nature portfolio

Peer Review File

Exploring the potential of molecular nanomagnets as quantum sensors of radiation

Corresponding Author: Professor Giuseppe Latino

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The manuscript of Cini et al, investigates the use of a Single Molecule Magnet (Mn12tBuAc) as quantum sensors for ionizing radiation, combining SQUID magnetometry and proton NMR relaxation measurements. The authors demonstrate that exposure to low-activity radiation sources leads to a reproducible reduction of the magnetization relaxation time tau_R by a factor of approximately 2–2.5. The effect is observed consistently across techniques and field values near quantum tunnelling anticrossings. I believe the MS is relevant, bridging molecular nanomagnets, quantum sensing, and particle detection together. Moreover, control experiments (non-emitting sources, thermal cycling, α-shielding) support the robustness and reproducibility of the results. The theoretical framework based on a giant-spin Hamiltonian, dipolar mean-field effects, and phonon-assisted relaxation is appropriate and successfully reproduces the main trends of the data. Despite my positive view of the overall manuscript, I find some points require further clarification as follows:
Major issues:
1. The sensing capability is presented mainly qualitatively. A quantitative estimate of sensitivity (minimum detectable energy or dose) is missing and would strengthen the claims. It is important for the reader and interested in the field to have a measure of the dosage employed during the study. This will further strengthen the observations if the dosages across the studies were maintained.
2. The radiation-induced effect is modeled phenomenologically via a two-temperature component; while reasonable, alternative mechanisms (e.g., radiation-induced disorder or local structural damage affecting transverse anisotropy) should be discussed more explicitly. In fact, I would argue that given the molecular nature of the complex used as a testbed, a high radiation might induce crystallographic changes (as often observed in structural data collection at synchrotron facilities), that might contribute to the observed differences. A simple crystal deterioration issue might induce local crystal distortions which might also contribute to the reported tau_R values.
3. The link between radiation dose, local heating, and the observed change in tau_R remains indirect. Clearer dose-rate estimates at the crystal and their relation to the measured effect would improve the manuscript.
4. Perhaps it was not clear, but I wonder whether the authors were able to perform tau_R data collection, without-with-without sample irradiation and how the tau_R compares for the three cases.
5. Given that the authors perform tau_R measurements using a SQUID magnetometer, I would have liked to see the hysteresis studies also under irradiation to see how the overall structure changes if any.
6. Although the authors claim a 2-2.5 change in tau_R, in table 1 it is shown that for the 0.96 T crossing, the non-emitting and emitting studies are both practically identical. Any explanation for this?
Minor issues:
• A likely typo is present in Fig. 4 caption (9.3 T instead of 0.93 T).
• A few statements (e.g., independence from Hamiltonian details) could be softened to avoid overgeneralization.
To summarize, the manuscript contains interesting experimental evidence and a plausible physical interpretation for radiation-induced acceleration of magnetization relaxation in SMMs. The work represents a novel proof of principle study proof of principle and is suitable for publication after minor-to-moderate revision, primarily aimed at strengthening quantitative aspects and clarifying the physical interpretation.

Reviewer #2

(Remarks to the Author)
In this article the authors present experiments showing a significant reduction in magnetic relaxation time of the single-

molecule magnet Mn12tBuAc in the presence of a γ radiation source, alongside theoretical simulations connecting the heating caused by the radiation to that reduction. While they do not see the magnetic "avalanche" behavior that can follow from other perturbations to the spins when in a metastable state, they do claim that the change in relaxation time is much greater than would be expected from the average amount of energy delivered by the radiation, and thus put this system forward as a possible sensor for detecting relatively small amounts of radiation. While I believe this article is mostly suitable for publication in this journal, I have a couple significant concerns that I would like to see addressed before it is accepted.

1. The main analysis focuses on modeling the relaxation using justified assumptions and fitting it to the data, but the fitting is made using effectively only four data points, two with radiation and two without (the three SQUID data points with radiation around 0.93 T are close enough that while they provide good evidence of repeatability, they don't give much of a sense of the broader field dependence). Ideally, data at more fields should be taken to provide more confirmation, but an alternative would be more concretely connecting the NMR data to these models, not quantitatively (as the authors point out this is not possible), but at least more qualitatively in the text. As it is the lack of data reduces confidence in the analysis.

