = 57.2 \pm 3.7$ J/g $= 6.4 \pm 0.4$ kJ/mol. The heats of fusion or crystallization are determined by integrating the corresponding peaks in the dT/dt curves, plotted as a function of time, and that area is multiplied by the average heat capacity C_p of the cell at that temperature:

$$\Delta H = \frac{1}{m} \int_{t_1}^{t_2} (dT/dt)dt \times C_p. \tag{4}$$

The crystal, obtained either from cooling or from heating the supercooled liquid, always melts at $T_m = 161.5$ K. The average value of enthalpy of melting, calculated on the basis of 18 different events of fusion, is $\Delta H_m = 75.7 \pm 2.9$ J/g $= 8.5 \pm 0.3$ kJ/mol. This result is in good agreement with the
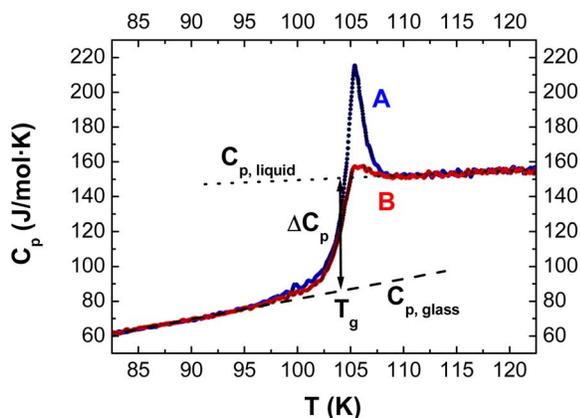
FIG. 3. Temperature dependence of the specific heat of ethylcyclohexane across the glass transition region for two different thermal histories. The glass (A) obtained by slow cooling (about −0.1 K/min) exhibits a more pronounced peak (overshoot) at T_g, compared to the sample quenched at −5 K/min (B). These heat-capacity measurements were performed consecutively using the continuous method at a heating rate of approximately +1 K/min. The method to determine T_g and $\Delta C_p(T_g)$, as the midpoint of the discontinuity, is graphically indicated.

literature values of 8.33 kJ/mol (by Huffman *et al.*[24]) and 8.28 kJ/mol (by Parks *et al.*[25]). As described above, in the present study, crystalline ethylcyclohexane has been formed experimentally in two different ways:

(I) supercooled liquid → crystal   [on cooling];

(II) glass → supercooled liquid → crystal   [on heating].

The experimental results indicate that the variation of enthalpy $\Delta H_{x,c}$ associated with the transition (I) from the liquid to the crystalline state is different from the enthalpy change $\Delta H_{x,h}$ associated with the phase transition (II). Both values are different from the enthalpy of melting ΔH_m, which corresponds to the reverse transition from the crystalline to the liquid state. However, this aspect can be easily explained if we assume a fixed entropy difference between liquid and crystal at any temperature. In fact, the relation $\Delta H = T\Delta S$ leads to $\Delta S_m = 52.1 \pm 2$ J/mol K at T_m, and hence, from the same relation, $\Delta H_{x,c} = 65.8 \pm 2.5$ J/g at 141 K and $\Delta H_{x,h} = 61.6 \pm 2.4$ J/g at 132 K, in agreement within experimental errors with the observed values. It is important to remark that the above determinations of heats of melting or crystallization are independent of the calorimetric cell, whose heat capacity influences the background of the curve but not the deviations observed due to endothermic or exothermic processes.

By using above-mentioned adiabatic and/or continuous methods, the heat capacities of several ethylcyclohexane glasses prepared by slow or fast cooling were measured. As expected, the thermal behavior of the glassy samples across the glass transition region depends on their thermal history. An example is shown in Fig. 3: glass A was obtained by slow cooling (about −0.1 K/min), whereas glass B was produced by quenching at −5 K/min. The specific heat of both samples was measured at an approximate rate of +1 K/min. The sample obtained by slow cooling exhibits a sudden peak (overshoot) at the glass transition (Fig. 3), while this feature
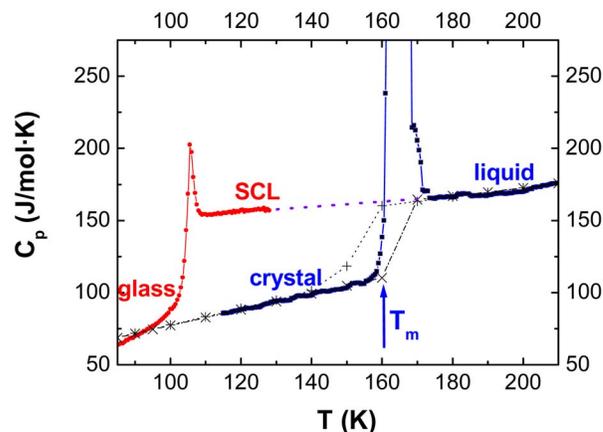

