

THERMAL STABILITY OF FULLERENE AMINES HOST-GUEST CRYSTALS

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Abstract

Fullerenes C₆₀ with adamantane (C₁₀H₁₆), hexamethyltetramine (HMT, C₆H₁₂N₄) or 1,4-diazabicyclooctane (DABCO, C₆H₁₂N₂) crystallize, at the relative concentration C₆₀/guest=2/1, in the pseudotetragonal lattice in which C₆₀ retains almost the same positions as in pure fullerenes. The 'guest' molecules occupy the octahedral interstitial sites. The mixed crystals which exhibit interesting physical properties are thermally unstable. The decomposition starts at 40–50°C.

Keywords: fullerenes

Introduction

Fullerenes C₆₀ of icosahedral symmetry are almost spherical and are weakly interacting with each other by van der Waals forces. Pure C₆₀ fullerene crystallizes in the cubic closed packed lattice (fcc) [1]. There are two different interstitial sites in the lattice: two tetrahedral and one octahedral site per each fullerene, they can be filled up with various dopants to control properties of fullerenes. Recently it was discovered that fullerenes doped with several amines like C₆₀:TDAE [2, 3] (TDAE=C₁₀H₂₄N₄) or C₆₀:DBU, C₆₀:DBN, [4] (DBU=C₉H₁₆N₂, DBN=C₇H₁₂N₂) reveal ferromagnetic properties. These results turned our attention to other fullerene-amine systems. In contrast to those works, for our investigations we looked for molecules of similar cage structure which fit to the interstitial octahedral sites of the fcc fullerene lattice. We hoped that differences in the structure of the similar 'guest' molecules could better probe intermolecular interaction. Those conditions are satisfied by adamantane (C₁₀H₁₆), hexamethyltetramine (HMT, C₆H₁₂N₄) and 1,4-diazabicyclooctane (DABCO, C₆H₁₂N₂) (Fig. 1). It was hoped that comparison of crystallographic structure, infrared properties or magnetic properties, if there were any, could shed some light on the origin of ferromagnetism in fullerene-amine systems. The comparison of adamantane and HMT derivatives could in particular answer the questions whether nitrogen lone pair electrons have any influence on fullerene. The organic molecules used here to modify fullerenes, can not be considered as good electron donors in contrast to those reported previously [2–4], whereas

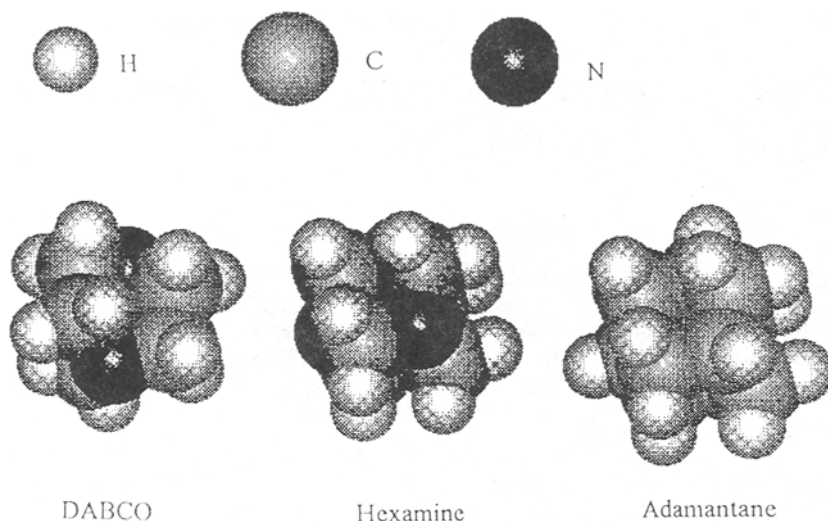


Fig. 1 The structure of the molecules used for investigations

the ferromagnetism in fullerides system is usually connected with amine \rightarrow fullerene electron transfer [3, 5]. Yet, it was found that C_{60} -HMT crystals exhibited magnetic hysteresis observed by ESR method [6, 7]. It could be also supposed that these molecules could be used to increase distances between fullerenes in superconducting fullerides.

Experimental results

Crystallization

The compounds which were used for growing C_{60} -amines crystals are similarly to fullerenes soluble in toluene, therefore the mixed crystals can be grown from the toluene solution. Since it was expected that the amines may be accommodate in the octahedral sites, the attempts to grow mixed crystals were started at the 1:1 C_{60} /amine concentration. It occurred, however, that in this case not whole amine was consumed by the growing crystals. With gradually decreasing amines relative concentration, the crystalline structure of the new compound remained the same, as verified by X-ray diffraction, but the amount of unused amines also decreased. Finally at the concentration C_{60} :amine=2:1 no more amines precipitates were detected in the X-ray patterns proving that all amine molecules were incorporated to the crystals.

