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# Solid-State Studies on a Cubic 1:1 Solvate of $C_{60}$ Grown from Dichloromethane and Leading to Another Hexagonal $C_{60}$ Polymorph

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Crystals of a $C_{60}$ 1:1 solvate (I-centered cubic, $a = 23.284(2)$ Å) were grown by evaporating solutions of $C_{60}$ in $H_2CCl_2$ at room temperature. Solvate crystals are not air stable and spontaneously transform into a hexagonal polymorph of $C_{60}$ ($a = 10.044(5)$ Å, $c = 16.404(8)$ Å, $c/a = 1.633(2)$) when extracted from the mother liquor at room temperature. Although solvate formation entails almost no volume change, desolvation enthalpy (59.2 kJ/mol of solvent) is found to be about twice as high as sublimation enthalpy for pure $H_2CCl_2$.

## 1. Introduction

The present work is part of a study on polymorphism and solvation of fullerene $C_{60}$, which was initiated by crystal photographs published by Krätschmer et al.[1] and the crystal appearance of early samples of solid $C_{60}$. The latter contained hexagonal-looking flat crystals, which were found afterward to be twinned fcc $C_{60}$ crystals with well-developed (111) faces.[2−6] It was also shown that the low-temperature freezing at about 90 K of the two-position orientational disorder in the simple cubic $C_{60}$ structure gave rise to a crystalline glassy state.[7−14] The occurrence of a glass transition can be considered as a clue for the existence of a transition to a more stable crystalline phase that is hindered because of kinetic reasons.[15] Thus, it can be thought that a low-temperature phase of $C_{60}$ (presumably hexagonal) is missing.

Another intriguing feature of early fcc $C_{60}$ powders obtained from solutions was their ability to trap solvent molecules;[16] particularities of X-ray profiles of these powders were related to hexagonal packing locally formed within the fcc lattice and solvent-induced defects.[17] However, until now, it remains unclear whether solvent molecules are retained through adsorption or solvation, perhaps because data on thermodynamic

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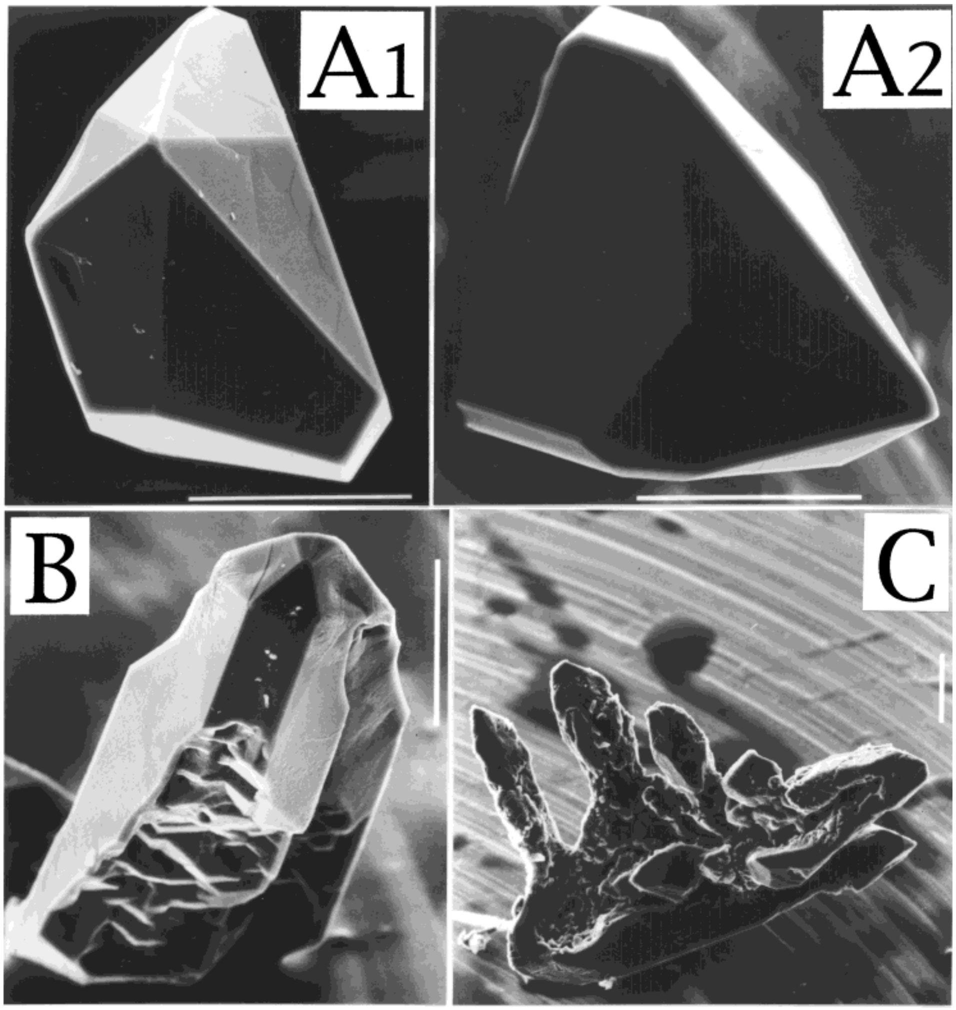