2. One of the most significant findings in the article is the substantial decrease in relaxation time compared to the average amount of energy being delivered by the radiation. Providing the answers to a few follow-up questions would help clarify how significant this is.
2a. If the change in τ_R were caused entirely by a bulk temperature increase, what would that temperature increase be, and in terms of average energy how much radiation would be required to cause it?
2b. How small is the level of detected radiation? The authors talk briefly about possible applications in sensing for fundamental physics research, how does the level of detected radiation compare to what might be necessary for such experiments? How does it compare to the sensitivity of the Mn12ac experiments from Refs. 32 and 33?
2c. Are the authors able to speculate about what level of radiation would be required to trigger an avalanche in this system, and connect that to possible applications?

I also have a number of more minor concerns that I list separately below.

Line 88: The relaxation time up to this line has been referred to as τ, but starting on this line it is called τ_R, with no explanation of the difference. Later on multiple different relaxation times are discussed, with τ_R being the main one under study, but no such distinction has yet been made. Some more clarity in the notation would be appreciated.

Fig. 3: The fits to the NMR data both with and without radiation are not great, and the authors do comment on the error size. However, the data with radiation almost appears to have an oscillatory component to it. Is this just a coincidence from the scatter in the data?

Line 170: If the main thing preventing the extraction of β from the NMR fits is the size of the noise, have the authors tried setting β from a similar SQUID run and fitting the NMR data with that value, to see whether the data is at least consistent with the SQUID β?

Fig. 4: The lines that are guides to the eye seem somewhat misleading, as they suggest a direct comparison between NMR and SQUID values of τ_R, and the authors previously state that no such direct comparison should be made. As the more impactful comparison is the change in τ_R with and without radiation within a single experiment type, the figure might be improved by highlighting those changes, perhaps as shaded bands.

Line 283: Is "the main of its field dependence" a typo? I think there might be a word missing.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have addressed all points raised by the referee; hence, I'm very happy to recommend this manuscript for publication

Reviewer #2

(Remarks to the Author)
The authors have addressed my concerns with the initial manuscript, through both some additional details in the main article, as well as additional data in the supplementary materials. I now believe the article is suitable for publication.

Dear Referees,

First, we wish to thank you for your constructive criticisms and valuable suggestions, which we found very useful to improve the clarity of the manuscript. In the following we discuss and reply point by point to your important comments. We detail the modifications we have made, where needed, to the manuscript and to the Supplementary Information to comply with your remarks. In red we include the new or modified text, in italics our answers. Where reported, line numbering refers to the first version of the draft.

Reviewer #1 (Remarks to the Author):

The manuscript of Cini et al, investigates the use of a Single Molecule Magnet (Mn12tBuAc) as quantum sensors for ionizing radiation, combining SQUID magnetometry and proton NMR relaxation measurements. The authors demonstrate that exposure to low-activity radiation sources leads to a reproducible reduction of the magnetization relaxation time tau_R by a factor of approximately 2–2.5. The effect is observed consistently across techniques and field values near quantum tunnelling anticrossings. I believe the MS is relevant, bridging molecular nanomagnets, quantum sensing, and particle detection together. Moreover, control experiments (non-emitting sources, thermal cycling, α-shielding) support the robustness and reproducibility of the results. The theoretical framework based on a giant-spin Hamiltonian, dipolar mean-field effects, and phonon-assisted relaxation is appropriate and successfully reproduces the main trends of the data. Despite my positive view of the overall manuscript, I find some points require further clarification as follows:

Major issues:
1. The sensing capability is presented mainly qualitatively. A quantitative estimate of sensitivity (minimum detectable energy or dose) is missing and would strengthen the claims. It is important for the reader and interested in the field to have a measure of the dosage employed during the study. This will further strengthen the observations if the dosages across the studies were maintained.

A.: *We agree with the reviewer that we only presented a qualitative estimation of sensing capability. The reason for this is that obtaining a quantitative estimate of sensitivity is not so straightforward. Indeed, from one hand we have a continuous emitting source, on the other (beside shielding for α particles) we do not have the technical possibility (given the lack of space within our apparatuses) to reduce the rate of γ incidence, to which the energy release in the crystals is mainly related. In short, with our current setup we can only give an estimate based on the evaluation of the minimum exposition time required to detect some effect. This yields an estimate of the upper limit for the minimum detectable energy, based on the observation that the recovery of the magnetization is systematically faster under irradiation in the very first part of data acquisition (lines 225-229): during the transient time of around 180 s required to get a stable B field at the required working value, the irradiated sample systematically recovers a higher fraction of the saturation magnetization with respect to the non-irradiated one. In short, the first measurement point for the irradiated sample always shows a sensible higher magnetization value (see Fig. 3 and Supplementary Fig. 1) than for the non-irradiated one. This makes us confident that we are at least sensitive to the total amount of energy released in the time (ca. 180 s) that the SQUID magnetometer needs to change field from B $\sim$0 T to a stable B field at the required value. Since it is not possible to have a shorter transient time with our setup, the estimate of the sensitivity we obtain should be considered as an upper limit. Furthermore, considering that the effect is seen also when shielding for α particles, the related energy release must be mainly attributed (as confirmed by the simulation) to γ irradiation. When considering the average dose rate estimate on the crystal, we get an upper limit estimate for the sensitivity of about 6.8 MeV.*

