EDITORIAL NOTE

There was a problem with the @ sign in the original article (published 9 January 2001). The entire corrected article is republished here. This article should be cited as M. Waiblinger, K. Lips, W. Harneit, A. Weidinger, E. Dietel, and A. Hirsch, Phys. Rev. B 63, 045421 (2001); 64, 159901(E) (2001).

Corrected Article: Thermal stability of the endohedral fullerenes N@C₆₀, N@C₇₀, and P@C₆₀ [Phys. Rev. B 63, 045421 (2001)]

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Nitrogen and phosphorus atoms enclosed in fullerenes keep their atomic ground-state configuration, and no charge transfer or covalent bonding to the cage occurs. These systems can be dissolved in organic solvents and reacted with addends without losing the atomic character of the guest atom. In this paper we present a detailed study of the annealing behavior of $N@C_{60}$, $N@C_{70}$, and $P@C_{60}$, and of some $N@C_{60}$ adducts. The disintegration of these systems, as recorded by electron paramagnetic resonance measurements, occurs in a temperature range between 400 and 600 K. The results are in qualitative agreement with potential-energy calculations, and confirm the proposed escape mechanism which proceeds via bond formation of the trapped atom with the cage. It is found that other combinations of group-V elements with fullerenes, e.g., $N@C_{84}$, $P@C_{70}$, and $As@C_{60}$, are not stable at room temperature. The escape mechanism and the possibility of disabling this path are discussed.

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I. INTRODUCTION

N@C₆₀, N@C₇₀, and P@C₆₀, produced by ion implantation,¹⁻⁴ have properties distinctly different from other endohedral fullerenes.⁵⁻⁸ Encapsulated in fullerenes, these highly reactive group-V atoms are uncharged and unbound, and they stay in the quartet ground state (⁴S_{3/2}) in the center of the fullerene.¹⁻³ Comparable properties were observed only for muonium encapsulated in C₆₀.⁹ All other endohedral fullerenes either contain noble gases,⁵ or else the enclosed atom leaves the central position and forms a bond with the fullerene shell.⁶⁻⁸

In this work, the escape behavior of an enclosed atom out of a cage is studied. Annealing curves using the electron paramagnetic resonance (EPR) signal intensity as a measure of the amount of endohedrals remaining in the sample were recorded. We find that the systems studied here become unstable below 600 K, i.e., much below the temperature at which the cage opening (window mechanism) was observed for He@C₆₀.⁵ This indicates that the mechanism by which the atoms leave the cage is quite different in the two cases. It will be shown that an intermediate bonding of the atom with the cage plays an essential role in the escape mechanism for nitrogen and phosphorus. A survey on the stability of group-V elements in fullerenes will be given.

II. EXPERIMENTAL SETUP

The production of encapsulated nitrogen and phosphorus was achieved by simultaneously evaporating fullerenes onto a substrate and irradiating the growing film by an intense nitrogen or phosphorus ion beam. The deposition rate and beam intensity were adjusted in such a way that approximately one ion per fullerene molecule arrived at the target. After several hours of bombardment the irradiated sample was removed from the substrate, dissolved in toluene or CS_2 , and filtered. Only the soluble part, which contains filled and empty fullerenes in the ratio of approximately 10^{-4} :1, was used for the subsequent experiments.

The encapsulated nitrogen or phosphorus is paramagnetic; therefore, the number of endohedrals in the sample can be derived from the EPR signal intensity. Figure 1 shows the EPR powder spectra of N@C₆₀ and P@C₆₀. No significant change in the linewidth occurred in the temperature region of the measurement. The number of endohedrals in the sample was determined by taking the area of the low-field EPR line and multiplying it by the absolute temperature to correct for the Curie dependence. The absolute number was determined by a comparison with an EPR standard.

The powder samples were obtained by evaporating the solvent from the solution, and carefully degassing the remaining powder for 2 h in a 10^{-7} -mbar vacuum and sealing it in a quartz ampoule without breaking the vacuum to avoid oxidation effects. The sample was inserted in an EPR *X*-band spectrometer (Bruker ELEXYS 500), and heated in a nitrogen-gas flow to temperatures ranging from 300 to 600 K. The temperature was measured by a Pt-100 thermometer.

