Polymeric alkali fullerides are stable in air

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Abstract

Infrared transmission, electron spin resonance, and X-ray diffraction measurements show unambiguously that RbC$_{60}$ and KC$_{60}$ are stable in air, in contrast to Rb$_6$C$_{60}$ which decomposes rapidly upon exposure. The specimens studied transform into pure C$_{60}$ and other byproducts when heated above 100°C, approximately the temperature of the orthorhombic-fcc phase transition. The stability of these compounds raises the possibility of applying them as protective layers for the superconducting fullerides.

The compounds of alkali metals (A) with fullerenes (C$_{60}$) are the subject of considerable recent interest. Superconductivity was discovered in A$_3$C$_{60}$, and a polymeric chain structure was seen in A$_1$C$_{60}$. Other fullerides of composition A$_4$C$_{60}$ and A$_6$C$_{60}$ have also been studied. Early investigations established that
some of these materials rapidly decompose if exposed to air, and extreme care has been taken to treat all samples in an inert atmosphere [2]. Yet here we report Infrared (IR) spectroscopy, Electron Spin Resonance (ESR) and X-ray diffraction experiments, indicating that two fullerides, RbC$_{60}$ and KC$_{60}$ are stable in air.

The A$_1$C$_{60}$ compounds have an fcc (rocksalt) structure at high temperature [7], and upon slow cooling they undergo a reversible first order phase transition to an orthorhombic state, where the C$_{60}$ molecules are chemically bonded to form linear chains [3,4]. This “polymeric” state is thermodynamically stable at room temperature for RbC$_{60}$. Phase separation of KC$_{60}$ to K$_3$C$_{60}$ and pure C$_{60}$ was reported by several authors [7–9]. However, for the slowly cooled samples in this study we consistently found large amounts of polymeric phase of both RbC$_{60}$ and KC$_{60}$ by ESR, X-ray diffraction [4] and IR spectroscopy. Further investigations are clearly needed in this respect, but the basic conclusions of the present work are not expected to change.

In the present study three separately prepared sets of samples were investigated. RbC$_{60}$ thin films (specimen S1) were made on Si substrates under vacuum in a special sample cell [10]. Doping was performed by exposing the films to Rb vapor. During doping the temperature of the film was 225°C and the composition was monitored in-situ by recording IR spectra, and following the evolution of the F$_{1u}(4)$ molecular vibration [9,11]. Polycrystalline KC$_{60}$ (specimen S2) was made by co-evaporation of stoichiometric amounts of the constituent materials in a sealed tube, placed in a gradient furnace [12]. Crystals of typical size $\sim$0.1mm grew at a temperature of about 300°C, while the C$_{60}$ and K were kept at 600°C and 150°C, respectively. During the course of the experiments samples S1 and S2 were first investigated under vacuum or inert atmosphere, and were later exposed to air. A part of the pristine S2 sample was further processed to produce iodine treated KC$_{60}$. The iodination was carried out in a glove box by immersing the co-evaporated crystals to a dilute solution of iodine in toluene for four days. The mixture was then repeatedly rinsed with toluene, ethanol and pentane in air. Specimen S3 was the insoluble residue, left behind after this process. This sample was stored in air for about a month before the measurements reported
here were completed.

IR transmission measurements were carried out on samples S1 and S3. First the spectrum of the pristine sample S1 was recorded. The low overall transmission and the characteristic resonance structure [6,13] of RbC$_{60}$ were clearly visible (lower curve of Fig. 1). The IR spectrum indicates that S1 also contains measurable amounts of Rb$_6$C$_{60}$ and pure C$_{60}$. Then the hermetically sealed sample cell was opened to air. The spectrum taken immediately afterwards (∼10 min) shows the same RbC$_{60}$ resonance lines, slightly increased transmission, and the absence of the Rb$_6$C$_{60}$ impurity phase (Fig. 1, upper curve). Therefore we conclude that Rb$_6$C$_{60}$ was destroyed and RbC$_{60}$ is stable. The small increase in overall transmission is most likely due to the removal of a small amount of metallic Rb$_3$C$_{60}$ from the pristine sample. The corresponding Rb$_3$C$_{60}$ resonance line, positioned at 1364 cm$^{-1}$, is expected to be below the noise level of the experiment. Pure C$_{60}$, most likely produced in the chemical reactions after air exposure, has a much weaker IR signal than Rb$_6$C$_{60}$ or Rb$_3$C$_{60}$ [9,11,14] and does not change the magnitude of the existing C$_{60}$ signal by any appreciable amount.

The IR spectrum of the iodine treated sample S3 is also dominated by the polymeric KC$_{60}$ signal (Fig. 2). This specimen was used to demonstrate that the compound is unstable if moderately heated. Upon heating the transmission increased dramatically, the split $F_{1u}(4)$ line of RbC$_{60}$ at 1387 cm$^{-1}$ and 1406 cm$^{-1}$ disappeared and a strong C$_{60}$ line appeared; i.e. the sample transformed into a mixture consisting of pure C$_{60}$ and other compounds with no strong IR resonances in the measured frequency range. The decomposition starts very slowly below 100°C, but it is complete at T=200°C. The sample was heated in several steps in the IR spectrometer, and it reached 200°C in about three hours. As illustrated by the uppermost spectrum at room temperature, the decomposition is irreversible.