**Figure 1.** Scanning electron microscopy photographs of crystals of cubic $C_{60}\cdot 1H_2CCl_2$. A: top view (1) with apparent 3-fold symmetry and lateral view (2) of a perfectly grown single crystal. B: another crystal where chaotic growth sits side by side with perfectly grown faces. C: dendritic growth of large polycrystalline agglomerates. Accelerating voltage: 25 kV. White bars correspond to 100 $\mu$m. magnification: 360× (A1 and A2), 240× (B), and 110× (C).

balances between adsorption and solvation are lacking.[18] Thus, polymorphism and solvation of $C_{60}$ remain open to question.

We found previously that thin needles grown by evaporating solutions of $C_{60}$ in dichloromethane[19] are single crystals of a hexagonal polymorph of $C_{60}$ with ratio $c/a < 1.633$ at room temperature. To try to obtain greater amounts of this phase, other evaporation experiments were undertaken, and crystals were grown, which proved to be different from the hexagonal needles obtained previously. This paper describes the resulting observations.

## 2. Experimental Section

**Techniques.** Crystal morphologies were examined by means of a JEOL JSM-35C scanning electron microscope.

An ENRAF-NONIUS Weissenberg camera ($\lambda$ Cu K$\alpha$ = 1.5418 Å) was used for preliminary X-ray diffraction studies on a single crystal.

High-resolution X-ray powder diffraction measurements using Debye–Scherrer geometry and transmission mode were performed with a horizontally mounted INEL cylindrical position-sensitive detector (CPS-120) made of 4096 channels (angular step of 0.029° in $2\theta$ degrees).[20] Cu K$\alpha_1$ radiation ($\lambda$ = 1.5406 Å) was selected by means of an asymmetric focusing incident-beam curved quartz monochromator. The generator power was set to 1.2 kW (40 kV and 30 mA). External calibration by means of cubic phase $Na_2Ca_3Al_2F_4$[21,22] was performed for channels to be converted into $2\theta$ degrees by means of cubic spline fittings. Peak positions were determined by Pseudo-Voigt fittings.

Samples were introduced into 0.5-mm-diameter Lindemann capillaries, which were rotated around their axes during data collections.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed under nitrogen or helium flux by means of thermobalance and DSC cell of a TA Instruments TA2000 system, respectively. A TA2910 system (also from TA Instruments) equipped with its cooling accessory was used for the low-temperature measurements (220–300 K). Heating and cooling rates of 5 and 10 K·min$^{-1}$ were used. Sample masses in the 2–5-mg range were weighed by means of 0.01-mg-sensitive microbalances.

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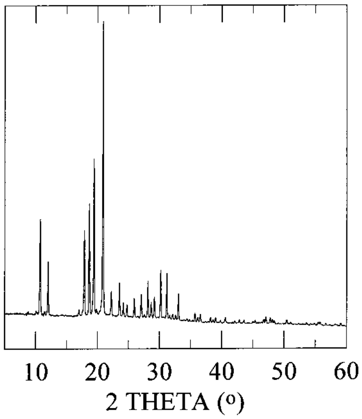

**Figure 2.** X-ray diffraction profile of the cubic $C_{60}\cdot 1H_2CCl_2$ solvate. This profile has been recorded from unground crystallites while a small excess of mother liquor was still in the Lindemann capillary.

**Sample Preparations.** Two methods were used to prepare the samples.

The first method consisted of evaporation of saturated solutions at room temperature. An excess (about 50 mg) of fcc $C_{60}$ (purity > 99.98%) from TermUSA was introduced into an Erlenmeyer flask (250-mL volume) filled with dichloromethane (Aldrich, purity >99.9%). After a 1-day contact, the solution was poured into several open beakers, which were left overnight in the dark at room temperature. Large transparent red-brown crystalline needles (Figure 1) were found in the saturated solutions whose evaporation was stopped before completion because preliminary experiments had shown that these crystals are not air stable.