To rule out crystal effects, these experiments were repeated with $N@C_{60}$ in 1-chloronaphthalene solution. This solvent was chosen because of its high boiling point



FIG. 1. X-band EPR powder spectra of N@C₆₀ and P@C₆₀ at room temperature. The triplet splitting (A = 5.67 G) in the upper panel is due to the hyperfine interaction of the electron spin with the nuclear spin I = 1 of ¹⁴N (natural abundance: 99.63%). The doublet splitting (A = 49.2 G) in the lower panel is due to the hyperfine interaction of the electron spin with the nuclear spin I = 1/2 of ³¹P (natural abundance: 100%).

 $(\sim\!532$ K). In this case the annealing curve was measured up to 520 K.

III. EXPERIMENTAL RESULTS

Figure 2 shows the amount of N@C₆₀ derived from the EPR signal for a solid sample and a sample in solution. In this isochronal annealing experiment the temperature was increased by 2 K every 82 sec. It can be seen that the main decay occurs around 500 K, but surprisingly, a prestage is seen around 440 K in the solid N@C₆₀ data.



FIG. 2. Number of N@C₆₀ as a function of temperature for a powder sample (circles) and a sample in 1-chloronaphthalene solution (squares). The temperature was raised in steps of 2 K per 84 sec. Note that the main decay step occurs slightly above 500 K in both cases.



FIG. 3. Annealing curve (heating rate 2 K per 84 sec) of a carefully purified $N@C_{60}$ sample (see the text). The annealing sequence was interrupted at 480 K, and restarted after dissolving and drying the sample in air. The difference in the number of $N@C_{60}$ molecules between the end of the first run and the beginning of the second is due to some loss of material during the treatment between the runs. In the lower part of the figure, the fractional loss per temperature step is shown.

N@C₆₀ in solution shows decomposition in a similar temperature range as in the solid sample, but the shape of the temperature dependence is somewhat different. Slight deviations are conceivable, since the surrounding of the cage may influence the escape. It seems that the prestage and the main stage come closer together in the solution curve, or that the prestage is missing and the main step is somewhat smeared out. However, it should be mentioned that the solution data are less reliable than those taken with the solid sample, since these experiments were performed close to the boiling point of the solvent, and thermal agitation may eject particles from the active EPR area, thus mimicking a decay of $N@C_{60}$. Another problem is the high electrical conductivity of the solvent, unfavorable for EPR measurements. However, in general the solution data confirm the results obtained for the solid sample, although the details are slightly different.

To figure out whether the two-step decay mentioned above is an intrinsic property of N@C₆₀ or, rather, reflects differences in the local environment, we repeated this experiment with a different sample under carefully controlled conditions. The sample was first run through a HPLC column, and only the C₆₀ peak containing filled and empty C₆₀ was cut out for further use. In this HPLC run, the solvent was saturated with He gas in order to get rid of other gases and to



FIG. 4. Annealing curve of $N@C_{70}$ (triangles) in comparison with that of $N@C_{60}$ (squares). The $N@C_{60}$ curve was taken after preannealing at 480 K. The heating rate was 2 K in 82 sec.

avoid oxidation effects. The C_{60} fraction was collected under Ar atmosphere, dried in an EPR quartz tube in a high vacuum line, and sealed off without allowing contact with air.

With this highly purified sample we repeated the annealing experiment. In a first run the heating was interrupted at 480 K. The sample was then rapidly cooled down, dissolved in CS_2 and treated with ultrasound, dried in air, filled in a quartz ampoule which was evacuated, and then sealed as described above. Then the annealing procedure was restarted. The results are shown in Fig. 3.

In the first run the loss of $N@C_{60}$ between 420 and 470 K is clearly seen, but this step is completely absent in the second run. This shows that one kind of $N@C_{60}$ has disappeared in the first run, and that this species cannot be reactivated by the usual treatment of our samples. This eliminates the possibility that a special environment is responsible for the observed difference in the stability, and is a strong indication that two species of $N@C_{60}$ exist. It should be emphasized that these data cannot be explained with two different escape mechanisms, but require the assumption of different kinds of $N@C_{60}$. An important aspect is also that the shape of the EPR spectra does not change in this prestep region.