The co-evaporated crystals (S2), as well as S3, were used in the ESR measurements. KC$_{60}$ and RbC$_{60}$ have a characteristically narrow ESR line [5,15]. The ESR spectrum of sample S1 was recorded at room temperature, with the sample sealed in a quartz tube. The tube was then opened to air, and the ESR signal was measured for several days. Figure 3 shows that the signal intensity a.) did not change after opening the sample to air and b.)
was independent of time within the accuracy of the measurement. The width of the signal was also unchanged. We emphasize that the most likely by-products of the disintegration of KC$_{60}$ (C$_{60}$ and K$_2$O or KOH) have no ESR signal. If free radicals or other paramagnetic materials are produced, then it is extremely unlikely that their signals mimic the KC$_{60}$ signal so accurately. The ESR signal of sample S3 is also characteristic of polymeric KC$_{60}$, and the magnetic susceptibility remains constant down to 50K, indicating the metallic nature of electrons, similar to pristine polymeric KC$_{60}$.

X-ray spectroscopy was also performed on the iodine treated sample, S3. The diffraction spectrum (Fig. 4.) shows an enhanced background, possibly due to a non-crystalline component, but the majority of the crystalline part is clearly orthorhombic KC$_{60}$. All three of the probes, X-ray, ESR and IR spectroscopy, sensitive to various physical properties of the sample, show that the air-exposed specimens are mostly polymeric A$_1$C$_{60}$.

The experimental data presently available to us is not sufficient to completely explain the unexpected stability of polymeric alkali metal fullerenes. Some C$_{60}$ salts with a C$^-$ anion, like the (TDAE)C$_{60}$ or the chromium(III) porphyrin salt, were found to be sensitive to air [16,17], while others, like (tetraphenyl phosphonium)C$_{60}$, are stable [17]. In principle, stability is observed if the material is in a thermodynamically favored configuration (like gold in air) or it may be covered by a protecting layer (like aluminum in air). The linear chain structure [4] and morphology [12] of the AC$_{60}$ compounds suggest a more exotic possibility: the long C$_{60}$ polymer chains inhibit the diffusion of the alkali metal or the oxygen, effectively leading to a much slower one-dimensional diffusion and hence a greatly enhanced lifetime.

The existence of a stable alkali metal fulleride may have far-reaching consequences for the study and application of fullerenes. Sample preparation procedures and measurements are much simpler if the specimens can be freely moved and exchanged in air. Investigation of the DC electrical properties will clarify if inter-grain potential barriers are present, possibly inhibiting the electronic transport. In any case, thermal, magnetic and optical studies are greatly simplified. The stable RbC$_{60}$ or KC$_{60}$ polymer may have applications as a protective skin for the superconducting K$_3$C$_{60}$ or Rb$_3$C$_{60}$ material. In fact, the present results may shed
some light on early reports of unexpected persistence of the superconducting Meissner signal in some air exposed $\text{A}_3\text{C}_{60}$ samples [18]. We hypothesize that a fraction of the material in those samples was doped incompletely, leading to the formation of $\text{A}_1\text{C}_{60}$, which then encapsulated the $\text{A}_3\text{C}_{60}$.

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FIGURES

FIG. 1. IR transmission spectra of a thin Rb-doped C\textsubscript{60} film (specimen S1). Inset shows the lower two vibrational modes on an expanded scale. The sample was cooled at a rate of \sim 10^\circ\text{C}/min to room temperature from the preparation temperature. The first spectrum (lower curve) was measured on the pristine film in vacuum. The lines at 1387cm\textsuperscript{-1} and 1406cm\textsuperscript{-1} derive from the F\textsubscript{1u}(4) molecular vibration, split by the polymerization. The F\textsubscript{1u}(2) and F\textsubscript{1u}(4) derived resonances corresponding the Rb\textsubscript{6}C\textsubscript{60} are also clearly visible. When the sample is exposed to air (upper curve), the Rb\textsubscript{6}C\textsubscript{60} is destroyed, while the RbC\textsubscript{60} remains.

FIG. 2. IR transmission of the iodine treated KC\textsubscript{60} powder (specimen S3) in a KBr pellet. The spectral features before heating indicate that the majority of the sample is KC\textsubscript{60}. Upon heating, the sample decomposes. The right side scale, which belongs to the lower two curves, is expanded by a factor of ten relative to the left side scale.

FIG. 3. Time dependence of the ESR intensity of a polycrystalline KC\textsubscript{60} sample (specimen S2) after exposure to air.

FIG. 4. X-ray diffractogram of the iodine exposed KC\textsubscript{60} (specimen S3), as compared to a pristine polycrystalline sample, used in the detailed Rietveld analysis of the polymeric structure (Ref. 4).