The second method was used to check whether an equilibrium between a $C_{60}$ solvate and its saturated solution could spontaneously occur from contact between an excess of cubic $C_{60}$ and dichloromethane. Two Erlenmeyer flasks filled with dichloromethane (250 mL) and an excess of fcc $C_{60}$ crystals (about 100 mg) were closed and stored in the dark at room temperature. After 45 days had elapsed, X-ray diffraction examination of the solid in excess revealed that it was made of the same phase as that resulting from the first method, although crystal morphologies (twinned cubocahedra and hexagonal-shaped plates) of initial fcc $C_{60}$ crystals were retained. One year later, the same result was found after the solid phase in the second Erlenmeyer was examined through X-ray diffraction.

## 3. Results

Preliminary X-ray diffraction experiments on a single crystal like that shown in Figure 1 revealed that the needle axis ($c_H = 20.1$ Å) about which it oscillated is not a symmetry axis. However, the 0-layer photograph normal to the needle axis exhibited symmetry axes at 60° from one another, from which it came $a_H = b_H = 33.3$ Å and $\gamma = 120°$. Then, the crystal deteriorated in air after about 8 h at 293 K.

For a high-resolution X-ray diffraction profile to be recorded, crystals were gently extracted together with solution and quickly introduced into a Lindemann capillary previously filled with the mother liquor. Then, the capillary was partially obstructed to slow solvent evaporation. The resulting X-ray profile is shown in Figure 2.

Program DICVOL-91[23] was used to determine crystal symmetry and lattice parameters. By using the first 22 stronger reflections, two solutions came out: a tetragonal unit cell with $a_T = 16.464$ Åand $c_T = 11.645$ Å (figures of merit: M(22) = 55.9, F(22) = 88.5) and a cubic unit cell with $a_C = 23.285$ Å (figures of merit: M(22) = 32.9, F(22) = 53.9). Subsequent least-squares refinements (63 reflections) by means of program AFFMAIL[24] yielded $a_T = 16.464(2)$ Å, $c_T = 11.645$ (2) Å ($V = 3156$ (1) Å$^3$) and $a_C = 23.284(2)$ Å ($V = 12623(4)$ Å$^3$) (Table 1).

Crystals as well as powders from both preparation methods underwent thermogravimetric measurements (at a 10 K·min$^{-1}$ rate), which started within <2 min after the samples were extracted from the mother liquor and put inside punctured aluminum pans. Whichever the sample, patterns such as curve A in Figure 3 were obtained. They showed that the sample mass decreases in two steps upon heating and levels off at about 473 K. The experimental weight loss (10.36% of the initial mass) is very close to the value (10.55%) calculated for ratio 1:1 between $C_{60}$ and $H_2CCl_2$ molecules.

Isothermal (298 K) gravimetric experiments were performed on powder samples (second method of preparation). They started 3 min or so after the samples were extracted from their mother liquor and the curve recording started a few minutes after it was observed that sample masses remained almost constant, which indicated that the excess of mother liquor had disappeared. Curves recorded for about 4000 min showed that weight losses of 10.3% occurred within about 500 min (Figure 4). These results show that the studied crystals and powders correspond to a new $C_{60}$ solvate.

To ascertain the 1:1 molar ratio between $C_{60}$ and dichloromethane, another isothermal (304 K) gravimetric experiment was performed on a heterogeneous sample made of powder extracted with an excess of the mother liquor and put into a Lindemann capillary (3-mm diameter, 11-mm length). Results are shown in Figure 5. It can be seen that a mass decrease occurs in two steps: the first step (steep decrease from origin to point “a”) is related to the evaporation of the mother liquor excess. Then, the mass decrease slows down all at once (point “a”), and the weight loss related to the second step is found to be 10.8% of the mass at point “a” (see inset, Figure 5). Then, the remaining powder was examined through X-ray diffraction. The resulting profile corresponds to profile A in Figure 6.

Both crystals and powders were also subjected to DSC analyses soon after they were extracted from mother liquors. No thermal effect was recorded upon cooling first to 220 K. Then, samples were heated to 523 K. Curve B in Figure 3 shows that two thermal events are associated with the two-step mass loss on the TG curve. For structure control after peak “a” in Figure 3 was recorded, another sample was heated to 363 K and then cooled to room temperature. Its X-ray diffraction profile (profile B in Figure 6) is very similar to the profiles attributed to mixtures of hexagonal and cubic $C_{60}$ by Vaughan et al.[17] The same result was obtained from another sample previously heated to 523 K (profile C in Figure 6), although better resolution on profile C indicates that crystallinity improved upon heating.