FIG. 4. Averaged specific heat data of ethylcyclohexane, measured on heating by the continuous method, in liquid, supercooled liquid (SCL), glassy, and crystalline states. Published data for the crystal and liquid phases are also shown (×, Ref. 24; +, Ref. 25).

is very less evident for the sample obtained by quenching, the reason being that in the former (latter) case the upward scan measuring rate is faster (slower) than the glass forming cooling rate. Considering several measurements on glassy samples obtained at different cooling rates (nine experimental runs ranging from −0.1 to −5 K/min, with an average cooling rate of −1 K/min, always being the heating rate of +1 K/min), the averaged glass transition temperature found is $T_g = 104.5 \pm 1$ K, and the discontinuity of the specific heat across the glass transition is $\Delta C_p(T_g) = 63$ J/mol K (see the method[26] used to determine the glass transition in Fig. 3 and the averaged data in Fig. 4). Contrary to the so-called "fictive temperature" T_f (defined as the intersection temperature of the extrapolated liquid and glass curves of *enthalpy*), the midpoint of the jump in the specific heat is much less dependent on the previous cooling rate employed since the liquid and glass $C_p(T)$ curves coincide in all cases beyond the transformation range. Uncertainties in this and next $\Delta C_p(T_g)$ values are estimated to be always below 6%.

As for glasses, a number of C_p measurements of the crystals were run, exhibiting very reproducible results. The specific heat of the crystals grown from cooling (route I) was found to be identical to that of the crystals obtained on heating (route II), showing that the two methods of preparation always provide the same crystalline phase. After the first-order transition peak due to melting (see Fig. 2), the heat capacity of the liquid could also be measured though the accuracy of calorimetric data decreases with increasing temperature. Thus the temperature-dependent specific heat of ethylcyclohexane has been measured in liquid, supercooled liquid, glassy, and crystalline state (Fig. 4). The results in the liquid and crystalline states are in agreement with the literature values,[24,25] while the thermal behavior in the glassy state had not been investigated previously to our knowledge.

B. Propylcyclohexane

Our calorimetric experiments on propylcyclohexane have shown that when slowly cooling the liquid from room temperature at typical rates of −0.2 K/min in the tempera-

ture region around 150 K, the substance does not crystallize, and a glass is finally obtained below 120 K. The glass transition temperature is $T_g = 118 \pm 1$ K and the discontinuity of the specific heat at T_g is $\Delta C_p(T_g) = 66$ J/mol K. In order to observe a crystallization, the liquid had to be cooled down and maintained in the region around 150 K. Crystallization starts at $T_{x,c} = 151$ K and the enthalpy change associated with the phase transition is $\Delta H_{x,c} = 71.5 \pm 4$ J/g $= 9.0 \pm 0.5$ kJ/mol. On the other hand, starting from the glassy state and heating the sample above the glass transition temperature, the supercooled liquid has regularly shown a crystallization with a typical onset temperature $T_{x,h} = 146$ K, and enthalpy change $\Delta H_{x,h} = 73.6 \pm 4$ J/g $= 9.3 \pm 0.5$ kJ/mol. The melting temperature of the crystal, made either by cooling the supercooled liquid or by heating the glass, is $T_m = 178$ K. The enthalpy of melting deduced from present experiments is $\Delta H_m = 84.3 \pm 3$ J/g $= 10.6 \pm 0.4$ kJ/mol, which corresponds to an entropy change $\Delta S_m = 59.7 \pm 2$ J/mol K at the melting temperature. Assuming a fixed entropy difference between liquid and crystal at any temperature and using again the relation $\Delta H = T\Delta S$, it follows that $\Delta H_x = 71 \pm 2.5$ J/g at 150 K, in agreement with both measured crystallization values.