On the nature of the different species we can only speculate. We presume that the main annealing step at 510 K is due to normal N@C₆₀, and that the prestep at 440 K refers to slightly modified N@C₆₀. The modification could be an isomer formed during the implantation by the opening and reclosing of the cage. Or the carbon isotopes could play a role in the sense that ¹³C containing C₆₀ molecules have a slightly different barrier for the escape. We have no independent confirmation of these hypotheses, nor can we exclude other explanations.

TABLE I. Stable endohedral compounds formed of group-V elements and fullerenes.

	Nitrogen	Phosphorus	Arsenic
C ₆₀ C ₇₀ C ₈₄	N@C ₆₀ N@C ₇₀ not stable	P@C ₆₀ not stable	not stable



FIG. 5. Annealing curves of the mono-adduct and hexa-adduct of $N@C_{60}$: $N@C_{61}(COOC_2H_5)_2$ and $N@C_{66}(COOC_2H_5)_{12}$ in comparison with that of $N@C_{60}$. The heating rate was 2 K in 82 sec.

N@C₇₀ and P@C₆₀ samples were prepared in the same way as described above for N@C₆₀. The N@C₇₀ annealing data are shown in Fig. 4, together with the N@C₆₀ data from the recovered fraction of Fig. 3. Clearly, N@C₇₀ is thermally less stable than N@C₆₀. P@C₆₀ starts to decay at 400 K. Since this material is very rare, and since we wanted to keep the existing sample for further investigations, no detailed annealing curve was taken. But it is completely clear that P@C₆₀ is the least stable compound of the three systems studied here.

We also tried to produce endohedrals with other combinations of group-V elements and fullerenes, but without success. For example, we operated the ion source with AsF₅ instead of N₂ or PH₃, but otherwise kept the conditions identical to the other implantation runs. No EPR signal related to As@C₆₀ was found, although signals of N and P in C₆₀ present from small contamination from previous runs were clearly seen, indicative of the high sensitivity of the measurement. Similarly, if higher fullerenes instead of C₆₀ or C₇₀ were used in N implantation, no signals related to these compounds were found. Thus it seems that, e.g., N@C₈₄, P@C₇₀, and As@C₆₀ are not stable at ambient conditions. Table I summarizes the status of these studies.

In an earlier paper¹⁰ we studied the $N@C_{60}$ mono-



FIG. 6. Arrhenius plot of the decay rates λ for N@C₆₀ and N@C₇₀. The solid lines are fits assuming a pre-exponential factor of $\lambda_0 = 5 \times 10^{-13} \text{ s}^{-1}$.

TABLE II. Activation energy for the escape of the enclosed atoms for different cages.

Molecule	Activation energy (eV)	
N@C ₆₀	1.57	
N@C ₇₀	1.39	
P@C ₆₀	\sim 1.2 $^{\rm a}$	
$N@C_{61}(COOC_2H_5)_2$	\sim 1.6 $^{\rm a}$	
$N@C_{66}(COOC_2H_5)_{12}$	\sim 1.8 a	

^aEstimated from the temperature of the main decay step assuming a pre-exponential factor of $\lambda_0 = 5 \times 10^{-13} \text{ s}^{-1}$.

malonates and hexamalonates: $N@C_{61}(COOC_2H_5)_2$ and $N@C_{66}(COOC_2H_5)_{12}$. The preparation of these materials and their properties are given in Ref. 10. Here we report on the stability of these compounds (see Fig. 5). It can be seen that the stability increases with the number of addends. The fast decay of the hexa-adducts above 570 K is probably due to a dissociation of the addends from the fullerene.

Figure 6 shows the decay rate λ as a function of the reciprocal temperature. λ was calculated according to

$$\lambda = \frac{I(n) - I(n+1)}{I(n)\Delta t},\tag{1}$$

where I(n) is the EPR intensity for the measurement number n, and Δt is the time between measurement numbers n and n+1. The results are summarized in Table II.