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**Table 1. X-ray Powder Diffraction Data for Cubic $C_{60}·1H_2CCl_2$ Solvate at Room Temperature (Observed ($d_{OBS}$) and Calculated ($d_{CAL}$) Interplanar Distances Correspond to the Profile in Figure 2; *h, k, l* = Miller Indices; $(I/I_o)$% = Relative Intensities)**

| *h k l* | $(I/I_o)$ % | $d_{OBS}$ (Å) | $d_{CAL}$ (Å) | $d_{OBS} - d_{CAL}$ (Å) |
|---|---|---|---|---|
| 2 2 0 | 32.4 | 8.2368 | 8.2322 | 0.0046 |
| 3 1 0 | 16.9 | 7.3638 | 7.3631 | 0.0007 |
| 4 2 0 | 1.7 | 5.2077 | 5.2065 | 0.0012 |
| 3 3 2 | 28.3 | 4.9640 | 4.9642 | −0.0002 |
| 4 2 2 | 35.2 | 4.7520 | 4.7528 | −0.0008 |
| 5 1 0 | 57.9 | 4.5659 | 4.5664 | −0.0005 |
| 5 2 1 | 100.0 | 4.2510 | 4.2511 | −0.0001 |
| 4 3 3 | 8.9 | 3.9952 | 3.9932 | 0.0020 |
| 6 1 1 | 11.0 | 3.7771 | 3.7772 | −0.0001 |
| 6 2 0 | 4.6 | 3.6809 | 3.6815 | −0.0006 |
| 5 4 1 | 3.9 | 3.5934 | 3.5928 | 0.0006 |
| 6 3 1 | 6.0 | 3.4332 | 3.4330 | 0.0002 |
| 4 4 4 | 0.3 | 3.3600 | 3.3608 | −0.0008 |
| 5 4 3 | 7.5 | 3.2921 | 3.2929 | −0.0008 |
| 6 3 3 | 11.0 | 3.1689 | 3.1686 | 0.0003 |
| 6 4 2 | 5.1 | 3.1114 | 3.1115 | −0.0001 |
| 7 3 0 | 6.3 | 3.0571 | 3.0573 | −0.0002 |
| 6 5 1 | 14.9 | 2.9571 | 2.9571 | 0.0000 |
| 8 1 1 | 14.2 | 2.8661 | 2.8661 | 0.0000 |
| 8 2 0 | 1.1 | 2.8246 | 2.8236 | 0.0010 |
| 6 5 3 | 1.7 | 2.7832 | 2.7830 | 0.0002 |
| 8 2 2 | 1.6 | 2.7434 | 2.7441 | −0.0007 |
| 8 3 1 | 8.7 | 2.7065 | 2.7067 | −0.0002 |
| 7 5 2 | 0.3 | 2.6360 | 2.6364 | −0.0004 |
| 8 4 0 | 0.8 | 2.6022 | 2.6032 | −0.0010 |
| 8 3 3 | 0.3 | 2.5720 | 2.5713 | 0.0007 |
| 8 4 2 | 0.4 | 2.5392 | 2.5405 | −0.0013 |
| 9 2 1 | 2.7 | 2.5111 | 2.5108 | 0.0002 |
| 6 6 4 | 1.5 | 2.4819 | 2.4821 | −0.0002 |
| 8 5 1 | 2.5 | 2.4543 | 2.4544 | −0.0001 |
| 7 6 3 | 0.1 | 2.4010 | 2.4016 | −0.0006 |
| 8 4 4 | 0.3 | 2.3770 | 2.3764 | 0.0006 |
| 8 5 3 | 1.5 | 2.3523 | 2.3521 | 0.0002 |
| 8 6 0 | 0.9 | 2.3284 | 2.3284 | −0.0000 |
| 7 7 2 | 1.5 | 2.3055 | 2.3055 | 0.0000 |
| 8 6 2 | 0.2 | 2.2830 | 2.2832 | −0.0002 |
| 9 5 0 | 0.7 | 2.2616 | 2.2615 | 0.0001 |
| 9 5 2 | 2.2 | 2.2197 | 2.2200 | −0.0003 |
| 8 6 4 | 0.2 | 2.1625 | 2.1619 | 0.0006 |
| 9 6 1 | 0.7 | 2.1432 | 2.1435 | −0.0002 |
| 9 5 4 | 1.2 | 2.1083 | 2.1080 | 0.0003 |
| 9 6 3 | 1.0 | 2.0743 | 2.0743 | 0.0000 |
| 9 7 2 | 0.4 | 2.0112 | 2.0114 | −0.0002 |
| 8 6 6 | 1.2 | 1.9964 | 1.9966 | −0.0002 |
| 8 8 4 | 1.7 | 1.9406 | 1.9403 | 0.0003 |
| 9 8 1 | 2.1 | 1.9269 | 1.9270 | −0.0001 |
| 10 5 5 | 2.1 | 1.9010 | 1.9011 | −0.0001 |
| 10 6 4 | 1.6 | 1.8883 | 1.8886 | −0.0003 |
| 9 8 3 | 0.9 | 1.8765 | 1.8763 | 0.0002 |
| 9 9 2 | 1.8 | 1.8069 | 1.8072 | −0.0003 |
| 9 8 5 | 0.4 | 1.7861 | 1.7858 | 0.0003 |
| 9 9 4 | 0.3 | 1.7457 | 1.7452 | 0.0005 |
| 11 7 4 | 0.4 | 1.7074 | 1.7073 | 0.0001 |
| 10 9 3 | 0.2 | 1.6893 | 1.6892 | 0.0001 |
| 9 8 7 | 0.5 | 1.6715 | 1.6717 | −0.0002 |
| 9 9 6 | 0.9 | 1.6546 | 1.6547 | −0.0001 |
| 10 10 0 | 1.1 | 1.6466 | 1.6464 | 0.0002 |
| 10 9 5 | 0.7 | 1.6221 | 1.6223 | −0.0002 |
| 13 5 4 | 0.7 | 1.6067 | 1.6067 | −0.0000 |
| 12 6 6 | 0.7 | 1.5839 | 1.5843 | −0.0004 |
| 11 9 4 | 0.4 | 1.5773 | 1.5770 | 0.0003 |
| 11 10 1 | 0.9 | 1.5627 | 1.5627 | 0.0000 |
| 14 5 3 | 0.6 | 1.5354 | 1.5353 | 0.0001 |

