PHYSICAL REVIEW B VOLUME 48, NUMBER 10 1 SEPTEMBER 1993-II

# Mechanically induced chemical decomposition of $C_{60}$-*n*-pentane clathrate at room temperature

G. Oszlányi, G. Bortel, G. Faigel, S. Pekker, and M. Tegze
*Research Institute for Solid State Physics, H-1525 Budapest, P.O. Box 49, Hungary*

R. J. Cernik
*Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom*

(Received 12 May 1993)

We report the mechanically induced chemical decomposition of $C_{60}$-*n*-pentane. This material is a typical $C_{60}$ clathrate with a well-characterized structure and is stable up to 400 K. However, at room temperature the grinding of $C_{60}$-*n*-pentane induces the loss of n-pentane from the originally orthorhombic structure and the material transforms to pure $C_{60}$ with the face-centered-cubic structure. The average crystallite size of the final powder is quite small, from x-ray powder diffraction peak widths it is estimated to be 150 Å. This unusual chemical decomposition at room temperature points to the highly strained nature of the structure. Similar chemical decomposition might exist for other $C_{60}$ clathrates such as $C_{60}$ acetone.

## I. INTRODUCTION

$C_{60}$-*n*-pentane crystals were first found in their highly twinned form.[1] Good quality single crystals were grown soon and it was realized that it is a clathrate-type molecular compound.[2] The structure can be envisaged as a skeleton $C_{60}$ structure that contains channels. However, this structure only exists if *n*-pentane molecules are situated in the channels and stabilize the structure. Thermal decomposition of $C_{60}$-*n*-pentane occurs at 400 K, which is much higher than the boiling point of *n*-pentane. This proves the van der Waals nature of the intermolecular forces in this material typical to clathrates.

Later followed the successful synthesis of a series of $C_{60}$-based clathrates formed by five-member linear molecules other than *n*-pentane.[3] Among this class of clathrate-type molecular compounds $C_{60}$-*n*-pentane can be taken as the model material showing a wide range of interesting structural characteristics. The full structural characterization of $C_{60}$-*n*-pentane at room temperature[4] and its low-temperature phase transition[5] is now nearly complete.

In this paper we report the mechanically induced chemical decomposition of $C_{60}$-*n*-pentane powder at room temperature.

## II. EXPERIMENT

$C_{60}$-*n*-pentane crystals were grown as described in Ref. 2. This method results in *n*-pentane single crystals which grow in the form of small plates (0.1–1 $mm^2$ area, 0.01–0.05 mm thickness) with shiny black faces. X-ray diffraction experiments were performed on both as-grown single crystals[2,5] and on powdered samples. Powder work was necessitated to determine the structural homogeneity of our samples used for further low-temperature differential scanning calorimetry measurements.

It proved to be a difficult task to obtain good quality powders from the initial batch of as-grown single crystals. First samples were powdered for very short times (10 sec) in agate mortar and then placed in 0.5 mm glass capillary. Powder-diffraction experiments were performed both in parallel beam geometry ($\lambda = 1.19929$ Å) at beamline 9.1 Daresbury Laboratory and in focusing geometry ($\lambda = 1.54056$ Å) in our laboratory. In both experiments the capillary was spinning during the measurement. Although the diffraction data reproduced quite well in both experiments (see Fig. 1), serious crystallite size problems were present.

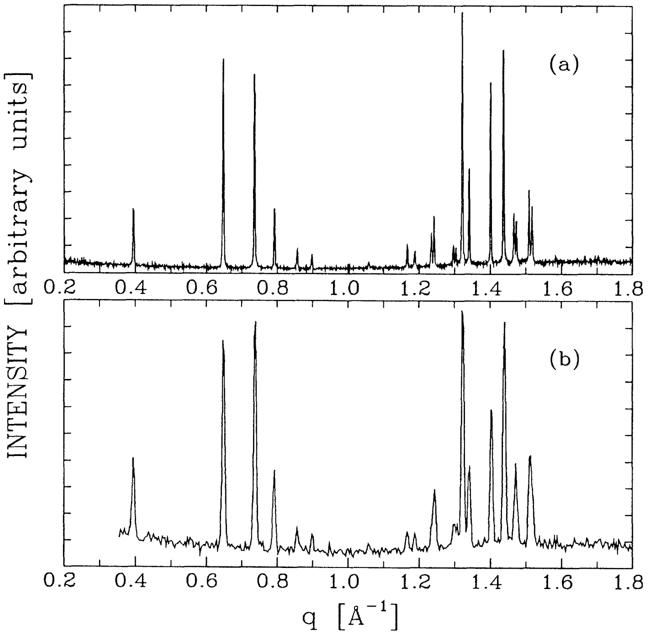

FIG. 1. Powder diffractogram of $C_{60}$-*n*-pentane powder measured (a) in parallel beam geometry at the Daresbury synchrotron source, and (b) in focusing geometry with Cu $K_{\alpha 1}$ radiation.

