

## Electron Delocalization and Dimerization in Solid C<sub>59</sub>N Doped C<sub>60</sub> Fullerene

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Electron spin resonance and *ab initio* electronic structure calculations show an intricate relation between molecular rotation and chemical bonding in the dilute solid solution. The unpaired electron of C<sub>59</sub>N is delocalized over several C<sub>60</sub> molecules above 700 K, while at lower temperatures it remains localized within short range. The data suggest that below 350 K rigid C<sub>59</sub>N-C<sub>60</sub> heterodimers are formed in thermodynamic equilibrium with dissociated rotating molecules. The structural fluctuations between heterodimers and dissociated molecules are accompanied by simultaneous electron spin transfer between C<sub>60</sub> and C<sub>59</sub>N molecules. The calculation confirms that in the C<sub>59</sub>N-C<sub>60</sub> heterodimer the spin density resides mostly on the C<sub>60</sub> moiety, while it is almost entirely on C<sub>59</sub>N in the dissociated case.

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Pure C<sub>60</sub> fullerene is an insulating solid with an energy gap of about 1.5 eV [1] between the valence and conduction bands. It is natural to expect that suitably doped fullerenes may be semiconductors. However, introducing donors or acceptors in a controllable way into C<sub>60</sub> is very difficult. Highly conducting alkali fulleride compounds and polymers are well known, but these are “line compounds” with well defined, fixed stoichiometry. Andreoni *et al.* [2] suggested as early as 1992 that the modified fullerene molecules, C<sub>59</sub>N and C<sub>59</sub>B, are electron and hole donors, respectively, and in their pure solid forms could be metallic or even superconducting. Unfortunately, C<sub>59</sub>B has not been synthesized in significant quantities [3] and pure C<sub>59</sub>N is an insulating crystal of covalent (C<sub>59</sub>N)<sub>2</sub> dimers [4,5].

The production of dilute solid solutions of monomeric C<sub>59</sub>N in C<sub>60</sub> (C<sub>59</sub>N : C<sub>60</sub>) in macroscopic quantities [6] opens a new possibility. A filled electron state 1.5 eV above the last filled shell is the main difference between C<sub>59</sub>N and C<sub>60</sub> and the distortion of the cage by the substitution of a nitrogen atom for carbon is small. The molecular energy scheme suggests that electrons may transfer from C<sub>59</sub>N to the surrounding C<sub>60</sub> molecules, but so far only neutral C<sub>59</sub>N was observed [6] in C<sub>59</sub>N : C<sub>60</sub>. In this Letter, we consider the interplay between chemical binding, rotation, and ionization of C<sub>59</sub>N and C<sub>60</sub> molecules. We argue that the ground state is a C<sub>59</sub>N-C<sub>60</sub> heterodimer. Below 350 K there are fluctuations between spatially fixed heterodimers and dissociated, rotating C<sub>59</sub>N. The structural fluctuations are accompanied by spin fluctuations between C<sub>60</sub> and C<sub>59</sub>N. The unpaired electrons are bound to C<sub>59</sub>N between 350 and 700 K, and are delocalized over several C<sub>60</sub> molecules above 700 K.

Most C<sub>59</sub>N : C<sub>60</sub> samples were produced by subliming pure C<sub>60</sub> in a N<sub>2</sub> gas electric discharge tube [6]. Some samples were made by dissolving pure (C<sub>59</sub>N)<sub>2</sub> and C<sub>60</sub> in toluene and then subliming the extracted mixture under vacuum. No difference was noted between the ESR spectra of samples made by the two methods. C<sub>59</sub>N concentrations determined from ESR spectral intensities range up to 2000 ppm. C<sub>59</sub>N is an extremely stable molecule that withstands temperatures of at least 1000 °C for a few minutes. Samples were purified by sublimation in dynamic vacuum at 560 °C and then sealed into quartz tubes under He atmosphere. C<sub>59</sub>N : C<sub>60</sub> is air sensitive at ambient temperatures but monomeric C<sub>59</sub>N is regenerated at high temperatures under vacuum. ESR spectra were recorded at 9, 36, 150, and 225 GHz frequencies.

*Ab initio* calculations of the molecular structure were performed using the Cambridge CASTEP plane-wave density functional theory code [7,8]. All calculations were done in a 12 × 12 × 22 Å orthorhombic unit cell using the Perdew–Burke–Ernzerhof gradient corrected functional [9] with a 240 eV energy cutoff and Vanderbilt ultrasoft pseudopotentials. The Brillouin zone was sampled at the  $\Gamma$  point. The <sup>14</sup>N hyperfine constant was calculated using the projector augmented wave (PAW) method as in Refs. [10,11] using the DFT++ package [12].