A sample recovered after an isothermal (298 K) gravimetry experiment was examined through DSC up to 523 K. No thermal effect was recorded (see curve C in Figure 3).

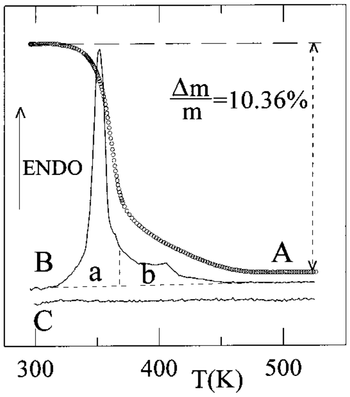

**Figure 3.** TG (A) and DSC (B) curves recorded upon heating cubic $C_{60}·1H_2CCl_2$ crystals gathered in punctured pans. C = DSC curve upon heating again the desolvated sample recovered from experiment B. ($N_2$ flow, 10 and 5 K·min$^{-1}$ rates for TG and DSC, respectively). Sample masses (A: 5.20 mg; B: 2.61 mg; C: 1.80 mg).

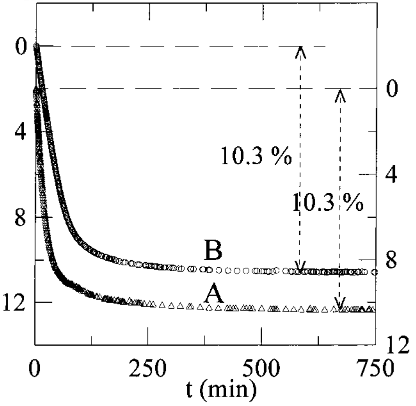

**Figure 4.** Isothermal (298 K) gravimetric curves. Powder samples of the cubic $C_{60}·1H_2CCl_2$ solvate have been gathered in an open pan (A) and in a pan with a punctured cover (B). Initial sample masses: 2.06 mg (A) and 3.72 mg (B).

To determine which phase(s) is (are) involved while mass loss occurs at room temperature, X-ray powder diffraction measurements were carried out as a function of time at 293 K. They show (Figure 7) that solvate crystals transform within 15 days or so at room temperature into a new $C_{60}$ phase, whose profile is very close to that obtained above (profile A in Figure 6).

## 4. Discussion

From gravimetric experiments, it can be concluded that solids obtained through both preparation methods are built with $C_{60}$ and $H_2CCl_2$ in the 1:1 molar ratio.