The detailed evaluation of the average dose rate estimate is now discussed in additional sentences added at line 415:

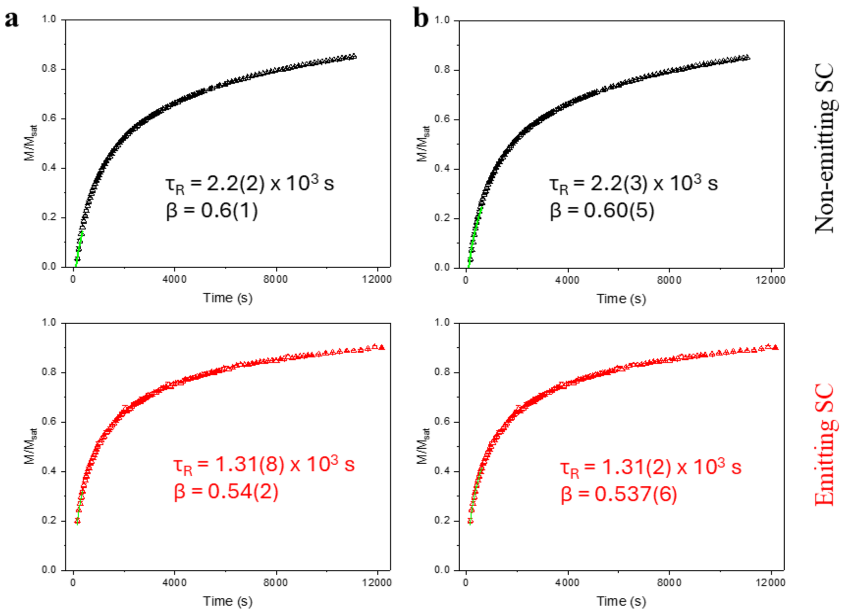
From this spectrum, a correction factor of about 1.3 has been derived for the γ surface flux, to account for the fraction of low energy photons ($E_\gamma < 59$ keV) not detected in the experimental characterization of the source. As a result, we finally estimated a dose rate on a single crystal of about $3\cdot10^{-8}$ Gy/min and $3.6\cdot10^{-7}$ Gy/min due to α and γ particles, respectively.

The upper limit estimate is now given in line 230:

Again, this difference was systematically found in all SQUID measurements (see Supplementary Fig. 1), also when shielding for α particles. From these observations, when considering the estimated dose rate on the crystals (see Materials and methods below), we can get an upper limit estimate for the sensitivity (minimum detectable energy release) of the crystals of about 6.8 MeV with our approach. This is close to the upper limit in sensitivity of 5.486 MeV reported in ref. 32-33, obtained with the magnetic avalanches approach for α particles absorption.

A mention to our upper limit estimate has also been added to the conclusions.

As a further check, not reported in the updated manuscript, we tried to perform the evaluation of τ_R by limiting the fit to the first 5 or 10 points, corresponding to about 200 or 400 s (see Fig. below): again, a sensible lower value for τ_R is observed for the irradiated crystal. This confirms that an effect can be seen (at least in the first part of the recovery curves) on a time span of order of few minutes or lower.