C. Butylcyclohexane

When cooling the liquid butylcyclohexane below around 200 K at moderate cooling rates as -0.5 K/min, the substance always crystallized. The found onset of the crystallization was $T_{x,c} = 182 \pm 2$ K and the measured enthalpy change $\Delta H_{x,c} = 100.5 \pm 2$ J/g $= 14.1 \pm 0.3$ kJ/mol. Crystallization on cooling was avoided by quenching the liquid at around -10 K/min, introducing helium as exchange gas between the cell and the liquid nitrogen external reservoir. On heating the glass, it undergoes the glass transition at 122 K with a change in specific heat $\Delta C_p(T_g) = 80$ J/mol K. The supercooled liquid obtained by heating the glass through the glass transition was not stable against crystallization. In fact, crystallization was always observed with a typical onset temperature of $T_{x,h} = 152$ K and enthalpy variation $\Delta H_{x,h} = 78 \pm 1$ J/g $= 11.0 \pm 1.5$ kJ/mol.

Independent of the route to the formation of the crystal, the latter was always found to melt at $T_m = 198$ K with an enthalpy of melting $\Delta H_m = 101 \pm 2$ J/g $= 14.2 \pm 0.3$ kJ/mol. The relation $\Delta H = T\Delta S$ leads to $\Delta S_m = 71.5 \pm 1.4$ J/mol K at T_m. As in the previous cases of ethylcyclohexane and propylcyclohexane, assuming a fixed entropy difference between liquid and crystal at any temperature, it follows that $\Delta H_{x,h} = 77.5$ J/g at 152 K and $\Delta H_{x,c} = 93$ J/g at 182 K in reasonable agreement with the observed crystallization values.

D. Methylcyclohexane

Contrary to ethyl- or propyl-cyclohexane, when slowly cooling liquid methylcyclohexane from room temperature (typically around -0.3 K/min in the relevant temperature range around 150 K), and even when quenching the liquid faster than -10 K/min, the substance always crystallized and it was not possible for us to obtain the glassy phase. It is known from the literature[27] that the glass transition occurs around 85 K. In the case of slow cooling, the onset of crys-
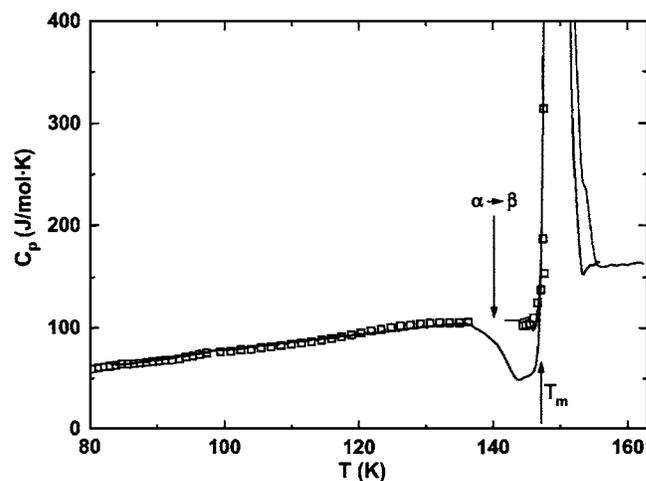

FIG. 5. Temperature dependence of the specific heat of methylcyclohexane from the crystalline to the liquid state. Solid lines: measured on heating by the continuous method. Squares: measured on heating by the adiabatic method. The region preceding the melting presumably corresponds to a transition from the stable α phase to a premelting β phase.

tallization is observed at $T_{x,c} = 138$ K. The enthalpy change associated with the phase transition is $\Delta H_{x,c} = 68.5 \pm 3.5$ J/g $= 6.7 \pm 0.3$ kJ/mol. The crystal melts at $T_m = 147$ K. The enthalpy of melting was found to be $\Delta H_m = 70.2 \pm 1.4$ J/g $= 6.89 \pm 0.14$ kJ/mol, corresponding to an entropy change of $\Delta S_m = 47 \pm 1$ J/mol K. Using again $\Delta H = T\Delta S$, it would follow that $\Delta H_{x,c} = 66$ J/g at 138 K, in good agreement with the observed crystallization values. The thermal behavior of crystalline methylcyclohexane is shown in Fig. 5. On heating the crystal, an exothermic process is observed in the temperature range above 140 K and just below the melting temperature. A previous investigation on methylcyclohexane based on Raman scattering experiments had pointed out the existence of a possible premelting crystal phase (β), different from the low-temperature stable crystal α. Thus the exothermic feature observed by adiabatic calorimetry below T_m can be tentatively identified as the transition from the α to the β phase of crystalline methylcyclohexane.