Below 350 K, two ESR active species appear in C<sub>59</sub>N : C<sub>60</sub> [Fig. 1(a)]. Both species are embedded in the C<sub>60</sub> matrix since their ESR spectra change abruptly at the  $T_c = 261$  K phase transition of solid C<sub>60</sub>. We assign one component of the ESR spectrum to C<sub>59</sub>N-C<sub>60</sub> heterodimers formed from C<sub>59</sub>N and one of its 12 C<sub>60</sub> neighbors. The other component arises from C<sub>59</sub>N free radicals and was investigated in detail in an earlier work [6].

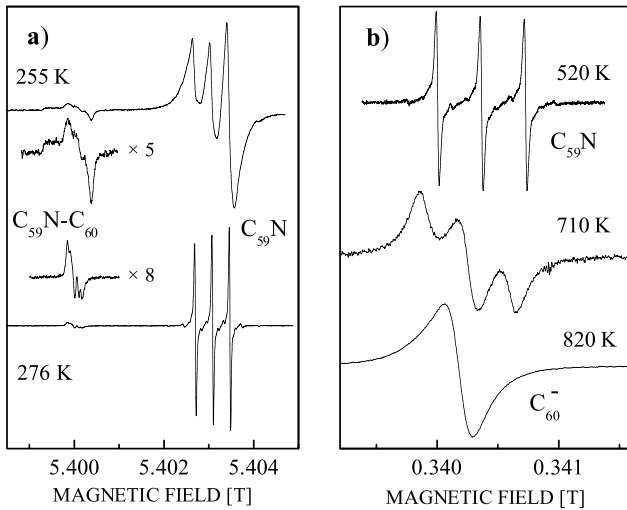


FIG. 1. ESR spectra in dilute  $C_{59}N:C_{60}$  solid solution. (a) Spectra at 150 GHz near the  $T_c = 261$  K phase transition of solid  $C_{60}$ . The two ESR lines are assigned to nonrotating  $C_{59}N-C_{60}$  heterodimers and neutral, rotating  $C_{59}N$ . We propose that structural fluctuations lead to a simultaneous observation of the two species. The  $C_{59}N-C_{60}$  signals are also shown magnified. (b) 9.4 GHz ESR spectra at high temperatures. Above 600 K the  $C_{59}N$  ESR is gradually replaced by the ESR of  $C_{60}^-$  anions. This is attributed to delocalization of electrons over many  $C_{60}$  sites.

Between 120 and 600 K the molecular dynamics of  $C_{59}N$  measured by ESR resembles the dynamics of neutral  $C_{60}$  in pure solid  $C_{60}$  measured by NMR [13]. At  $T_c$ , the  $sc$  phase with a well defined order of  $C_{60}$  molecular orientations changes to the  $fcc$  phase where molecules rotate quasi-independently. The activation energies of rotational correlation times of  $C_{60}$  and  $C_{59}N$  molecules are similar both above and below  $T_c$ . Below 200 K, the large  $g$  factor and hyperfine anisotropies of  $C_{59}N$  result in a broad ESR line with a complicated structure in the powder samples. Between 220 and 261 K, the frequency of  $C_{59}N$  rotations between energetically similar positions becomes faster than the frequency spread of the anisotropy, and the ESR spectrum gradually narrows. Above  $T_c$ , the  $C_{59}N$  molecules rotate nearly freely and the ESR spectrum consists of extremely narrow lines of a  $^{14}N$  triplet and a series of weak satellites from  $^{13}C$  doublets.

We find a dramatic change in the ESR spectrum between 600 and 820 K [Fig. 1(b)]. The  $^{14}N$  triplet with an isotropic  $g$  factor of 2.00137 transforms gradually into a single line shifted to lower fields at  $g = 2.0024$ . We are not simply dealing with a lifetime broadening of the hyperfine components. Rather, a new line emerges and the  $C_{59}N$  spectrum disappears. The same reversible transformation was found in various samples. We explain these observations as a delocalization of electrons, first over a cluster of  $C_{59}N$  and 12 first neighbor  $C_{60}$  molecules and then at higher temperatures to larger distances. The reason for the somewhat higher  $g$  factor of  $C_{60}^-$  at high temperatures in a  $C_{60}$

matrix with respect to values of about 2.000 measured in frozen solutions [14] is unclear. The decrease of free energy associated with this delocalization overcomes the Coulomb attraction of the  $C_{59}N^+$  ion left behind.

