

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/233758319>

# Relaxation Processes and Structural Changes in Li- and Na-Doped Fullerenes for Hydrogen Storage

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY C · AUGUST 2012

Impact Factor: 4.77 · DOI: 10.1021/jp304552r

CITATIONS

12

READS

20

9 AUTHORS, INCLUDING:



**Annalisa Paolone**

Italian National Research Council

131 PUBLICATIONS 959 CITATIONS

SEE PROFILE



**Francesca Teocoli**

Technical University of Denmark

14 PUBLICATIONS 175 CITATIONS

SEE PROFILE



**O. Palumbo**

Italian National Research Council

58 PUBLICATIONS 399 CITATIONS

SEE PROFILE



**R. Cantelli**

Sapienza University of Rome

209 PUBLICATIONS 1,683 CITATIONS

SEE PROFILE

# Relaxation Processes and Structural Changes in Li- and Na-Doped Fullerenes for Hydrogen Storage

A. Paolone,<sup>\*,†,‡</sup> F. Vico,<sup>†</sup> F. Teocoli,<sup>§</sup> S. Sanna,<sup>†</sup> O. Palumbo,<sup>†,‡</sup> R. Cantelli,<sup>†</sup> D. A. Knight,<sup>⊥</sup> J. A. Teprovich, Jr.,<sup>⊥</sup> and R. Zidan<sup>⊥</sup>

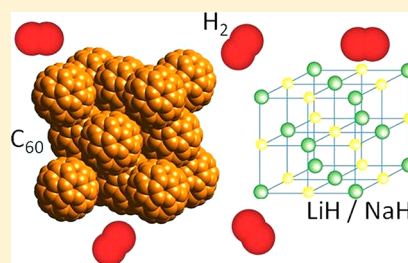
<sup>†</sup>Department of Physics, Sapienza University of Rome, Piazzale A. Moro 5, 00185 Rome, Italy

<sup>‡</sup>CNR-ISC, UOS Sapienza, Piazzale A. Moro 5, 00185 Rome, Italy

<sup>§</sup>Research Center Hydro-ECO, Sapienza University of Rome, Piazzale A. Moro 5, 00185 Rome, Italy

<sup>⊥</sup>Clean Energy Directorate, Savannah River National Laboratory, Aiken, South Carolina 29801, United States

**ABSTRACT:** The anelastic spectra of  $\text{Li}_6\text{C}_{60}\text{H}_x$  and  $\text{Na}_6\text{C}_{60}\text{H}_x$  have been measured for the first time. The spectra of composite materials obtained by mixing of LiH and NaH with  $\text{C}_{60}$  in a solvent still show the structural phase transition around 260 K and preserve the buckyball dynamics of pure fullerenes but do not show the spectral features of the hydrides. This observation suggests that the composite materials are homogeneous samples in which the hydrides are finely dispersed in the fullerene crystal and therefore lose their features. However, after dehydrogenation and after rehydrogenation both the phase transition and the dynamic process are completely suppressed, indicating a deep modification of the lattice structure, possibly due to polymerization. The present study indicates that  $\text{Li}_6\text{C}_{60}\text{H}_x$  and  $\text{Na}_6\text{C}_{60}\text{H}_x$  are homogeneous materials and cannot be considered as constituted by bulk  $\text{C}_{60}\text{H}_n$  and  $\text{Li}(\text{Na})\text{H}_x$ , as suggested by a previous study.



## INTRODUCTION

The development of hydrogen-absorbing storage media fulfilling international targets is currently considered one of the most technologically challenging obstacles in the way of achieving a hydrogen-based economy. The main requirements for such hydrogen absorbers are a high storage capacity, practical working temperatures and pressures, fast kinetics of hydrogenation and dehydrogenation, and a high resistance to degradation and contamination during hydrogen absorption–desorption cycles. In recent years many materials, such as alanates,<sup>1–3</sup> amides,<sup>4,5</sup> aluminum hydride,<sup>6–9</sup> ammonia borane,<sup>10–12</sup> and borohydrides,<sup>13</sup> have been considered as promising storage media. However, none of these compounds can fulfill the strict international requirements for mobile applications of hydrogen.

Consequently, new, efficient, and nontraditional manipulation methods of traditional hydrides have been recently proposed in order to obtain composite systems with improved storage properties.<sup>14,15</sup> Among these methods, showing good performances materials, are nanoinfiltration and hybridization with carbon-based systems. In order to optimize such nano and hybridized systems for hydrogen storage, a fundamental understanding of hydrogen interaction with these systems is needed.