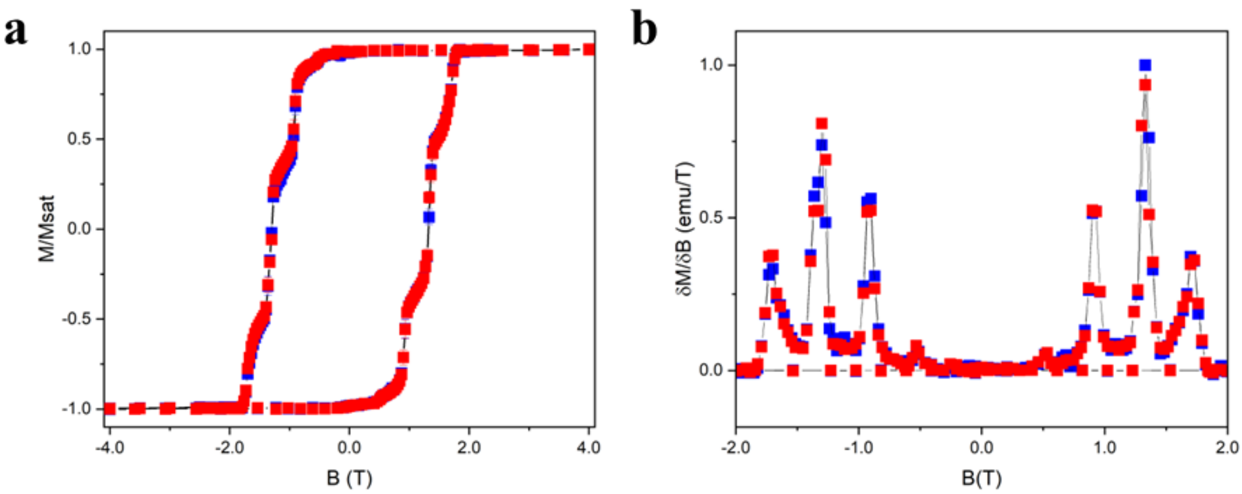


Magnetization dynamics at B = 0.93 T with and without irradiation. SQUID recovery curves acquired with B = 0.93 T at T = 2.2 K with the $Mn_{12}{}^tBuAc$ crystal facing the non-emitting (black points) and emitting SC (red points). Green lines are fits according to Eq. (3B) considering: (**a**) the first five points of the measurement (approximately the first 200 s of each recovery curve) and (**b**) the first ten points (about 400 s).

2. The radiation-induced effect is modeled phenomenologically via a two-temperature component; while reasonable, alternative mechanisms (e.g., radiation-induced disorder or local structural damage affecting transverse anisotropy) should be discussed more explicitly. In fact, I would argue that given the molecular nature of the complex used as a testbed, a high radiation might induce crystallographic changes (as often observed in structural data collection at synchrotron facilities), that might contribute to the observed differences. A simple crystal deterioration issue might induce local crystal distortions which might also contribute to the reported tau_R values.

A.: *We agree with the Reviewer on the fact that a priori a high radiation dose can induce crystal deterioration. Anyway, it should be noticed that our source is characterized by a very low dose release (see table 3 and comments at lines 417-421). Furthermore, as from lines 225-229, the source effect is already seen after about 3 minutes of irradiation, which corresponds to a relatively low number of absorbed ionizing particles (around 4 α and 200 γ). A control-check was indeed performed by comparing the hysteresis curves before and after about 10 h of continuous irradiation: this is shown in the new Supplementary Fig. 5 (also reported below). The two hysteresis curves and the corresponding dM/dB vs B curves practically coincide, indicating the absence of any macroscopic crystal deterioration during our measurement's time span.*
While we agree that a detailed study of the impact of radiation damage on Mn12 crystals, to the best of our knowledge hitherto unreported in literature, needs to be performed in the near future, for instance by using high intensity radiation sources, however, it is clearly beyond the scope of this study.
For better clarification, we added the following paragraph, summarizing the above discussion, at the end of the Experimental results section (at line 244):

Furthermore, we can *a priori* be confident that the observed effect is not due to a crystal deterioration induced by the radiation, given that the source is characterized by a very low dose release and its effect is already seen after about 3 minutes of exposition, in correspondence of which there is a relatively low number of absorbed ionizing particles (around 4 α and 200 γ). This hypothesis is confirmed by the comparison of the hysteresis curves before and after about 10 hours of continuous irradiation. As shown in Supplementary Fig. 5, the two hysteresis curves practically coincide, as well as the d*M*/d*B vs B* curves, indicating no occurrence of a macroscopic crystal deterioration at least during our measurements time, as expected for the low dose released by the source. A detailed study of the impact of radiation damage on $Mn_{12}{}^tBuAc$ crystals, to the best of our knowledge hitherto unreported in literature, needs to be performed in the near future and it is beyond the scope of this study.



Supplementary Figure 5. Magnetization hysteresis cycle for $Mn_{12}{}^tBuAc$ under irradiation. **a:** single crystal SQUID measurements acquired at $T = 2.2$ K with the *B* field applied along the easy axis: the red curve was measured about 10 hours after the blue one, *i.e.* after 10 hours of exposition to the radioactive source. The reported values are normalized to M_{sat}. **b:** plot of d*M*/d*B vs B* from the same hystereses, showing the *B* values at which the anticrossing occurs.