IV. DISCUSSION

Glass-forming ability of alkylcyclohexanes appears to be sensitive to systematic changes of the molecular structure. Using the present kind of calorimetric cells, it has been observed that methylcyclohexane cannot be cooled down to the glassy phase avoiding crystallization, even at cooling rates as high as -10 K/min. Comparatively, ethylcyclohexane is a good glass former because it reaches the glassy phase at moderate cooling rates such as -0.2 K/min. Nevertheless, in some occasions, when working on the liquid after melting the crystal, ethylcyclohexane has been observed to crystallize at the same cooling rates. When the length of the alkyl side chain is increased, propylcyclohexane shows an even better glass forming ability since it never crystallizes on cooling at slow rates. However, the next substance in the series, butylcyclohexane, can lead to the glassy phase only by relatively fast quenching. Thus the glass forming ability of alkylcyclohexanes is improved by increasing the length of
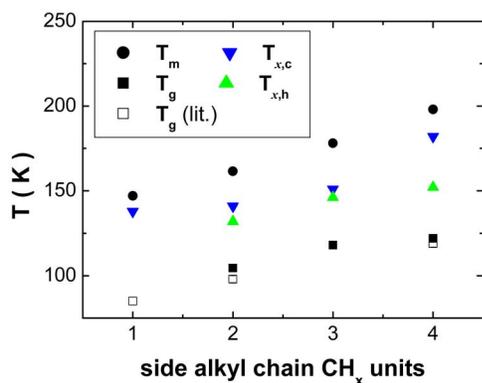
FIG. 6. Melting temperature T_m and glass transition temperature T_g of alkylcyclohexanes as a function of the alkyl-chain length. Glass transition temperatures from previous literature (Ref. 27) (□) are shown for a comparison. The plot also shows the onset of crystallization observed on cooling the liquid T_{xc} (▼), as well as the temperature of crystallization T_{xh} (▲) observed on heating the supercooled liquid coming from the glass.

the alkyl chain from methylcyclohexane to propylcyclohexane, but this trend is interrupted for a longer alkyl chain in butylcyclohexane. It is interesting to notice that exactly the same pattern holds in the case of the first four monoalcohols, from methanol up to *n*-buthanol.[17,27] Apparently, when the hydrocarbon molecules are long enough, they begin to find it easier to align themselves and crystallize.

The temperatures of crystallization, glass transition, and melting for the series of alkylcyclohexanes are shown as a function of increasing alkyl-chain length in Fig. 6. Both the melting temperature and the glass transition temperature increase when the length of the alkyl chain is increased. This is in agreement with the general trend of small molecule glass formers.[27] In Fig. 6, it can be observed that the higher the glass forming ability is, the lower the difference between the temperatures $T_{x,c}$ and $T_{x,h}$, is which mark the onset of crystallization on cooling from the liquid and on heating from the glass, respectively. Moreover, the glass forming ability does correlate with the ratio T_g/T_m (see Table I), i.e., the narrower the temperature window for crystallization is, the easier the glass can be obtained. Again, we can mention that the simplest monoalcohols exhibit the same correlation[17,27] and even very similar figures of T_g/T_m for the corresponding number of carbons.

On the basis of the present calorimetric results on the alkylcyclohexanes, we conclude that the crystalline phases obtained following the two different thermal routes (either cooling the liquid or by heating the glass) are the same, since

no further transitions are observed and they exhibit indeed the same values of specific heat. In the previous section it has been pointed out that, for each of the substances investigated, depending on the temperature at which the phase transition between crystal and liquid occurs, different values of the measured enthalpy variation ΔH are obtained. At the melting temperature the relation $\Delta H_m = T_m \Delta S_m$ allows to use the heat of melting to evaluate the entropy difference between the liquid and the crystal, ΔS_m. At the other relevant temperatures, i.e., $T_{x,c}$ and $T_{x,h}$, the experimental results are consistent with the hypothesis that the entropy difference, ΔS_m between the liquid and the crystal is essentially constant in the considered temperature interval and mainly due to a variation in configurational entropy. This observation provides further support to the conclusion that both routes to crystallization bring to the same crystalline stable phase, since a single value of ΔS_m can account for the measured values of ΔH concerning all the different crystal-to-liquid and liquid-to-crystal transition events.