In the framework of hybridization, the mixing of  $\text{C}_{60}$ <sup>16</sup> and alkali hydrides (NaH and LiH) has been considered.<sup>17,18</sup> Both fullerene and NaH/LiH are able to store hydrogen, but their major drawback is the extremely high desorption temperatures ( $T_d > 500$  °C for hydrofullerene,  $\text{C}_{60}\text{H}_x$ ;  $T_d > 450$  °C for NaH;  $T_d > 720$  °C for LiH). However, it has been reported that

composite samples can reversibly store 5.0 and 2.5 wt % hydrogen in the case of  $\text{Li}_6\text{C}_{60}\text{H}_x$  and  $\text{Na}_6\text{C}_{60}\text{H}_x$ , respectively; in addition, the desorption temperatures are reduced to <300 °C.<sup>17</sup>

The same desorption temperature was observed for hydrogenated lithium fulleride formed by the reaction of  $\text{C}_{60}$  with 10 wt % of lithium metal. In the latter case, an amount of 2.59 wt % hydrogen is released after hydrogenation at 523 K and 3 MPa of  $\text{H}_2$ . For those samples, NMR measurements suggest that  $\text{C}_{60}\text{H}_n$  and LiH were formed after hydrogenation.<sup>19</sup>

In the present paper, we report dynamic and structural information on novel  $\text{Li}_6\text{C}_{60}\text{H}_x$  and  $\text{Na}_6\text{C}_{60}\text{H}_x$ , obtained by means of anelastic spectroscopy, which seem to differ from the picture suggested by NMR results and indicate that a quite different material is formed after hydrogenation.

## EXPERIMENTAL SECTION

$\text{C}_{60}$ , LiH, and NaH were purchased from Sigma-Aldrich and used as received. All of the materials and synthesis were performed under an argon atmosphere in a glovebox or on a Schlenk line.

Composite materials (starting materials) were obtained by dissolution and mixing of fullerene and LiH or NaH in molar ratios of 1:6 in THF or toluene, respectively. The removal of the solvent was accomplished by vacuum evaporation and heating at ~70 °C (typically 2–5 wt % solvent remains in the

Received: May 10, 2012

Revised: July 5, 2012

Published: July 18, 2012



samples). Those samples will be called 6LiH:C<sub>60</sub> and 6NaH:C<sub>60</sub> in the following. The starting materials were heated at 500 °C to allow the release of residual solvents and hydrogen. Rehydrogenation was obtained by applying a pressure of 100 bar hydrogen at 350 °C for the lithium material and at 275 °C for the sodium material with each for 11 h. For comparison, the same conditions were also utilized for the synthesis of the undoped hydrofullerene (C<sub>60</sub>H<sub>x</sub>).<sup>17</sup>

The consolidated samples necessary to perform anelastic spectroscopy measurements were obtained by pressing the powders in a die at 4 kbar, following a well-established procedure for anelastic spectroscopy experiments on complex hydrides.<sup>20–26</sup> The samples are rectangular bars 25–40 mm long, 6 mm wide, and 0.7–1.5 mm thick. All the material handling was performed in a glovebag in flowing inert gas atmospheres to avoid contamination.

Anelastic spectroscopy measurements were conducted by suspending the bars on thin wires located at the nodal lines of flexural vibration modes. The suspended bars were electrostatically excited to the corresponding mechanical resonances of the samples; in the present work the first and third flexural modes were excited. The sample vibration produces an alternate stress which interacts with the local lattice distortions, introduced by the mobile entities. The alternate stress perturbs their site energies in such a way that the sites that are energetically favored in the first half period become unfavored in the second half. The system then attempts to reach an equilibrium redistribution among the perturbed levels. When the system reaches a temperature at which the relaxation rate  $\tau^{-1}$  of the mobile atoms is equal to the angular vibration frequency  $\omega$  (i.e., at the Debye relaxation condition  $\omega\tau = 1$ , the stimulated atomic migration follows, by thermal activation), the coefficient of elastic energy dissipation  $Q^{-1}$  reaches its maximum value. The energy dissipation (or reciprocal of the mechanical quality factor  $Q$ ) is measured from the decay of the free oscillations or from the width of the resonance peak. The dynamic Young's modulus  $E'$  is obtained concomitantly with  $Q^{-1}$  from the angular vibration frequency,  $E' = \omega^2 \rho / z$ , where  $\rho$  is the mass density and  $z$  a numerical factor depending on the sample geometry.<sup>27</sup> The independent and concomitant measurements of  $Q^{-1}$  and  $E'$  allow the complex modulus  $E = E' + iE''$  to be derived from  $Q^{-1} = E''/E'$ .