3. The link between radiation dose, local heating, and the observed change in tau_R remains indirect. Clearer dose-rate estimates at the crystal and their relation to the measured effect would improve the manuscript.

A.: *We thank the Reviewer for raising this important point. Based on our PHITS simulation for the interaction of radiation with the crystals and on the measured emission rates, we are able to perform a direct dose-rate estimate. We made this quantitatively clearer in the text by adding the following sentences at line 415:*

From this spectrum, a correction factor of about 1.3 has been derived for the γ surface flux, to account for the fraction of low energy photons ($E_\gamma < 59$ keV) not detected in the experimental characterization of the source. As a result, we finally estimated a dose rate on a single crystal of about $3 \cdot 10^{-8}$ Gy/min and $3.6 \cdot 10^{-7}$ Gy/min due to α and γ particles, respectively.

At the moment, we cannot perform a more detailed study of the effect vs. dose-rate, given that we have only one radiation source. This could be the subject of a separate study, performed by using several sources with different activities. Furthermore, a proper description of the link between the dose-rate deposit on the crystal and its relation to the measured effect requires a more detailed model with respect to the simple "two" component one proposed in the current paper. Indeed, such model is currently under study, based on a "reaction-diffusion" theory for the simulation of thermal transport processes triggered by the energy deposition due to the interaction of ionizing particles with Mn12-tBu; this will be the subject of a separate publication.

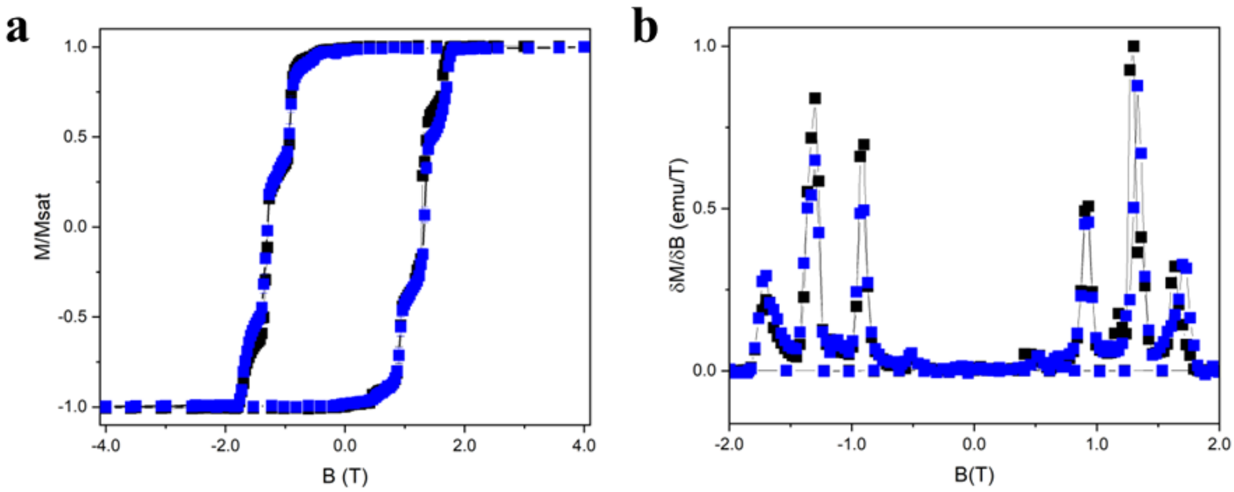
4. Perhaps it was not clear, but I wonder whether the authors were able to perform tau_R data collection, without-with-without sample irradiation and how the tau_R compares for the three cases.

A.: *Considering the intrinsic crystal fragility and given the required multiple thermal cycles and exposure to air, we decided to avoid the potential stress related to mounting/dismounting the same crystal on different (emitting/not-emitting) setups. Anyway, given there is no evidence of substantial radiation damage on the exposed crystals, we are confident about the reproducibility of the* τ_R *measurement without irradiation after exposition to radiation. Furthermore, the consistent results obtained with NMR and SQUID techniques in different measurement campaigns performed with different crystals (also from different production batches), clearly point to the observed effect being not attributable to potential intrinsic* τ_R *differences among different crystals.*

5. Given that the authors perform tau_R measurements using a SQUID magnetometer, I would have liked to see the hysteresis studies also under irradiation to see how the overall structure changes if any.