Search for metrics resulted in two (cubic or tetragonal) possible unit cells. The tetragonal metrics was found to be almost the same as that found by Janssen and Waidmann,[25] although according to these authors, thermal analyses and density measurements led to a different stoichiometry ($C_{60}·2H_2CCl_2$). It can be seen that all observed reflections correspond to a primitive (P) lattice in the tetragonal setting and obey the condition $h + k + l = 2n$ in the cubic setting (Table 1). This corresponds to a body-centered (I) cubic cell related to the hexagonal setting of the rhombohedral lattice found from single-crystal X-ray measurements by the

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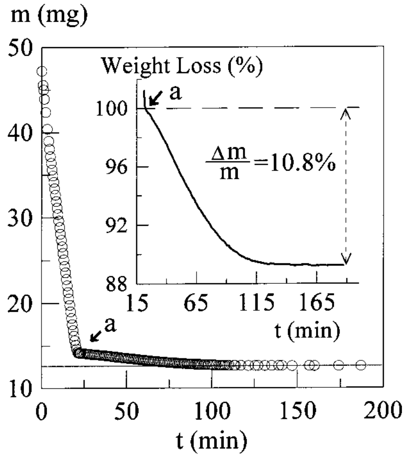

**Figure 5.** Isothermal (303 K) evaporation curve of a heterogeneous sample made of cubic $C_{60}\cdot 1H_2CCl_2$ powder and excess of the mother liquor (vertical axis: sample mass). Evaporation rate: −1.55 and −0.022 mg·min$^{-1}$ in the first part ($t = 0$ to $t = t_a$) and at the beginning of the second part ($t_a$ to $t = 60$ min) of the curve, respectively. Inset: detail of the second part of the curve (mass loss is expressed in % of the weight at point a).

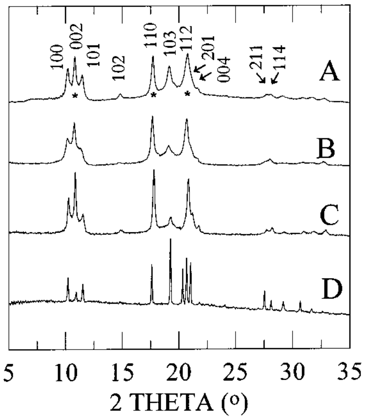

**Figure 6.** X-ray diffraction profiles of powders recovered at room temperature after desolvation at 304 K (A), 363 K (B), and 523 K (C). X-ray diffraction profile (D) of another hexagonal phase of $C_{60}$ obtained previously.[18] Stars indicate peaks that may be ascribed to fcc $C_{60}$.

following relationships: $a_H = \sqrt{2}\cdot a_C$ and $c_H = \sqrt{3}\cdot a_C/2$, while there are no crystallographic relationships between tetragonal P and cubic I lattices. This suggests that the single crystal was oscillated about direction <111>, that is, a 3-fold axis, of the cubic setting. It was also checked that reflections observed in the hexagonal 0-layer comply with the condition $h + k + l = 2n$ after indexing in the bcc setting. Thus, a bcc packing for solvate $C_{60}\cdot 1H_2CCl_2$ solvate is to be preferred.

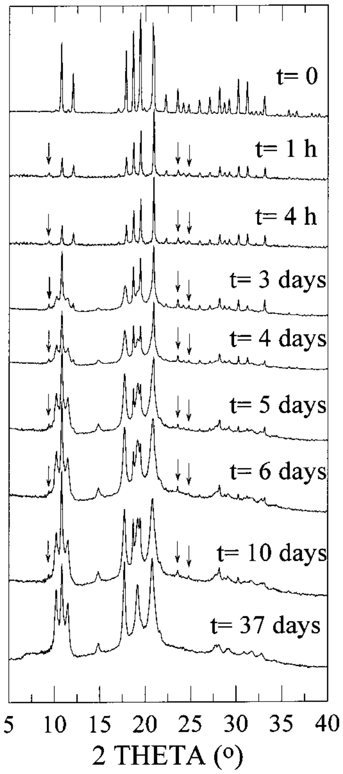

**Figure 7.** Isothermal (293 K) desolvation process for cubic $C_{60}\cdot 1H_2CCl_2$ examined through high-resolution X-ray diffraction as a function of time. Arrows indicate peaks that are not observed at the initial and final states of the process.