IV. DISCUSSION

We have shown above that endohedral fullerenes containing group-V elements decay below 600 K on a time scale of minutes. In a comparable situation, He@C_{60} is stable up to 1200 K.¹¹ It has been proposed that He escapes by a window mechanism, where one or more bonds of the fullerene break up opening a larger ring through which the trapped He atom escapes.⁵ If nitrogen were to leave the cage by the same mechanism, the stability should be similar. The much lower stability of the group-V endohedrals has to do with the active role of the enclosed atoms in the escape process.

We assume that the disintegration of N@C₆₀ occurs via the process depicted in Fig. 7. The nitrogen atom moves away from the center, forms a bond with two carbon atoms, and then swings through the bond to the outside of the cage. It has been shown by theoretical calculations¹⁰ that the energy for this escape path is lower than for an escape through the center of a five- or six-membered ring. The proposed



FIG. 7. Proposed escape path for nitrogen out of C_{60} . First the nitrogen breaks a double bond of the cage and forms an azabridge with two carbon atoms from the inside of the cage, and then it leaves the cage by swinging through the bridge to the outside.



FIG. 8. Calculated heat of formation for nitrogen in C_{60} as a function of displacement from the center toward a 6-6 double bond, adapted from Ref. 10. Open squares represent the calculated potential for the quartet state, and open circles that for the doublet state. The dashed line at 3.6 Å corresponds to the radius of the fullerene.

escape path can qualitatively explain the rather low temperature at which $N@C_{60}$ disintegrates.

Figure 8 shows the calculated potential (PM3-UHF calculation; for details, see Ref. 10) for two specific escape paths out of the fullerene. Inside the cage, the lowest energy is obtained for the quartet (S=3/2) state in the center of the cage. The energy rises continuously with the displacement of the atom. Coming closer to the cage, the nitrogen forms an endohedral complex with two carbon atoms, and reaches a local minimum for the doublet (S = 1/2) configuration. In the last step the nitrogen atom swings through the bridge to the outside. The N atom stays only a very short time in the bound state on the inner wall, and then either falls back to the center of the cage or swings to the outside. Thus, in accordance with the experiment, this intermediate state will not be visible in the EPR measurement. The configuration after the escape is not known, but it is plausible that a diamagnetic state, resulting in no EPR signal, is formed via a reaction with already present paramagnetic states, e.g., from previously decayed N@C₆₀. Such diamagnetic configurations may be formed either by transporting electrons or by rearranging the atoms.

Within this picture, the experimentally observed trends in the stability can be explained as follows. The decreasing stability with increasing mass of the enclosed atom is a consequence of the larger overlap of electron shells of atom and cage, thus enabling bond formation. The surprising finding that the stability also decreases with the increasing size of the fullerene cage is due to the fact that the bending of the cage decreases with an increasing number of C atoms, an effect which facilitates bond formation. Finally, the blocking of double bonds by addends is the reason for the increase of the stability of the adducts. It seems that the formation of the bond from the inside is the decisive step in the decay of the endohedral systems with group-V elements.

V. CONCLUSION

 $N@C_{60}$ disintegrates at rather low temperatures (around 500 K) compared to, e.g., He@C₆₀, which is stable up to

1100 to 1200 K. The reason for this is that the escape process is quite different for these endohedral systems. Whereas He is a passive partner which takes the chance to escape by thermal excitation after the cage has opened, nitrogen actively takes part in the opening of the shell by forming a bond with carbon atoms and thereby lowering the barrier for the escape.

Exohedral addends at the outside of the cage can effectively block this escape path, thus leading to an enhanced stability of this kind of atom trap. Furthermore, we find that the stability decreases if one goes to higher fullerenes or to higher masses of the enclosed atoms. Whereas for nitrogen both $N@C_{60}$ and $N@C_{70}$ are found to be stable, for phosphorus only $P@C_{60}$ exists, and arsenic forms no stable endohedral fullerene. We suggest that the decrease of the chemical inertness of the inner wall of the cages from C_{60} to C_{70} , etc., and the increase of the radius of the enclosed atom from N to P to As are responsible for this tendency. A preannealing step has been observed in case of $N@C_{60}$. The origin of this step is not clear.

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