Lattice structure

Although the crystallites powder was of good quality for the X-ray powder diffraction analyses we were unable to select any single crystallite which could

be used for single crystal diffractometry method in order to determine unambiguously the lattice structure. We therefore had to rely on the powder diffraction patterns only. The analyses of the obtained diffractograms suggests the pseudotetragonal lattice of the new crystals (Table 1), which is determined by arrangements of fullerenes. In this 'host' structure, the fullerenes remain in the fcc lattice in which every second octahedral site is occupied by the 'guest' molecule.

Table 1 The lattice parameters

| | $a/\text{Å}$ | $b/\text{Å}$ | $c/\text{Å}$ | β |
|-------------------------------------|--------------|--------------|--------------|---------------|
| $\text{C}_{10}\text{H}_{16}$ | 10.34 | 31.69 | 10.15 | 90.63° |
| $\text{C}_6\text{H}_{12}\text{N}_4$ | 10.35 | 31.71 | 10.16 | 90.43° |
| $\text{C}_6\text{H}_{12}\text{N}_2$ | 10.37 | 31.72 | 10.17 | 90.26° |

The diffractograms could be also interpreted in terms of a monoclinic lattice (similar to those of C_{60} :TDAE [2]) with the following lattice parameters $a=16.03\text{Å}$, $b=10.27\text{Å}$, $c=13.73\text{Å}$, $\beta=94.83^\circ$, for $(\text{C}_{60})_2:\text{C}_{10}\text{H}_{16}$.

In this lattice C_{60} are arranged in the distorted body centered cubic lattice with the amines built in the octahedral sites. Because in the two lattices fullerenes form substantially different 'host' lattice, one may hope that experiments on thermal decomposition of the mixed crystals can supply further arguments supporting one of the models.

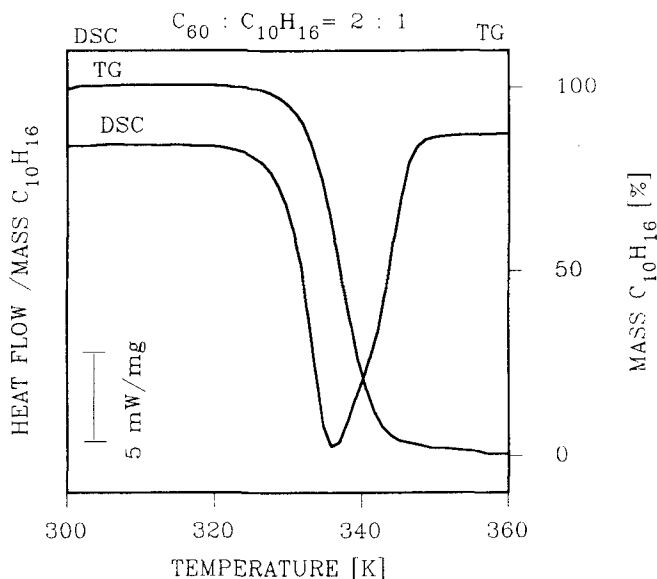


Fig. 2 The DSC and TG runs of the decomposition reaction of C_{60} :adamantane samples

Thermal analysis

The crystals were analyzed by thermal method with the use of Du Pont 1090 analyzer with the DSC unit in the temperature range 153–573 K. The DSC and TG measurements were performed with samples weighting 10 mg in the helium atmosphere at heating rates $a=1,2,5,10,20$ deg·min⁻¹ for DSC, and $a=10$ deg·min⁻¹ for TG with the helium flow 25 ml·min⁻¹.

The mixed fullerene-amine crystallites are thermally unstable. They start to decompose above 320 K. The DSC and TG runs for fullerene 2:adamantane is shown in Fig. 2. The mass loss of 8.6% results from the release of adamantane molecules from the crystalline structure. A maximum of mass loss rate coincides (within 1 K) with the maximum of the DSC run. Since the decomposition rate depends on the temperature and the position of the peak varies with the heating rate it is justified to use the activation energy (E_a) and to apply the Kissinger method [8] for analyzing the thermal effects data. Then the heating rate (a) and the temperature at the reaction rate maximum (=DSC maximum, T_m) obey the equation:

$$a/RT_m^2 = A \exp(E_a/RT_m);$$

where $a=dT/dt$, R —gas constant, A —coefficient.

The experimental results for $(C_{60})_2:C_{10}H_{16}$ decomposition at various heating rates are shown in Fig. 3, and the relation $\ln(a/T_m^2)$ vs. $(1/T)$ in Fig. 4, which was used to determine the activation energy.