Assuming $Z = 16$ formula units in the bcc cell of the solvate and a volume of 710 Å$^3$ per $C_{60}$ molecule as in its fcc cell ($a = 14.16$ Å$^3$), it comes that about 79 Å$^3$ per $H_2CCl_2$ molecule in the solvate lattice is available per solvent molecule.This is close to 83 Å$^3$, calculated from the density value (20 kmol·m$^{-3}$ at 178 K) for solid $H_2CCl_2$.[26] Thus, it can be inferred that solvate formation is accompanied by almost zero or weakly negative excess volume (about 4 Å$^3$ per formula unit). This might explain why crystallization solvent is lost spontaneously, as it is from cubic solvates ($C_{60}\cdot 12$ cyclohexane,[27] $C_{60}\cdot 12CCl_4$[25,28,29]) that form with no or positive excess volume, and also for triclinic $C_{60}\cdot 4$ benzene[30,31] that forms with a weakly negative excess volume, although benzene molecules were found to pack in this solvate as they do within the high-pressure monoclinic benzene.[32]

From DSC, TG, and X-ray measurements, it may be concluded that the whole effect (peak a + peak b) in the DSC curve (curve B, Figure 3) is related to the desolvation enthalpy (73.5 J/g of initial sample, i.e., (59.2 ± 3.0) kJ/mol of solvent (or mol of 1:1 solvate) while peak b has to be assigned to the desorption of the solvent trapped inside the $C_{60}$ powder formed when the solvate lattice is destroyed upon heating. Since peaks a and b are accompanied 70.6% and 29.4% losses of the initial amount of solvent, respectively, it comes that peak b (20.2 J/initial g of solvate) corresponds to (55.3 ± 2.8) kJ/mol of desorbed solvent. It is to be emphasized that these results were found to be the same whatever

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the sample examined was (crystals and powders from both preparation methods).

The sublimation enthalpy for $H_2CCl_2$ is calculated to be about $+34$ kJ·mol$^{-1}$ by adding its melting enthalpy and its vaporization enthalpy.[33] It comes that the desolvation enthalpy ($+59.2$ kJ·mol$^{-1}$) is about twice as high as the sublimation enthalpy. This indicates that strong interactions between $C_{60}$ and solvent molecules may be inferred from thermodynamics while weak or no interactions may be inferred from crystallography. This paradoxical finding is the opposite of previous (albeit paradoxical too) conclusions attained for other solvates ($C_{60}$·2$CCl_4$,[34] $C_{60}$·1 *n*-heptane,[35] C60·1 *n*-octane,[36] $C_{60}$·1 trichlorethylene,[37] $C_{60}$·1 1,2-dichloroethane,[18] and $C_{60}$·2$S_8$[38]) for which weak and strong interactions were inferred from thermodynamics and crystallography, respectively.

It is found that solvation of solid $C_{60}$ into cubic $C_{60}$ by $H_2CCl_2$ solvate is preferred to adsorption of $H_2CCl_2$ on $C_{60}$ powders by about 4 kJ/mol of solvent, although this solvate is not air stable and spontaneously loses its crystallization solvent within a short time. This does not go along with previous conclusions[18] according to which $C_{60}$ solvates remain unchanged—even for years[39]—when solvation is thermodynamically preferred to adsorption.

Avgul and Kiselev[40] determined adsorption enthalpies ($\Delta_{\mathrm{ads}}H$) on thermal graphitic carbon black for compounds of the $H_{4-n}CCl_n$ ($n = 0, 1, 3, 4$) series. Results can be summed up by equation $|\Delta_{\mathrm{ads}}H|$ (kJ·mol$^{-1}$) $= 11.51 + 13.53n - 1.60n^2$ ($R^2 = 0.9992$). It becomes $|\Delta_{\mathrm{ads}}H| = 32.2$ kJ/mol of $H_2CCl_2$. Thus, adsorption of dichloromethane on $C_{60}$ is about twice as high as it is on thermal graphitic carbon black.

Let us now consider the X-ray profile of the phase that remains after solvent loss has occurred at room temperature. This profile is very similar to that assigned by Arkhangel'skii et al.[41] to a hexagonal $C_{60}$ phase (hereafter called H$\alpha$). From a least-squares refinement using $2\theta$ values of 12 reflections (Table 2), the profile became $a = 10.044(5)$ Å and $c = 16.404(8)$ Å ($V = 1433(1)$ Å$^3$ and $c/a = 1.633(2)$, close to the values found by Arkhangel'skii et al.[41] This indicates that hexagonal phase H$\alpha$ is different from that found previously.[19] Observation of reflection 102 also supports this conclusion (compare profiles A and D in Figure 6).