For a single relaxation time,  $\tau$ ,  $Q^{-1}$  is given by

$$Q^{-1} = g\nu_0(\lambda_1 - \lambda_2)^2 \frac{cn_1n_2}{kT} E' \frac{(\omega\tau)^\alpha}{1 + (\omega\tau)^{2\alpha}} \quad (1)$$

where  $c$  is the molar concentration of the jumping atoms and  $n_1$  and  $n_2$  are their equilibrium fractions in sites 1 and 2;  $\lambda_1$  and  $\lambda_2$  are the elastic dipoles<sup>27</sup> of the defects in their two configurations;  $g$  is a factor of the order of  $1/2$  depending on the geometry of the jump and the type of sample vibration,  $\nu_0$  the unit cell volume,  $\alpha$  a parameter equal to 1 for a single Debye process, and  $k$  the Boltzmann constant. For classical processes  $\tau = \tau_0 e^{W/kT}$ , with  $W$  being the activation energy. As  $\tau$  is temperature dependent for thermally activated processes, the relaxation condition ( $\omega\tau = 1$ ) is satisfied at lower temperatures for fast processes and at higher temperatures for slow processes. In many cases the experimental peaks are broader than a Debye peak, and they can be described by means of a Fuoss–Kirkwood model, in which the parameter  $\alpha$  in eq 1 becomes smaller than 1. Fuoss–Kirkwood peaks are broader than Debye peaks by a factor  $1/\alpha$ , and they physically describe processes in

which  $W$  and  $\tau_0$  do not have a single value, but they are expressed by a distribution function.

The relaxation intensity in eq 1 decreases with increasing  $T$ , thus leading to a higher intensity for the peaks measured at lower frequencies, where the relaxation condition  $\omega\tau = 1$  is satisfied at lower temperatures. However, in the case of hopping between two nonequivalent sites 1 and 2 with energy separation  $\Delta E$ , the relaxation intensity, which is proportional to the product of the respective populations, becomes<sup>28</sup>

$$\frac{cn_1n_2}{T} \alpha \frac{c}{T} \sec h^2\left(\frac{\Delta E}{2kT}\right) \quad (2)$$

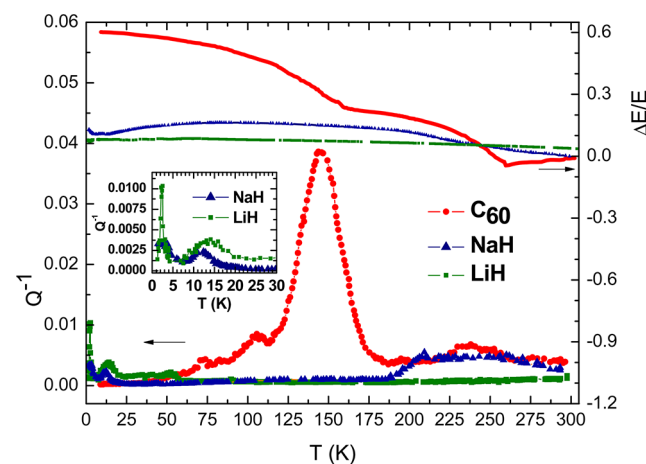
In this case, assuming the Arrhenius law, the relaxation time becomes

$$\tau^{-1} = \tau_{12}^{-1} + \tau_{21}^{-1} = \tau_0^{-1} e^{-W/kT} \cosh\left(\frac{\Delta E}{2kT}\right) \quad (3)$$

where  $W$  is the mean activation energy for hopping between the two nonequivalent sites. This dependence for jumps between two nonequivalent sites results therefore in a higher intensity for the peaks measured at higher frequencies.

## RESULTS AND DISCUSSION

The anelastic spectrum of the parent materials, i.e., pure C<sub>60</sub>, LiH, and NaH, was measured in the temperature range between 1.3 and 300 K at temperature rates ranging between 0.3 and 1 K/min, and the data are reported in Figure 1. Upon cooling

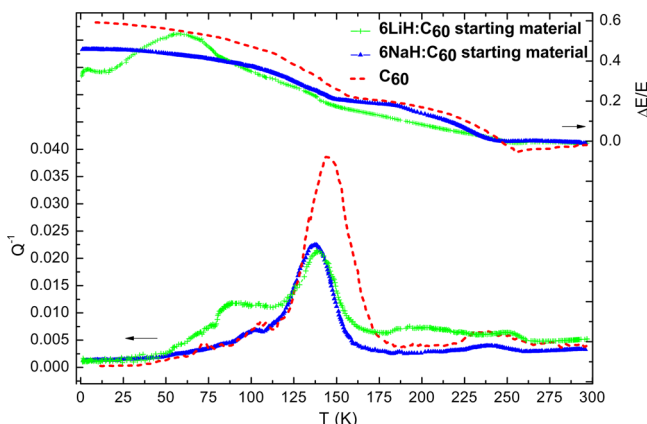


**Figure 1.** Temperature dependence of the Young modulus and of the elastic energy dissipation of pure C<sub>60</sub> (red dots), LiH (green squares), and NaH (blue triangles). The inset shows the detail of the low-temperature part of  $Q^{-1}$  for LiH and NaH.