We now turn to the assignment of the second ESR active species as  $C_{59}N-C_{60}$  heterodimers that form below 340 K. The highest resolution (3 ppm) spectra indicate more than one very similar species. At a somewhat poorer resolution of 6 ppm a single (average) species describes well the spectra with  $g$  factors of 2.00232, 2.00245, 2.00265 just below  $T_c$  and 2.00240, 2.00247, 2.00251 above  $T_c$ . At 261 K the extra line changes abruptly [Fig. 1(a)]; the  $g$  factor anisotropy narrows but does not disappear. This  $g$  factor anisotropy is due to a molecular distortion; the  $g$  factor of an undistorted  $C_{60}^-$  ion would be isotropic. Thus the second species does not rotate freely since in that case the  $g$  factor distribution would be motionally narrowed.

We suggest that this complex ESR spectrum reflects a thermal distribution of two molecular structures: a ground state  $C_{59}N-C_{60}$  heterodimer with a covalent bond between the component molecules and a higher energy state of dissociated neutral molecules. The heterodimer appears as a distorted  $C_{60}$  molecule in the ESR spectrum as the unpaired electron spin resides mostly on the  $C_{60}$  moiety while in the dissociated state the spin is on the  $C_{59}N$  molecule. This spin transfer is plausible since the covalent bond takes one electron from the  $C_{59}N$  and the other from the  $C_{60}$  moiety. There is a structural change of the heterodimer at the 261 K phase transition.

In the following, we discuss observations supporting the assignment. The extra line is intrinsic to  $C_{59}N:C_{60}$  since its intensity relative to the  $C_{59}N$  line is sample independent. We measured—mostly at temperatures above  $T_c$ —a large number of samples of various purity and made by different methods. The samples had a wide range of  $C_{59}N$  radical concentrations between less than 100 ppm and 2000 ppm. Yet, for all samples,  $R(T)$ , the concentration ratio of the species of the extra line to monomeric  $C_{59}N$  is the same at any given temperature,  $T$ . [ $R(T)$  is measured by the relative ESR spectral intensities of the two species.] Degrading the sample in air reduces both the ESR active  $C_{59}N$  concentration and the intensity of the extra line, leaving  $R(T)$  unchanged.  $R(T)$  is well explained if the unpaired electron spin hops with a low frequency between two states: in one it is localized to  $C_{59}N$  and in the other mainly to a neighboring  $C_{60}$ . Since the observed  $C_{60}$ -like radical has a static distortion, it is natural to assign it to  $C_{60}$  covalently bound to the neighboring  $C_{59}N$  molecule. The sample independent intensity ratio rules out the earlier assumption [6] that the extra line is from impurities.

$R(T)$ , the concentration ratio of  $C_{59}N-C_{60}$  to  $C_{59}N$  is determined by a dynamic thermal equilibrium between the two states. Above  $T_c$ ,  $R(T)$  decreases rapidly with increasing temperature and is independent of the ESR resonance frequency (Fig. 2); the heterodimer line is no more de-

tected above 360 K. There is no hysteresis in  $R(T)$  when the temperature is cycled between 270 and 350 K. The decrease of the ESR line intensity reflects a decrease of the heterodimer concentration and not an excessive line broadening which could result in an apparent intensity loss. Only above 315 K is the transverse spin relaxation time short enough to broaden the 9 GHz line measurably.

Dimerization (and polymerization) of both charged and neutral  $C_{60}$  molecules are well known in compounds [15];  $KC_{60}$  is a well studied example. Depolymerization is an endothermic phase transition where the binding energy of the intermolecular covalent bond is overcome by the rotational entropy gain. We suggest that a similar phenomenon is observed in  $C_{59}N : C_{60}$ . However, instead of a phase transition, in the small clusters of  $C_{59}N$  and neighboring  $C_{60}$  molecules fluctuate between the heterodimer and the dissociated state in a broad temperature range. The dissociation of rigid  $C_{59}N-C_{60}$  heterodimers into rotating neutral  $C_{59}N$  and  $C_{60}$  molecules increases the entropy and thus decreases  $R(T)$  at high  $T$ . Denoting the binding energy and entropy differences between the dissociated and heterodimer states by  $\Delta E_b$  and  $\Delta S$  respectively, and neglecting their  $T$  dependence, the concentration ratio is  $R(T) = \exp(\Delta E_b/k_B T - \Delta S/k_B)$ . The experimental values are:  $\Delta E_{b>}/k_B = 2400 \pm 600$  K,  $\Delta S_{>}/k_B = 11 \pm 2$  and  $\Delta E_{b<}/k_B = 600 \pm 100$  K,  $\Delta S_{<}/k_B = 5.3 \pm 0.4$  where the subscript “>” (“<”) denotes above (below) the transition.