0163-1829/93/48(10)/7682(3)/$06.00

Once sample spinning was switched off and the detector $2\theta$ was set to a diffraction peak, then sample $\omega$ scans revealed sharp, intense peaks from single crystallites in the powder. This is a well known symptom of poor powder quality, which simply requires further grinding.[6] To improve the quality of the powder we ground the sample for the second time for 20 sec. However, instead of improving the powder quality we obtained a two-phase sample consisting of $C_{60}$-$n$-pentane and fcc $C_{60}$. We set the detector $2\theta$ on several diffraction peaks of both phases and checked the powder quality with sample $\omega$ scans again. While $\omega$ scans on the fcc $C_{60}$ peaks gave essentially constant intensity, $\omega$ scans on $C_{60}$-$n$-pentane showed again sharp, intense peaks from single crystallites. This means that the powder quality of $C_{60}$-$n$-pentane did not improve with grinding but some of it decomposed to very fine fcc $C_{60}$ powder. After a final grinding the sample was almost entirely fcc $C_{60}$. Figure 2 shows the powder diffractogram at different levels of grinding.

We estimate the average crystallite size ($D$) of both the initial $C_{60}$-$n$-pentane and the final fcc $C_{60}$ powder from the $D \sim \lambda/[\mathrm{FWHM} \times \cos(\theta)]$ relationship[7] (where FWHM is full width at half maximum). The synchrotron data set a lower limit of 2000 Å on the crystallite size of $C_{60}$-$n$-pentane. The crystallite size of fcc $C_{60}$ is estimated from laboratory data to be 150 Å. In both cases instrumental broadening is taken into account.

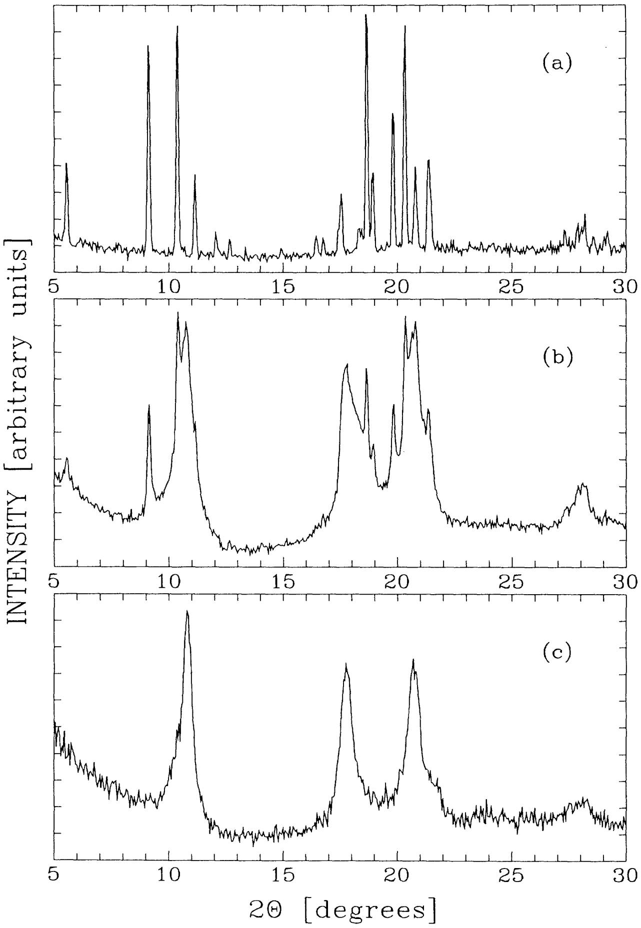

FIG. 2. Powder diffractograms of $C_{60}$-$n$-pentane measured on the same sample after successive grindings: (a) first, (b) second, (c) third.

## III. DISCUSSION

Our results can only be explained with chemical decomposition of the original sample. Both the known structure of $C_{60}$-$n$-pentane and the small crystallite size of the end product support this view.