pure fullerene from room temperature, the elastic modulus decreases, showing a trend opposite to that followed by the standard linear solid, but at 260 K this trend is abruptly inverted. Such a behavior, which is typical of a phase transformation, was attributed<sup>29</sup> to the occurrence of a structural transition between an orientationally disordered phase at high  $T$ 's and an ordered phase at low  $T$ 's. Moreover, fullerene displays an intense relaxation peak, centered around 150 K for a vibration frequency of  $\sim 2.8$  kHz, which is compatible with the previous report<sup>29</sup> of a relaxation process, attributed to the rotation of C<sub>60</sub> molecules between energetically inequivalent positions.<sup>16,29</sup>

The anelastic spectra of pure LiH and NaH are reported for the first time in the present work. The spectra of both compounds display two sharp maxima centered around 13 and 3 K, whose physical origin requires further investigation.

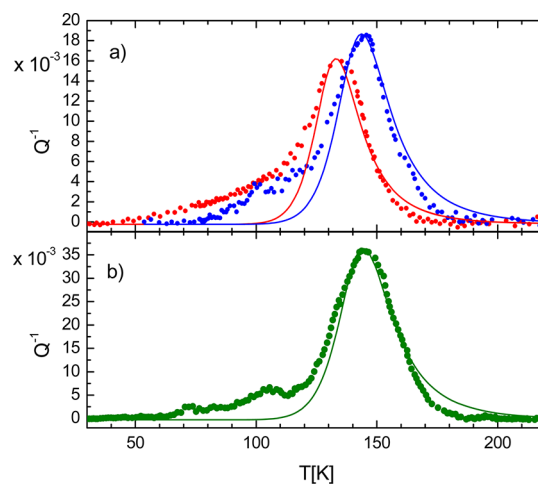
Figure 2 shows the anelastic spectra of the starting materials, 6LiH:C<sub>60</sub> and 6NaH:C<sub>60</sub>, obtained by mixing LiH and NaH



**Figure 2.** Temperature dependence of the variation of the Young modulus and elastic energy dissipation of pure fullerene (red line), 6LiH:C<sub>60</sub> (green crosses), and 6NaH:C<sub>60</sub> (blue triangles).

with C<sub>60</sub> in THF or toluene, in molar ratio 6:1. It should be noted that both compounds show an anelastic spectrum similar to that of pure C<sub>60</sub>. Indeed, both materials present the inflection of the Young modulus around 260 K displayed by pure fullerene, attributed to the occurrence of the structural phase transition. Moreover, both 6LiH:C<sub>60</sub> and 6NaH:C<sub>60</sub> show an intense relaxation peak, which is slightly shifted to lower temperature (by 10 K) with respect to pure C<sub>60</sub>. It should be noted that the height of the relaxation peak is about 1/2 of that of pure fullerene even though C<sub>60</sub> is the minor component of the materials in terms of molar fraction. This is a consistent indication that the crystal structure of the mixture is very similar to that of pure fullerene. In spite of the high sensitivity of our elastic energy loss measurements, the low-temperature peaks displayed by pure LiH and NaH completely disappeared in the composite materials. This observation demonstrates that, in the composite materials, the hydrides lose their lattice structure. A possible interpretation is that NaH and LiH are finely dispersed in the fullerene crystal structure, possibly occupying interstitial positions, so that the anelastic properties of the composite materials are mainly those of the host matrix.

The close similarity between pure fullerene and the starting composite materials mixture is also evident from the analysis of the relaxation peak centered around 140–150 K, which in pure fullerene was attributed to the rotations of buckyballs between inequivalent configurations.<sup>29</sup> The temperature dependence of the elastic energy dissipation of 6NaH:C<sub>60</sub> measured for the first (~1.0 kHz) and third (~5.4 kHz) vibration modes are reported in Figure 3. After subtraction of a polynomial background from the experimental data, we performed a fit using the Fuoss–Kirkwood model (eq 1), assuming hopping between two nonequivalent sites (eqs 2 and 3), as suggested by crystallographic mapping (ref 16), in order to reproduce the higher intensity displayed by the peak measured at the higher frequency (Figure 3). The best fit curves displayed in Figure 3 obtained by the fitting procedure gave the values  $W = 0.27$  eV,  $\Delta E = 0.04$  eV,  $\tau_0 = 1.25 \times 10^{-14}$  s, and  $\alpha = 0.71$ , which are very



**Figure 3.** Elastic energy dissipation (after subtraction of a polynomial background from the experimental data) and best fit curves of 6NaH:C<sub>60</sub> (panel a; red dots: first flexural mode, blue dots: third flexural mode) and C<sub>60</sub> (panel b).