The entropy variation ΔS_m associated with either melting or crystallization, as well as the molar specific-heat discontinuity $\Delta C_p(T_g)$, clearly increases with the side chain length (see Table I). These magnitudes have been traditionally rationalized in terms of "beads," i.e., more or less spherical and compact units that conform the molecule and their corresponding degrees of freedom. In Table I, we can see that $\Delta C_p(T_g)/R$ gives approximately the number of carbons per molecule. Lubchenko and Wolynes[28] have recently proposed to count beads from the entropy of fusion instead of at the glass transition. Assuming an entropy of fusion per particle for Lennard-Jones spheres, $s_{LJ} = 1.68k_B$, they proposed hence $N_{beads} = \Delta S_m/1.68R$. So-obtained numbers of beads are roughly one-half of the former ones. These authors also successfully predicted a correlation between the supercooled-liquid fragility[3] m (essentially the activation energy at the glass transition in units of $k_B T_g$) and the basic thermodynamic magnitudes:

$$m = 34.7 \frac{T_m}{\Delta H_m} \Delta C_p \equiv 34.7 \frac{\Delta C_p}{\Delta S_m}. \tag{5}$$

We also show in Table I these predicted fragility parameters for the studied alkyl-cyclohexanes. To our knowledge, there are no kinetic measurements to compare with. Thus we find that alkyl-cyclohexanes are moderately strong liquids, rather than fragile, with fragility indices very similar to that of *n*-propanol.[29,30]

TABLE I. Summary of thermodynamic parameters concerning the glass transition and the stable crystal-to-liquid transition in the cyclohexane derivatives investigated in the present work. R is the ideal gas constant. The number of beads N_{beads} and the predicted fragility index m from Eq. (5), after Lubchenko and Wolynes (Ref. 28), are also given.

	M_W (g/mol)	T_m (K)	T_g (K)	T_g/T_m	$\Delta C_p (T_g)$ (J/mol K)	ΔS_m (J/mol K)	$\Delta C_p/R$	$N_{beads} = \Delta S_m/1.68R$	m
MCH	98.19	147	85[a]	0.59	···	47	···	3.4	···
ECH	112.21	161.5	104.5	0.65	63	52.1	7.6	3.7	42
PCH	126.24	178	118	0.66	66	59.7	7.9	4.3	38
BCH	140.27	198	122	0.62	80	71.5	9.6	5.1	39

[a]See Ref. 27.

The smallest molecule of the series, methylcyclohexane, with minimum difference in entropy between the crystal and the liquid is also the only substance which has shown a transition to a premelting crystalline structure. The onset temperature of this premelting feature coincides with the temperature at which Abramczik et al.[18] firstly reported a sudden and significant change in the vibrational spectrum of methylcyclohexane. Interestingly, the authors of these Raman investigations on methylcyclohexane also reported that the glassy state could be achieved at a cooling rate of -3 K/min.[18,19] In the present study instead, it was impossible to get the sample in the glassy state even at cooling rates as high as -10 K/min. The reason of this different behavior might depend on the different experimental cells employed. A glass ampoule was used for the optical measurements. This implies that the optical sample had a smaller volume, a larger surface to volume ratio, and the liquid was in contact with clean, smooth walls made of vitreous material. In contrast, calorimetric cells are made of copper, are larger, and the liquid faces metallic protuberances that may promote heterogeneous crystallization. Indeed, very similar findings have been reported and discussed for experiments conducted on ethanol:[31] experimental cells for x-ray diffraction and Brillouin measurements allowed to obtain the glassy phase at very moderate cooling rates, whereas calorimetric ones required much higher quenching rates.

V. CONCLUSIONS

Thermodynamic properties of a series of cyclohexane derivatives have been studied by both adiabatic and continuous calorimetries. The specific heat of ethylcyclohexane, n-propylcyclohexane, and n-butylcyclohexane has been measured for the first time also in the glassy phase. The results clearly indicate that the glass-forming ability of alkylcyclohexanes depends on the size of the alkyl chain: it is improved on going from methylcyclohexane to propylcyclohexane, but the trend is inverted with butylcyclohexane. Only one stable crystalline phase is found for ethylcyclohexane, propylcyclohexane, and butylcyclohexane, independent of the thermal history of the material. In the case of methylcyclohexane a transition from the stable crystalline α phase to a premelting, crystalline structure β is found around 140 K, in agreement with the results of a previous Raman-spectroscopy investigation. On the other hand, melting (T_m) and glass (T_g) temperatures, enthalpies (ΔH_m), and entropies (ΔS_m) of melting, as well as specific-heat discontinuities $\Delta C_p(T_g)$ at the glass transition, increase more or less linearly with the length of the alkyl chain and with the corresponding number of beads constituting the molecule.