The structure ($A$—centered orthorhombic unit cell, $a$ = 10.10 Å, $b$ = 10.16 Å, $c$ = 31.71 Å) is based on slightly distorted square planar layers of $C_{60}$ molecules which can follow in alternating close and loose packing. The ideal close and loose packing are described by relative shifts of $(1,1,\sqrt{2})R$ and $(1,0,\sqrt{3})R$, respectively ($\sqrt{2}$ and $\sqrt{3}$ for short), where $R$ is the van der Waals radius of the $C_{60}$ molecule. The $C_{60}$-$n$-pentane structure can be constructed with a $\sqrt{2}\sqrt{3}\sqrt{2}\sqrt{3}$ sequence of shifts leaving two channels per cell for the $n$-pentane molecules. The ideal fcc $C_{60}$ structure is based on close packed layers with $\sqrt{2}$ shifts only. This close relation of the two structures explains that with a loss of $n$-pentane molecules from the channels, the square layers described by $\sqrt{3}$ shifts can slip in the easy direction and transform to $\sqrt{2}$ shifts. How the actual dynamics of decomposition takes place is not clear yet, but the structure is very dense at room temperature and $n$-pentane molecules must flip between two positions to maintain orthorhombicity.[5] The small crystallite size of the fcc $C_{60}$ end product (~10 cell edges) shows that during the loss of $n$-pentane the original crystallites break into small ones to let the $n$-pentane out of the structure.

As the thermal decomposition of $C_{60}$-$n$-pentane occurs at 400 K we must discuss whether a significant temperature rise was possible during the grinding process. The grinding was very gentle and under an optical microscope we observed that the slightest pressure caused the originally black crystallites to "explode" and transform to fine brownish powder. This phenomenon can even be induced on single crystallites using an ordinary pin. So the

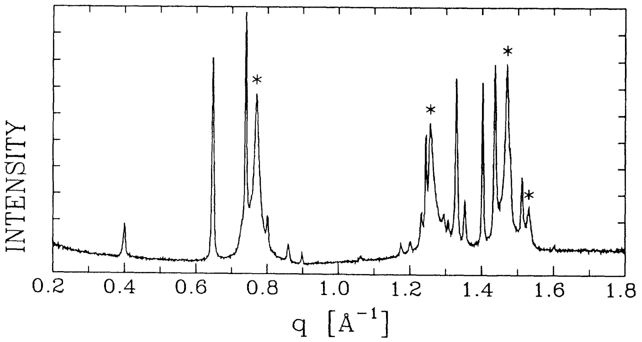

FIG. 3. Powder diffractogram of $C_{60}$-acetone measured in parallel beam geometry at the Daresbury synchrotron.

chemical decomposition is induced by pressure and not heat, that means, thermal decomposition of the sample can be ruled out.

The mechanically induced chemical decomposition described is probably not unique to $C_{60}$-$n$-pentane since in most of the clathrate samples measured after grinding we have seen traces of fcc $C_{60}$. As an example we show in Fig. 3 a synchrotron spectrum of $C_{60}$-acetone which has a very similar unit cell to $n$-pentane ($a$ = 10.10 Å, $b$ = 10.20 Å, $c$ = 31.37 Å). Although this clathrate is not investigated in great detail yet, its powder diffractogram shows two phases: one that can be indexed with the above mentioned unit cell and the other fcc $C_{60}$ with much smaller crystallite size. It is very likely that the second phase is the result of grinding again.

## IV. SUMMARY

In this paper we have reported the mechanically induced chemical decomposition of $C_{60}$-$n$-pentane. A qualitative understanding of the phenomenon can be reached on the basis of the known structure of the material. This surprising phenomenon might be not unique to $C_{60}$-$n$-pentane only, but characteristic to similar $C_{60}$ based clathrates.

## ACKNOWLEDGMENTS

This work has been supported by OTKA grants under Contract Nos. 2943, T4222 and Daresbury Grant No. 21/102.

---

[1] R. M. Fleming, A. R. Kortan, B. Hessen, T. Siegrist, F. A. Thiel, P. Marsh, R. C. Haddon, R. Tycko, G. Dabbagh, M. L. Kaplan, and A. M. Mujsce, Phys. Rev. B **44**, 888 (1991).

[2] S. Pekker, G. Faigel, K. Fodor-Csorba, L. Gránásy, E. Jakab, and M. Tegze, Solid State Commun. **83**, 423 (1992).

[3] S. Pekker, G. Faigel, G. Oszlányi, M. Tegze, T. Kemény, and E. Jakab, Synth. Met. **56**, 3014 (1993).

[4] G. Oszlányi *et al.* (unpublished).

[5] G. Faigel *et al.* (unpublished).

[6] W. Parrish, M. Hart, and T. C. Huang, J. Appl. Cryst. **19**, 92 (1986).

[7] L. V. Azaroff, *Elements of X-Ray Crystallography* (McGraw-Hill, New York, 1968).