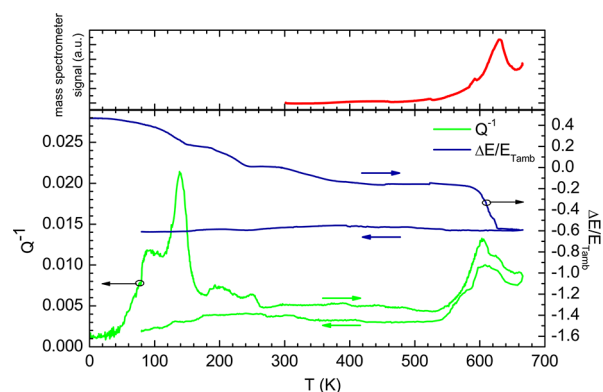
close to those reported in ref 29 for pure C<sub>60</sub> ( $W = 0.29$  eV,  $\tau_0 = 3 \times 10^{-14}$  s). Actually, the contribution from ref 29 did not perform the peak shape analysis, and thus much information was not obtainable, particularly that concerning the peak broadening due to the interaction among the relaxing units. Indeed, this interaction is not negligible, as the value of  $\alpha$  is quite different from 1, indicating that both the activation energy,  $W$ , and the pre-exponential factor of the relaxation time,  $\tau_0$ , have a wide distribution.

In order to ascertain whether a distribution of  $W$  is needed in a pure fullerene sample, an analysis of the peak measured in pure C<sub>60</sub> in the present work was performed. We were able to precisely measure the dissipation curve only for the first flexural vibration (~2.8 kHz). Therefore, we fixed the parameter  $\tau_0$  to the value reported by the previous literature and allowed  $W$  and  $\alpha$  to vary. The best fit parameters obtained are  $W = 0.284$  eV and  $\alpha = 0.69$ . The fact that  $\alpha$  is much lower than 1 clearly shows that a wide distribution of the activation energy is present in pure fullerene.

Figures 2 and 3 clearly show that the relaxation peak is asymmetric and presents a broad shoulder on the low-temperature side which is particularly pronounced in the 6LiH:C<sub>60</sub> compound. While the height of the relaxation peak centered around 140 K is time-independent, a variation of the dissipation of the low-temperature shoulder was detected as the samples were kept in vacuum for subsequent measurements (results not shown). This observation suggests that the shoulder could be attributed to the presence of the solvents used to mix hydrides with fullerene, which are slowly released in vacuum, similarly to the case of calcium borohydride.<sup>26</sup> Details about the nature of the shoulder of the main dissipation peak are outside the aim of the present paper and will not be discussed.

Figure 4 reports the temperature dependence of  $Q^{-1}$  and of the Young modulus of 6LiH:C<sub>60</sub>, during a thermal treatment in vacuum up to 690 K, which removes hydrogen and leaves the sample in the dehydrogenated state. The increase of  $Q^{-1}$  above 580 K and the sharp decrease of  $Y$  above 600 K are due to the dehydrogenation, as monitored by a mass spectrometer (upper panel in Figure 4). When the sample was cooled back below room temperature, we did not observe either the phase



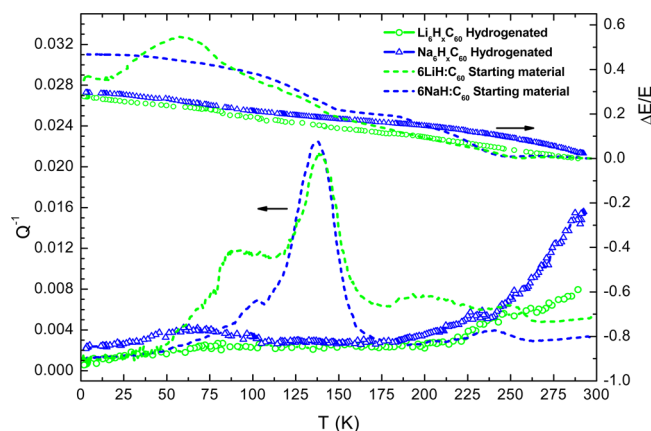


**Figure 4.** Lower panel: temperature dependence of the elastic energy loss (green line) and of the variation of the Young modulus (blue line) of 6LiH:C<sub>60</sub> during the dehydrogenation process. Upper panel: temperature evolution of the mass spectrometer signal for  $m/z = 2$  during the measurement above room temperature.

