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Interactive comment on "Room temperature hyperpolarization of polycrystalline samples with optically polarized triplet electrons: Pentacene or Nitrogen-Vacancy center in diamond?" *by* Koichiro Miyanishi et al.

Anonymous Referee #2

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The authors use optically polarized electron triplets in combination with integrated solid-effect DNP to polarize 13C nuclei in NV- doped diamond and also in pentacene doped benzoic acid. The authors extract spin exchange probabilities from the EPR and NMR data and calculate 13C spin diffusion coefficients for each sample in order to assess the suitability of each system for generating bulk 13C polarization in the host matrix. The exchange probability is extracted by modeling the build-up of 13C polarization in the rapid-diffusion limit and spin diffusion coefficients are calculated from the Lowe-Gade formula for the NV case and estimated based on previous works for the

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Discussion paper

pentacene case. The authors suggest that the triplet state lifetime and the presence of heteronuclear dipolar coupling accounts for the difference in observed exchange probabilities for the two systems.

This work calls attention to several parameters (source lifetime, T1n, spin-spin coupling effect) that should be considered when choosing a polarized electron triplet source and matrix to maximize the bulk polarization of a particular nucleus in a sample, specifically low gamma. Most interestingly, this work shows how the exchange probability can be extracted from NMR/EPR data and presents a metric to assess the general suitability of optically hyperpolarized systems for efficient nuclear polarization of the surrounding matrix.

The paper is well-written and of interest to the MR community though it is lacking in some areas with respect to proper references and literature knowledge.

Specific comments and also technical/reference comments:

1. Line 22. The optically generated spin polarization does depend on the magnetic field in specific instances when one considers level crossings and spin mixing effects.

2. Line 25. Triplet-DNP was not originally demonstrated in a single crystal of naptha-lene with pentacene, there is at least one earlier reference to the case where Kesteren, Wenckebach and Schmidt acheived this in a different system (Fluorene doped with deuterated phenanthrene)[https://doi.org/10.1103/PhysRevLett.55.1642].

3. Line 45. Needs a reference for order of singlet states [https://doi.org/10.1103/PhysRevB.98.085207]

4. Line 59. I'm repeating J. Reimer's comment here, this is not DNP, no microwaves were used in this experiment by King 2010.

5. Line 66. As J. Reimer said, Ajoy paper is first example of ISE used in NV diamond, though detection done at higher field, and was frequency swept not field swept.

6. Paragraph starting at line 74 provides context that is not relevant to the study, I would suggest removing it.

7. Line 99. The authors should be more specific about the rapid diffusion model when it is first introduced, under what specific conditions is it valid?

8. When extracting spin diffusion coefficients the authors do not include the effect of paramagnetic sinks, could the authors clarify this point?

9. Line 163: The authors state: "we estimated the initial electron polarization PNVe of the NV− center between the mS = 0 and the mS = −1 states right after laser irradiation to be 13 % from the ratio of the area intensity of the EPR line of the NV− centers integrated over the field-sweep range to the area intensity of the EPR lines of all S = 1/2 electron spins (177 ppm)." I am not sure this is entirely valid unless one includes the effects of optical density and scatter. The entire volume of S=1/2 electron spins is measured in the EPR cavity, however wouldn't only a fraction of NV- spins be excited based on scattering, optical density and the laser spot size of the sample? Could the authors clarify this point?

10. From what I understand, the 13% value is extracted from the data shown in 3b, for the nanodiamonds. Why is this same value applied to the microdiamonds as opposed to using the data from 3c and known P1 concentrations in the microdiamonds? I would also expect the penetration depth to be quite different for the microdiamonds.

11. Line 385, Though this is the first report I've seen to haev used a ns pulsed laser source, there are many other cases in which laser schemes are used with gating for the laser + RF + microwaves to polarize a small number of neighbouring 13C nuclei. (e.g. https://doi.org/10.1103/PhysRevLett.120.060405). I would suggest changing the 'continuous light irradiation' to continuous wave laser light sources to be more clear.

12. Line 405. There have been a number of studies focused on methods to eliminate surface defects in diamond as this can be lead to very short coherence lifetimes for

NV centers near the surface, this has included different baking/oxidizing techniques as well as different surface coating methods. [e.g. a few ref: Analytical and Bioanalytical Chemistry volume 407, pages7521–7536(2015), and also Nano Lett. 2013, 13, 10, 4733–4738] In addition, there have been a number of proposed schemes for transferring polarization from the diamond matrix to external spins, though none have been applied successfully to a larger volume. [Nano Lett. 2014, 14, 5, 2471–2478; Nano Lett. 2018, 18, 3, 1882–1887]

13. Line 413.The quest to find new defects in semiconductors that can be optically polarized has been ongoing for at least a decade, though it is found more so in the quantum information processing literature (Nature Physics volume 3, pages153–159(2007).

14. The authors may find the following (very) recently published work interesting: "Scaling analyses for hyperpolarization transfer across a spin-diffusion barrier and into bulk solid media" https://doi.org/10.1039/D0CP03195J

Comments on supplementary:

1. I would suggest that the authors add a reference to the following paper [E. Rej et al. J. Am. Chem. Soc. 2017, 139, 1, 193–199] (in which the ESR of dangling bonds in nanodiamonds are discussed and shows the g-factors and where ESR lineshapes of P1 and surface radicals overlap). 2. Line 9: there are more than three lines here, if the authors include all the features of dangling bonds, one is dealing with multiple overlapping resonances (E. Rej: J. Am. Chem. Soc. 2017, 139, 1, 193–199). 3. In the supplementary text the authors report $T_{1,C}$ in microdiamonds to be 99 +/- 14 s but then in figure 3(c) the authors show $T_{1,C}$ to be 85+/- 5 s. Please clarify this point.