The entropy jump at the phase transition,  $\Delta S_{>} - \Delta S_{<} \approx 6k_B$ , is roughly twice the measured entropy change in  $C_{60}$  fullerene,  $\Delta S_{C_{60}} = 2-3k_B$  [16,17].  $\Delta S_{>} - \Delta S_{<}$  arises mainly from the change in the dissociated state since the entropy of the heterodimer is small. The entropy change of  $C_{59}N$  is similar to that of  $C_{60}$  since activation

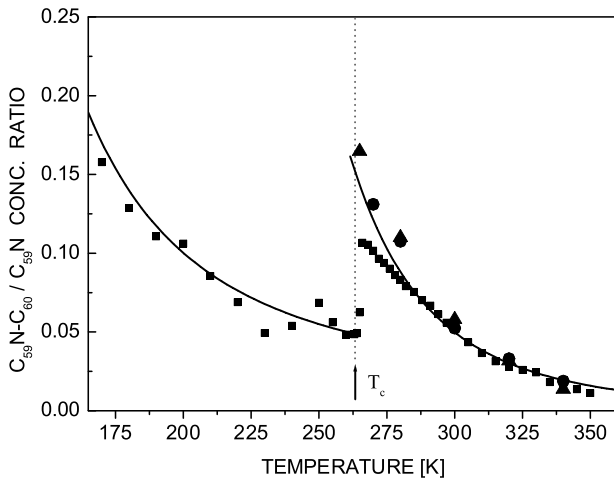


FIG. 2. Temperature dependence of the ESR intensity ratio,  $R(T)$ , of the species attributed to  $C_{59}N-C_{60}$  heterodimers and  $C_{59}N$  at 9 (squares), 75 (dots), and 225 (triangles) GHz.  $R(T)$  is approximately proportional to the heterodimer concentration. Solid lines: calculated curves; see text.

energies of the molecular rotation are similar both above and below  $T_c$ . The large value  $\Delta S_{>}/k_B = 11$  for the dissociated  $C_{59}N$  and  $C_{60}$  molecules is in qualitative agreement with a simple model of solid  $C_{60}$  [18] which assumes that above the phase transition the rotational entropy is  $\ln 90 = 4.5$  per molecule.

Figure 3 summarizes the energy scheme with approximate entropies when the particular levels are occupied. The large entropy differences allow the observation of the various configurations at moderate temperatures. Above  $T_i = 700$  K electrons become delocalized over the cluster of 12 first neighbor  $C_{60}$  molecules and  $C_{59}N$ . As a rough estimate, the corresponding entropy gain is  $\Delta S_i = \ln 13$  and the approximate energy difference  $E_i - E_{>} = T_i * \Delta S_i = 1800$  K. Finally, the electrostatic energy of the electron to escape from the first neighbor is  $E_{free} - E_i = e^2/(\epsilon a_0)$  (with  $\epsilon = 4.4$  [19] and the first neighbor distance  $a_0 = 1$  nm).

The *ab initio* calculation of the electronic structure with all atomic positions relaxed shows a  $C_{59}N-C_{60}$  heterodimer with a  $d_0 = 0.164$  nm long C-C covalent bond between the C1 first neighbor to the nitrogen atom of  $C_{59}N$  (in the notation of [6]) and a C atom of  $C_{60}$  [Fig. 4(a)]. It has a mirror plane that includes the N atom and the C atoms of the intermolecular covalent bond. Twisting the  $C_{60}$  and  $C_{59}N$  molecules around the bond confirms that the minimum energy configuration is the *trans* conformation with a mirror plane, shown in Fig. 4(a). This type of bonding is expected since C1 is the most reactive atom, as it has the largest spin density in the isolated  $C_{59}N$  molecule. Figure 4(a) also shows the extra spin density,  $\rho(z)$ , along the molecular bond direction  $z$ , integrated over  $(x, y)$  planes perpendicular to  $z$ . Remarkably,  $\rho(z)$  is almost entirely on the  $C_{60}$  moiety and is not at all spherically distributed. These characteristics are in agreement with the