transition around 240 K or the rotational dynamical process around 140 K, indicating that the crystal structure of the sample was modified by the dehydrogenation process. The diffraction data reported in ref 17 for Li<sub>6</sub>C<sub>60</sub>H<sub>x</sub> show that both the starting material and the dehydrogenated samples have a fcc structure, while the hydrogenated material has a bcc structure. However, the diffraction peaks of dehydrogenated samples are broader than in the starting materials, so that some modification of the crystal structure is expected. The present anelastic spectroscopy measurements strongly indicate that noticeable changes indeed occur, and they lead to the suppression of the rotational dynamics both in Li<sub>6</sub>C<sub>60</sub>H<sub>x</sub> and in Na<sub>6</sub>C<sub>60</sub>H<sub>x</sub>. A possible explanation is that in the dehydrogenated compounds some bonds can be formed between the buckyballs, possibly leading to polymerization. Indeed, polymerization has been reported for pure C<sub>60</sub> when the material is pressed at high temperatures and pressures. Moreover, the phase diagrams of Na<sub>x</sub>C<sub>60</sub> and Li<sub>x</sub>C<sub>60</sub> obtained by means of diffraction measurements present wide regions of polymerization.<sup>16</sup> In particular, the absence of any feature related to the rotational motions of C<sub>60</sub> molecules in the anelastic spectrum of fullerene films deposited under *in situ* photoirradiation<sup>30</sup> was attributed to the occurrence of uniform dimerization in the C<sub>60</sub> films. It should be pointed out that even the simple bonding of the buckyballs can lead to the suppression of the rotational dynamics, without the need of a long-range order.

Raman characterizations reported in ref 17 showed the presence of some cross-linking of the fullerenes with the appearance of broad bands at  $\sim 1335$  and  $\sim 1585$  cm<sup>-1</sup> that are consistent with polymerization and/or cage modification.

The anelastic spectra of the rehydrogenated compounds are similar to those of the dehydrogenated samples. The rehydrogenated samples (Figure 5) do not present the inflection of the Young modulus around 260 K and the intense relaxation peak around 150 K. Again, our data indicate that in the hydrogenated compounds the lattice presents deep modifications compared to that of pure fullerene and to that of the composite materials obtained by mixing LiH and NaH with C<sub>60</sub>. The diffraction data reported in ref 17 indicate a bcc structure of the sample hydrogenated at 350 °C, with broad diffraction peaks. From the present anelastic spectroscopy measurements we cannot suggest a crystal structure for the hydrogenated compounds; however, the experiments clearly



**Figure 5.** Temperature dependence of the variation of the Young modulus and of the elastic energy dissipation in the starting materials and in the rehydrogenated compounds: 6LiH:C<sub>60</sub> starting material (green line); 6NaH:C<sub>60</sub> starting material (blue line); Li<sub>6</sub>H<sub>x</sub>C<sub>60</sub> (open green dots); Na<sub>6</sub>H<sub>x</sub>C<sub>60</sub> (open blue triangles).

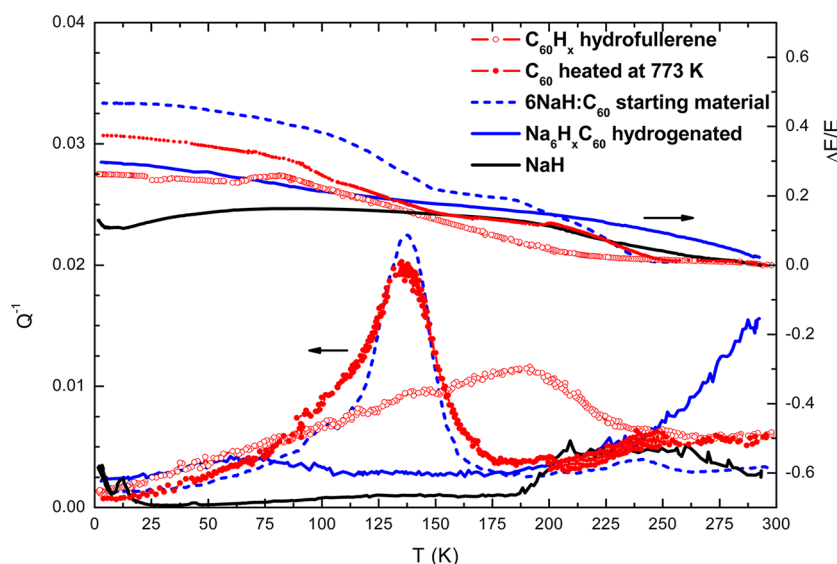
indicate that they do not undergo phase transitions between 4 and 300 K and do not show any relaxation of the buckyballs, consistent with a polymerization of the samples.