**Table 2. X-ray Powder Diffraction Data for a Hexagonal Phase of $C_{60}$ at Room Temperature (Observed ($d_{\mathrm{OBS}}$) and Calculated ($d_{\mathrm{CAL}}$) Interplanar Distances Correspond to Profile A in Figure 6; *h*, *k*, *l* = Miller Indices; Symbol * Indicates Reflections Not Used for Least-Squares Refinement; $(I/I_o)$% = Relative Intensities)**

| *h k l* | $(I/I_o)$ % | $d_{\mathrm{OBS}}$ (Å) | $d_{\mathrm{CAL}}$ (Å) | $d_{\mathrm{OBS}} - d_{\mathrm{CAL}}$ (Å) |
|---|---|---|---|---|
| 1 0 0 | 76.3 | 8.6857 | 8.6988 | −0.0131 |
| 0 0 2 | 79.9 | 8.1807 | 8.2019 | −0.0212 |
| 1 0 1 | 69.5 | 7.7172 | 7.6851 | 0.0321 |
| 1 0 2 | 10.1 | 5.9723 | 5.9676 | 0.0047 |
| 1 1 0 | 100 | 5.0119 | 5.0222 | −0.0103 |
| 1 0 3 | 81.2 | 4.6302 | 4.6293 | 0.0009 |
| 1 1 2 | 75.0 | 4.2803 | 4.2831 | −0.0027 |
| 2 0 1 | 29.7 | 4.2073 | 4.2041 | 0.0032 |
| 0 0 4 | 5.4 | 4.1041 | 4.1010 | 0.0031 |
| 2 1 1 | 6.3 | 3.2240 | 3.2237 | 0.0003 |
| 1 1 4 | 8.5 | 3.1779 | 3.1765 | 0.0014 |
| 1 0 5 | 7.5 | 3.0677 | 3.0697 | −0.0020 |
| 2 1 3 | 10.1 | 2.8217* | 2.8177 | 0.0040 |
| 0 0 6 | 8.1 | 2.7317* | 2.7340 | −0.0023 |
| 3 0 2 | | | 2.7338 | −0.0021 |
| 2 0 5 | 2.1 | 2.6119* | 2.6192 | −0.0073 |
| 1 0 6 | | | 2.6082 | 0.0037 |

## 5. Concluding Remarks

The cubic solvate described here has been shown to form equally by evaporation of saturated solutions and by slow transformation of the excess of the fcc $C_{60}$ phase in contact with dichloromethane solution at room temperature. This indicates that the initial solid−liquid heterogeneous equilibrium (fcc $C_{60}$ + saturated solution) transforms into a more stable equilibrium between solid $C_{60}$·1$H_2CCl_2$ solvate and saturated solution. This is generally accompanied with a solubility decrease (as was shown in the case of the $C_{60}$·1,1,2-trichloroethane system[42]) and this may be related to the reported anomalous[43] solubility of $C_{60}$, as suggested previously.[44,45]

Dichloromethane is the first solvent to prove unambiguously that polymorphism of $C_{60}$ really occurs at room temperature and that it is solvent dependent. Moreover, two hexagonal polymorphs of $C_{60}$ have been characterized from solutions in dichloromethane. One of them[19] has been shown to grow by quickly evaporating solutions in dichloromethane and the other one (H$\alpha$) to form by desolvation of a cubic $C_{60}$·1$H_2CCl_2$ solvate. These two hexagonal phases are (meta)stable at room temperature so that none of them can be the low-temperature phase, which is expected because of the occurrence of the glass transition near 90 K.

However, formation of polymorph H$\alpha$ through desolvation might involve another phase as a transient species in the transformation of the bcc solvate. This is suggested by a few weak reflections that grow on X-ray profiles recorded while transformation goes along with desolvation and that are no longer observed as soon as

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Hα samples become solvent free (see arrows in Figure 7). This transient phase might be another $C_{60}$ solvate with a lower $C_{60}$ content (although no inflection point was observed on the isothermal desolvation curves) or another $C_{60}$ polymorph that remains to be isolated and characterized.

Arkhangel'skii et al.[41] cautiously wrote that their powders might be made of mixtures of fcc and hcp phases. This is also supported by the change in relative intensities that occurs when solvent-free $C_{60}$ is obtained through desolvation upon heating. Comparison of profiles A and C in Figure 6 indicates that the peaks assigned to polymorph Hα become weaker as temperature increases. However, heating unground Hα powders up to 523 K did not reveal any DSC peak that might be related to Hα transformation into fcc $C_{60}$. Furthermore, DSC and TG experiments show that hexagonal phase Hα obtained from desolvation at room temperature does not trap solvent molecules, as the fcc $C_{60}$ phase obtained from solutions does. Thus, it might be inferred that the desorption-related effect (peak b on curve B in Figure 3) should be assigned to the cubic part of the cubic and hexagonal phase mixture that forms during desolvation of solvate $C_{60}\cdot 1H_2CCl_2$.

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