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Response to “Comment on ‘Laser controlled magnetism in hydrogenated fullerene films’” [J. Appl. Phys. 113, 036101 (2013)]

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In the paper “Laser controlled magnetism in hydrogenated fullerene films,”¹ we reported on room temperature magnetism of fullerenes treated with mono-atomic hydrogen. The study was motivated by the earlier theoretical predictions^{2,3} that unpaired spins on fullerene molecules in the polymerized solid phases show long range exchange interaction, which is strong enough to expect ferromagnetism at room temperatures. In Ref. 1, we reported that after treatment with monoatomic hydrogen and polymerization, fullerene films show well pronounced magnetic hysteresis and the saturation magnetization corresponds to 0.1–0.2 bohr magneton per fullerene molecule.

The observed magnetism in our hydrogenated samples—magnetically inert before the treatment—has been interpreted in the physical picture where the unpaired spins are due to hydrogen atoms attached to fullerenes, $C_{60}H$ being the simplest possibility as a magnetic building block. In accordance with *ab initio* calculations, these states are thermodynamically unstable. Our treatment with monoatomic hydrogen creates metastable complexes, which are long lived due to a high barrier (~ 2 eV, in accordance with *ab initio* calculations) on the path from the unstable configuration $C_{60}H + C_{60}H$ to the stable one $C_{60}H_2 + C_{60}$.

We do not think that it is of much interest for the reader to discuss if our results “...contradict the existing experimental knowledge” of the Comment’s author. Our paper¹ is concentrated on magnetism with the structural data presented rather sketchy, and we are grateful to the author of the Comment for the opportunity to discuss structural properties and show our data in more detail.

In Fig. 1(a), we show the Raman spectrum of a pristine film. These data were not included in our publication,¹ as the Comment quite rightly states. In the region from 1650 to 4000 cm^{-1} , the spectrum in Fig. 1(a) is featureless in contrast to the spectrum of a hydrogenated film in Fig. 1(a), inset. We emphasize that the two spectra were measured in identical conditions at the same very low laser intensity (1% of the

maximum He-Ne laser power where the full power is 50 mW/ cm^2).

The assignment of the Raman peaks seen in our freshly hydrogenated samples in Fig. 1(a), inset, indeed requires discussion. Leaving aside “...unknown effects...” suggested in the Comment, we are aware of two mechanisms: (i) intrinsic one, that is, due to the vibration modes related to hydrogen(s) attached to fullerenes; (ii) second or higher order Raman processes,⁴ an extrinsic mechanism in this context.

The vibrational frequencies and the corresponding Raman intensities have been computed in Ref. 1, and Fig. 1(b) presents the simulated spectra. The calculations predict the C-H stretching modes in the frequency range 2800–3100 cm^{-1} at the positions which turn out to be rather close to the following second-order Raman modes: $2H_g(7)$; $A_g(2) + H_g(7)$; $2A_g(2)$; $H_g(7) + H_g(8)$, and $A_g(2) + H_g(7)$. The latter were observed in Ref. 4 on fullerene films exposed to high laser excitation intensities. Admittedly, this near coincidence creates ambiguity in the interpretation. Although the appearance of the second order modes at the very low laser intensity is very unlikely in our measurements, we cannot exclude the contribution of C_{60} silent modes which become weakly active when attached hydrogens reduce the space symmetry; in a sense, this mechanism is also intrinsic. The peaks in the C-H stretching vibrations region are much stronger than other features in the 1800–4000 cm^{-1} region,¹ and we believe that the spectrum is the superposition of the mechanisms, intrinsic mechanism being a prevailing one.

Further, in Fig. 1(c), we show the Raman spectrum of pristine and hydrogenated films in the 200–1800 cm^{-1} range. In this range, *ab initio* calculations predict the following changes in the Raman spectra due to hydrogenation: (i) lifting the degeneracy of the $H_g(1)$, $H_g(7)$, and $H_g(8)$ modes, (ii) strong enhancement of the latter mode in intensity, and (iii) an appearance of large amount of spectral features around the $H_g(5)$ and $H_g(6)$ modes. The predicted features, although expectedly weak in intensity, can be identified from the comparison of the spectra of pristine and hydrogen

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FIG. 1. (a) Experimental Raman spectrum of C_{60} film. Inset: Part of the spectrum of the same film before and after the hydrogen plasma treatment. (b) Theoretical Raman spectra for $C_{60}H_1$ (upper curve) and $C_{60}H_2$ (lower curve) calculated using the *ab initio* DFT/B3LYP/3-21G method by PC GAMESS version 7.0 and GAUSSIAN 03 suite of programs. (c) Experimental Raman spectrum of C_{60} film before (lower curve) and after (upper curve) the hydrogen plasma treatment. Inset: Enlarged part of the spectra of the same films; Lower panel of the inset: Theoretical Raman spectra for $C_{60}H_1$ shown as partial peaks.

treated samples. Splitting of the $H_g(1)$ mode around 270 cm^{-1} and the $H_g(7)$ around 1425 cm^{-1} modes as well as a threefold enhancement in intensity of the $H_g(8)$ mode at 1575 cm^{-1} (marked by the ovals) are clearly seen in Fig. 1(c). Closer look at the $1000\text{--}1400\text{ cm}^{-1}$ region (Fig. 1(c), inset) provides further arguments: below 1000 cm^{-1} , the spectra of pristine and treated samples are nearly identical being noticeably different around 1100 , 1200 , 1250 cm^{-1} , i.e., in the region predicted by the theory (lower panel in the inset).

In the hydrogenated samples, the Raman measurements in the region from 260 to 3200 cm^{-1} reveal a number of peaks that can be assigned to the predicted hydrogen modes. As expected, these additional peaks disappear with aging of our samples.

We emphasize that the aging effects are seen simultaneously in magnetic properties and the Raman spectra.² These findings unequivocally indicate that both magnetic and structural changes are due to the hydrogen treatment, and we assert that the data support our physical picture.

The Comment's author claims he is in possession of commercial fullerene samples in which the characteristic Raman peaks similar to that in Fig. 1(a) were seen without any treatment. We are not in position to discuss unpublished results obtained on uncharacterized samples by an undocumented procedure. It could be that these samples contained hydrogen-rich impurities and/or high order Raman processes contributed to the spectra.

In conclusion, we thank the Comment's author for attention and invaluable advices but we find no convincing argument in the Comment that makes us change the point of view presented in Ref. 1.

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