Recently, Yoshida et al. reported NMR experiments on a Li<sub>x</sub>C<sub>60</sub>H<sub>n</sub> ( $x \approx 15$ ), obtained by a different chemical procedure, i.e., the reaction of C<sub>60</sub> with 10 wt % of lithium metal followed by hydrogenation, and found that 2.59 wt % H<sub>2</sub> is desorbed at  $\sim 560$  K.<sup>18</sup> These authors suggest that after hydrogenation LiH and C<sub>60</sub>H<sub>n</sub> are formed and molecular hydrogen is stored as a proton (H<sup>+</sup>) incorporated in C<sub>60</sub> and as a hydride (H<sup>-</sup>) incorporated with the Li ion. Our present anelastic measurements suggest a different environment in the Li<sub>6</sub>C<sub>60</sub>H<sub>n</sub> and Na<sub>6</sub>C<sub>60</sub>H<sub>n</sub> materials. Indeed, in Figure 6 we report the variation of the Young modulus and the elastic energy dissipation of hydrofullerene in the temperature range between 4 and 300 K. One can note that the anelastic spectrum of hydrofullerene presents a change of slope of the modulus below 250 K and a very broad relaxation peak below the same temperature. In Figure 2, the elastic energy dissipation of pure LiH and NaH displayed the presence of two relaxation peaks below 20 K. The flat spectra of Na<sub>6</sub>C<sub>60</sub>H<sub>n</sub> and Li<sub>6</sub>C<sub>60</sub>H<sub>n</sub> are very different from both hydrofullerene and pure alkali hydrides spectra, indicating that the hydrogenated samples studied in the present work are not the simple mix of individual bulk hydrofullerene and alkali hydrides.

One can speculate whether the heat treatments used to dehydrogenate and rehydrogenate the fullerene samples can change the C<sub>60</sub> crystal structure and suppress the structural phase transition and the rotational dynamics. Therefore, we heated pure fullerene at 773 K in an argon atmosphere for 15 min, in order to reproduce just the thermal treatment on the sample during dehydrogenation. The  $Q^{-1}$  and  $Y$  curves vs  $T$  of heated C<sub>60</sub> from 4 to 300 K drawn in Figure 6 show that the rotational dynamics in fullerene persists also after the thermal treatment. In view of those results it can be asserted that the presence of Li, Na, and H is a key ingredient to induce the structural changes, demonstrating that they remarkably interact with the C lattice.

## CONCLUSIONS

Composite materials obtained by mixing LiH in THF or NaH in toluene with C<sub>60</sub> (6:1 mole ratio) show the structural phase



**Figure 6.** Temperature dependence of the variation of the Young modulus and of the elastic energy dissipation in  $C_{60}H_x$  (open red dots);  $C_{60}$  heated at 773 K (full red dots);  $6NaH:C_{60}$  starting material (blue dashed line);  $Na_6H_xC_{60}$  (blue solid line); NaH (black solid line).

transition and the buckyball rotational dynamic previously reported for pure fullerene. Our results indicate that the lattice of the composite materials is very similar to that of  $C_{60}$  for the as prepared materials. LiH and NaH lose their identity and likely go in fine dispersion in the  $C_{60}$  lattice. However, after dehydrogenation and rehydrogenation the crystal structure is deeply modified because both the phase transition and the relaxation dynamics are no longer observed in these samples, possibly due to polymerization. The present data also indicate that the rehydrogenated compounds are new homogeneous materials formed during the desorption and absorption of hydrogen and cannot be regarded as individual bulk hydrofullerene and alkali hydride.

## AUTHOR INFORMATION

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The present work was partially supported by the Project Industria 2015 “HYDROSTORE” funded by the Italian ministry of Economic Development. D.A.K., J.A.T., and R.Z. thank the US-DOE, Office of Basic Energy Science, for funding.

## REFERENCES

- (1) Palumbo, O.; Cantelli, R.; Paolone, A.; Jensen, C. M.; Sulic, M. J. *Phys. Chem. B* **2006**, *110*, 9105–9111.
- (2) Mohtadi, R.; Sivasubramanian, P.; Hwang, S.-J.; Stowe, A.; Gray, J.; Matsunaga, T.; Zidan, R. *Int. J. Hydrogen Energy* **2012**, *37*, 2388–2396.
- (3) Johnson, T. A.; Kanouff, M. P.; Dedrick, D. E.; Evans, G. H.; Jorgensen, S. W. *Int. J. Hydrogen Energy* **2012**, *37*, 2835–2849.
- (4) Zhang, J.-X.; Cerny, R.; Villero, B.; Godart, C.; Chandra, D.; Latroche, M. J. *Alloys Compd.* **2011**, *509S*, S732–S735.
- (5) Palumbo, O.; Paolone, A.; Rispoli, P.; D’Orazio, A.; Cantelli, R.; Chandra, D. *Int. J. Mater. Res.* **2008**, *99*, 487–490.
- (6) Zidan, R.; Knight, D. A.; Dinh, L. V. U.S. Pat. Appl. Publ. US 20120141363 A1 20120607, 2012.
- (7) Dinh, L. V.; Knight, D. A.; Paskevicius, M.; Buckley, C. E.; Zidan, R. *Appl. Phys. A: Mater. Sci. Process.* **2012**, *107*, 173–181.