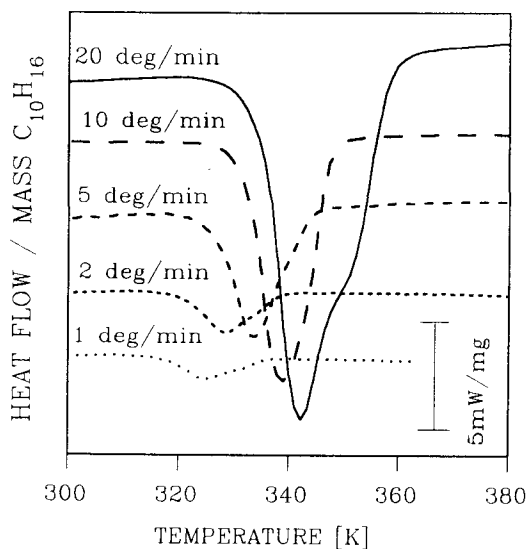


Fig. 3 The DSC runs obtained for C_{60} :adamantane samples at various heating rates

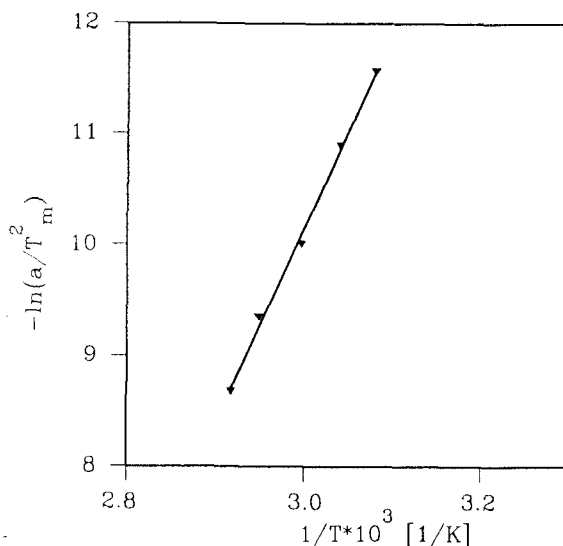


Fig. 4 Kissinger's plot for C_{60} :adamantane host-guest crystals

Here the activation energy is interpreted as the thermal energy needed to activate the migration of the guest molecules between equivalent 'host' lattice sites until they escape the crystallite. Because the samples after thermal experiments did not contain the 'guest' compounds and were well crystallized in the fcc structure, the following two approximations were used:

1. The enthalpy (ΔH) of thermal dissociation was identified with the binding energy (E_b) of the 'guest' molecules in the 'host' lattice ($\Delta H = E_b$), and the energy involved with the change of the C_{60} - C_{60} -distance ($\approx 4\%$) was neglected.
2. Prior and after the thermal process organic molecules did not interact with each other – they were in a 'vapor' state when they were evenly distributed in the mixed crystals lattice and after the decomposition.

The energies determined from such analyses for C_{60} -HMT, -DABCO and -adamantane crystals are summarized in the Table 2.

Table 2 Thermal decomposition data of $(C_{60})_2$:amine compounds

| | T_m/K | $\Delta H/kJ \cdot mole^{-1}$ | $E_a/kJ \cdot mole^{-1}$ |
|----------------|---------|-------------------------------|--------------------------|
| $C_{10}H_{16}$ | 339 | 100.2 | 146.1 |
| $C_6H_{12}N_4$ | 334 | 99.7 | 139.2 |
| $C_6H_{12}N_2$ | 337 | 101.3 | 140.8 |

The fact that, the annealing temperature in these experiments was very low and C_{60} was well crystallized after the thermal reaction we consider as an indirect proof that mixed crystals had pseudotetragonal lattice where fullerene molecules were arranged in the same lattice as in pure material.

Discussion

Our experiments on the mixed crystals, show that the intermolecular bonding of amines in fulleride lattice is very weak. The infrared absorption of these mixed crystals [9] exhibits new modes which can be ascribed to the deformed fullerene. Then the deformation can either originate from C_{60} - C_{60} interaction or C_{60} -amine (or adamantane) interaction. In the later case hydrogen of organic molecule might be responsible for fullerene deformation. Other experiments on hydrogen transfer to C_{60} from saturated hydrocarbons (decaline $C_{10}H_{18}$, cyclohexane C_6H_{12}) at elevated temperatures [10], proved that this interaction might be very effective. However these experiments do not supply enough information on the nature of the interaction. It remains also unclear why only every other octahedral site in the 'host' lattice can accommodate the 'guest' molecules.

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Zusammenfassung — Fullerene C_{60} kristallisieren mit Adamantan ($C_{10}H_{16}$), Hexamethylotetramin (HMT, $C_6H_{12}N_4$) oder 1,4-Diazabicyclooktan (DABCO, $C_6H_{12}N_2$) bei der relativen Konzentration $C_{60}/\text{Gast} = 2/1$ in einem pseudotetragonalen Gitter, in dem C_{60} die gleiche Position beibehält, wie in reinen Fullerenen. Die 'Gast'-Moleküle nehmen die oktaedrisch interstitialen Stellen ein. Diese Mischkristalle mit interessanten physikalischen Eigenschaften sind thermisch instabil. Die Zersetzung setzt bei 40–50°C ein.