[1] P. W. Anderson, Science **267**, 1615 (1995).

[2] D. Turnbull, Contemp. Phys. **10**, 473 (1969).

[3] C. A. Angell, J. Non-Cryst. Solids **102**, 205 (1988).

[4] I. Gutzow and J. Schmelzer, *The Vitreous State* (Springer, Berlin, 1995).

[5] P. G. Debenedetti, *Metastable Liquids: Concepts and Principles* (Princeton University Press, Princeton, 1996).

[6] C. Alba-Simionesco, J. Fan, and C. A. Angell, J. Chem. Phys. **110**, 5262 (1999).

[7] G. Harrison, *The Dynamic Properties of Supercooled Liquids* (Academic, New York, 1976).

[8] S. R. Elliott, *Physics of Amorphous Materials*, 2nd ed. (Longman, Essex, 1990).

[9] G. B. McKenna, in *Glass Formation and Glassy Behavior*, Comprehensive Polymer Science Vol. 2, edited by C. Booth and C. Price (Pergamon Press, Oxford, 1989), pp. 311–362.

[10] A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, J. Appl. Phys. **88**, 3113 (2000).

[11] J. H. Crowe, J. F. Carpenter, and L. M. Crowe, Annu. Rev. Physiol. **60**, 73 (1998).

[12] *The Glassy State in Foods*, edited by J. M. C. Blanshard and P. Lillford (Nottingham University Press, Nottingham, 1993).

[13] *Glasses and Amorphous Materials*, Materials Science and Technology Vol. 9, edited by J. Zarzycki (VCH, Weinheim, 1991).

[14] H. Suga, J. Therm Anal. Calorim. **80**, 49 (2005); O. Haida, H. Suga, and S. Seki, J. Chem. Thermodyn. **9**, 1133 (1977).

[15] C. Talón, M. A. Ramos, S. Vieira, G. J. Cuello, F. J. Bermejo, A. Criado, M. L. Senent, S. M. Bennington, H. E. Fischer, and H. Schober, Phys. Rev. B **58**, 745 (1998).

[16] C. Talón, M. A. Ramos, and S. Vieira, Phys. Rev. B **66**, 012201 (2002).

[17] M. A. Ramos, C. Talón, R. J. Jiménez-Riobóo, and S. Vieira, J. Phys.: Condens. Matter **15**, S1007 (2003).

[18] H. Abramczik, K. Paradowska-Moszkowska, and G. Wiosna, J. Chem. Phys. **118**, 4169 (2003).

[19] H. Abramczik and K. Paradowska-Moszkowska, J. Chem. Phys. **115**, 11221 (2001).

[20] M. Cutroni and A. Mandanici, J. Phys. Chem. (submitted).

[21] A. Mandanici, M. Cutroni, and R. Richert (unpublished).

[22] E. Gmelin, Thermochim. Acta **29**, 1 (1979).

[23] T. H. K. Barron and G. K. White, *Heat Capacity and Thermal Expansion at Low Temperatures* (Kluwer Academic, New York, 1999), Chap. 3.

[24] H. M. Huffman, S. S. Todd, and G. D. Oliver, J. Am. Chem. Soc. **71**, 584 (1949).

[25] G. S. Parks, G. E. Moore, M. L. Renquist, B. F. Naylor, L. A. McClaine, P. S. Fujii, and J. A. Hatton, J. Am. Chem. Soc. **71**, 3386 (1949).

[26] D. R. Uhlmann, A. G. Kolbeck, and D. L. De Witte, J. Non-Cryst. Solids **5**, 426 (1971).

[27] C. A. Angell, J. M. Sare, and E. J. Sare, J. Phys. Chem. **82**, 2622 (1978).

[28] V. Lubchenko and P. G. Wolynes, J. Chem. Phys. **119**, 9088 (2003).

[29] C. A. Angell, J. Res. Natl. Inst. Stand. Technol. **102**, 171 (1997).

[30] J. D. Stevenson and P. G. Wolynes, J. Phys. Chem. B **109**, 15093 (2005).

[31] M. A. Ramos, I. M. Shmyt'ko, E. A. Arnautova, R. J. Jiménez-Riobóo, V. Rodríguez-Mora, S. Vieira, and M. J. Capitán, J. Non-Cryst. Solids (in press).