- (8) Martinez-Rodriguez, M. J.; Garcia-Diaz, B. L.; Teprovich, J. A., Jr.; Knight, D. A.; Zidan, R. *Appl. Phys. A: Mater. Sci. Process.* **2012**, *106*, 545–550.
- (9) Teprovich, J. A., Jr.; Motyka, T.; Zidan, R. *Int. J. Hydrogen Energy* **2012**, *37*, 1594–1603.
- (10) Autrey, T.; Bowden, M.; Karkamkar, A. *Faraday Discuss.* **2011**, *151*, 157–169.
- (11) Shaw, W. J.; Bowden, M.; Karkamkar, A.; Howard, C. J.; Heldebrant, D. J.; Hess, N. J.; Linehan, J. C.; Autrey, T. *Energy Environ. Sci.* **2010**, *3*, 796–804.
- (12) Palumbo, O.; Paolone, A.; Rispoli, P.; Cantelli, R.; Autrey, T. *J. Power Sources* **2010**, *195*, 1615–1618.
- (13) Paolone, A.; Palumbo, O.; Rispoli, P.; Miriametro, A.; Cantelli, R.; Rönnebro, E.; Chandra, D. *J. Alloys Compd.* **2011**, *509S*, S691–S693.
- (14) Gutowska, A.; Liyu, L.; Shin, Y.; Chongmin, M.; Wang, X.; Li, S.; Linehan, J.; Smith, S.; Kay, B. D.; Schmid, B.; Shaw, W.; Gutowski, M.; Autrey, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 3578–3582.
- (15) Zheng, S.; Fanf, F.; Zhou, G.; Chen, G.; Ouyang, L.; Zhu, M.; Sun, D. *Chem. Mater.* **2008**, *20*, 3954.
- (16) Andreoni, W. *The Physics of Fullerene-Based and Fullerene-Related Materials*; Kluwer Academic: Dordrecht, 2000.
- (17) Teprovich, J. A., Jr.; Wellons, M. S.; Lascola, R.; Hwang, S.-J.; Ward, P. A.; Compton, R. N.; Zidan, R. *Nano Lett.* **2012**, *12*, 582–589.
- (18) Teprovich, J. A., Jr.; Knight, D. A.; Wellons, M. S.; Zidan, R. *J. Alloys Compd.* **2011**, *509S*, S562–S566.
- (19) Yoshida, A.; Okuyama, T.; Terada, T.; Naito, S. *J. Mater. Chem.* **2011**, *21*, 9480–9482.
- (20) Palumbo, O.; Paolone, A.; Cantelli, R.; Jensen, C. M.; Ayabe, R. *Mater. Sci. Eng., A* **2006**, *442*, 75–78.
- (21) Palumbo, O.; Cantelli, R.; Paolone, A.; Jensen, C. M.; Srinivasan, S. S. *J. Phys. Chem. B* **2005**, *109*, 1168–1173.
- (22) Palumbo, O.; Paolone, A.; Cantelli, R.; Chandra, D. *Int. J. Hydrogen Energy* **2008**, *33*, 3107–3110.
- (23) Paolone, A.; Palumbo, O.; Rispoli, P.; Cantelli, R.; Autrey, T. *J. Phys. Chem. C* **2009**, *113*, 5872–5878.
- (24) Paolone, A.; Palumbo, O.; Rispoli, P.; Cantelli, R.; Autrey, T.; Karkamkar, A. *J. Phys. Chem. C* **2009**, *113*, 10319–10321.
- (25) Cantelli, R.; Palumbo, O.; Paolone, A.; Jensen, C. M.; Kuba, M. T.; Ayabe, R. *J. Alloys Compd.* **2007**, *446–447*, 260–263.
- (26) Paolone, A.; Palumbo, O.; Rispoli, P.; Cantelli, R.; Rönnebro, E.; Luedtke, A.; Chandra, D. *Solid State Phenomena* **2012**, *184*, 24–32.
- (27) Nowick, A. S.; Berry, B. S. *Anelastic Relaxation in Crystalline Solids*; Academic Press: New York, 1972.

- (28) Cannelli, G.; Cantelli, R.; Cordero, F.; Trequattrini, F. *Phys. Rev. B* **1997**, *55*, 14865–14871.
- (29) Shi, X. D.; Kortan, A. R.; Williams, J. M.; Kini, A. M.; Savall, B. M.; Chaikin, P. M. *Phys. Rev. Lett.* **1992**, *68*, 827–830.
- (30) Tanimoto, H.; Yamada, K.; Mizubayashi, H.; Matsumoto, Y.; Naramoto, H.; Sakai, S. *Appl. Phys. Lett.* **2008**, *93*, 151919.