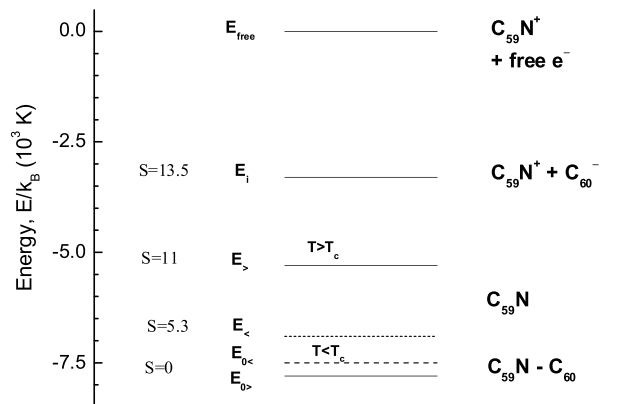


FIG. 3. Proposed energy level diagram of  $C_{59}N : C_{60}$ .  $E_{0>}(E_{0<})$ : heterodimer  $T > T_c$ , ( $T < T_c$ );  $E_{>}(E_{<})$ : dissociated neutral  $C_{59}N$  free radical  $T > T_c$ , ( $T < T_c$ );  $E_i$ : pair of  $C_{59}N+$  and first neighbor  $C_{60}^-$  ions (electron delocalized to a cluster of  $C_{59}N$  and 12  $C_{60}$  molecules);  $E_{free}$ : electron delocalized over large distances.

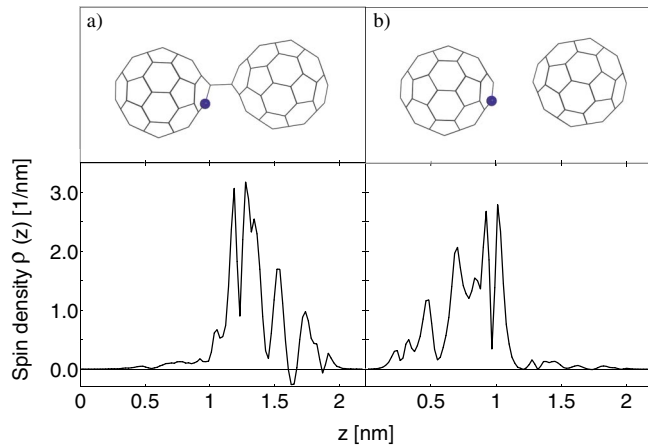


FIG. 4 (color online). *Ab initio* calculation of molecular structures and the spin densities,  $\rho(z)$ , along the molecular axis  $z$  integrated in the plane perpendicular to  $z$ . (a) The ground state heterodimer and (b) the dissociated pair with a fixed intermolecular C-C separation  $d = 0.30$  nm. Note the almost complete transfer of an electron spin from C<sub>60</sub> to C<sub>59</sub>N with the dissociation of the heterodimer.

ESR assignment of a distorted C<sub>60</sub>-like molecule. We calculated a very small <sup>14</sup>N hyperfine constant of  $A = 0.016$  mT from the 10% spin density remaining on the C<sub>59</sub>N molecule. We observed, however, no hyperfine splitting with a precision of 0.01 mT above and 0.05 mT below  $T_c$ , showing again that the spin transfer to the C<sub>60</sub> moiety is nearly complete.

We calculated the way the heterodimer is torn apart by fixing larger and larger nearest intermolecular C-C distances,  $d$ , while relaxing all other atomic positions. Figure 4(b) shows the structure of the dissociated molecule for  $d = 0.30$  nm; this is about the nearest neighbor distance in solid C<sub>60</sub>. In contrast to the heterodimer, in the dissociated case most of the spin density resides on the C<sub>59</sub>N molecule. The energy difference between the heterodimer and the dissociated pair of C<sub>59</sub>N and C<sub>60</sub> molecules is small. We find a barrier between the heterodimer and the dissociated pair with an energy maximum of 0.5 eV at  $d = 0.21$  nm.

Thus, the calculation is in qualitative agreement with the picture derived from the experiment. At finite temperatures the configuration fluctuates between the covalently bonded heterodimer and dissociated molecules since these configurations have similar energies and the barrier between them is small. Dissociation of the heterodimer is accompanied by transfer of an electron spin. In the experiments at intermediate temperatures we detect simultaneously the distorted C<sub>60</sub> moiety of the heterodimer and the neutral

C<sub>59</sub>N of the dissociated pair. The spin lifetime of the heterodimer is limited by the lifetime of the heterodimer itself. From the increase of the spin-spin relaxation time measured at 9 GHz we estimate a slow fluctuation frequency of the order of  $10^7$  Hz at 350 K. The extra electron is localized to C<sub>59</sub>N from 350 K to about 700 K and only above this high temperature is C<sub>59</sub>N:C<sub>60</sub> a doped semiconductor.

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