A.: *The Reviewer raises here an important point. To comply with this request, we have updated Supplementary Fig. 2 (now Supplementary Fig. 7, see below). The hysteresis acquired at 2.2 K with one crystal on the non-emitting semicylinder (SC) is now compared with the one acquired with another crystal, from the same production batch, mounted on the emitting SC. The two curves show an overall overlapping. Minimal discrepancies in the hysteresis curves may be ascribed to the non-complete reproducibility of the mounting, which may result in a few degrees angle between the c axes of the two crystals. Despite this, the dM/dB vs B curves show that the anticrossings occur at essentially the same B values. In conclusion, no structure change is observed, as expected, given the low dose of the source. This is also evidenced by the new Supplementary Fig. 5, cited in the answer to question 2. We added the following sentence at line 386:*

This figure also evidences that the overall shape of the hysteresis curve (*i.e.* anticrossing B values) does not change for irradiated crystals. This indicating that (at least under the low dose rates of our sources) the irradiation does not produce any relevant damage possibly bringing to changes in the energy level structure of the molecular cluster.



Supplementary Figure 7. Magnetization hysteresis cycle for a single $Mn_{12}{}^{t}BuAc$ crystal mounted on the non-emitting (black) and emitting (blue) SC. **a:** SQUID measurement acquired at $T = 2.2$ K with the B field applied along the easy axis. The reported values are normalized to M_{sat}. The two measurements were acquired with different crystals from the same production batch. **b:** plot of dM/dB *vs* B from the same hysteresis, showing the B values at which the anticrossing occurs.

6. Although the authors claim a 2-2.5 change in tau_R, in table 1 it is shown that for the 0.96 T crossing, the non-emitting and emitting studies are both practically identical. Any explanation for this?

***A.**: The reviewer notes here an important and a somehow puzzling point: we have no clear answer to this question, since we could not perform another measurement at this B value in a second campaign to firmly conclude that this is an experimental artifact. However, the fact that an additional measurement at B = 0.95 T gave evidence of the presence of the effect with both methods, as shown in the new Supplementary Fig. 3, suggests that this might be the case.*

Minor issues:

• A likely typo is present in Fig. 4 caption (9.3 T instead of 0.93 T).
A.: *Thanks for noting it. This is now fixed.*

• A few statements (e.g., independence from Hamiltonian details) could be softened to avoid overgeneralization.

***A.**: the characteristic features reported after eq. 6 at lines 279-282 do not depend on the details of the Hamiltonian and of spin-phonon coupling, provided the structure of these two terms is not strongly altered (e.g. the tunnelling part is no more a small perturbation wrt the axial part).*
At any rate, to avoid any misunderstanding on this, we substituted "specific details" with "fine details" at line 283. The sentence now reads as follows:

This well-established behaviour, and the way τ depends on the B field, are independent of the fine details of the spin-Hamiltonian (Eq. (4)) and the spin-phonon coupling (Eqs. (5) and (6)).

To summarize, the manuscript contains interesting experimental evidence and a plausible physical interpretation for radiation-induced acceleration of magnetization relaxation in SMMs. The work represents a novel proof of principle study proof of principle and is suitable for publication after minor-to-moderate revision, primarily aimed at strengthening quantitative aspects and clarifying the physical interpretation.

We thank the reviewer for the kind appreciation of our work.

Reviewer #2 (Remarks to the Author):

In this article the authors present experiments showing a significant reduction in magnetic relaxation time of the single-molecule magnet Mn12tBuAc in the presence of a γ radiation source, alongside theoretical simulations connecting the heating caused by the radiation to that reduction. While they do not see the magnetic "avalanche" behavior that can follow from other perturbations to the spins when in a metastable state, they do claim that the change in relaxation time is much greater than would be expected from the average amount of energy delivered by the radiation, and thus put this system forward as a possible sensor for detecting relatively small amounts of radiation. While I believe this article is mostly suitable for publication in this journal, I have a couple significant concerns that I would like to see addressed before it is accepted.

1. The main analysis focuses on modeling the relaxation using justified assumptions and fitting it to the data, but the fitting is made using effectively only four data points, two with radiation and two without (the three SQUID data points with radiation around 0.93 T are close enough that while they provide good evidence of repeatability, they don't give much of a sense of the broader field dependence). Ideally, data at more fields should be taken to provide more confirmation, but an alternative would be more concretely connecting the NMR data to these models, not quantitatively (as the authors point out this is not possible), but at least more qualitatively in the text. As it is the lack of data reduces confidence in the analysis.

A.: *We thank the reviewer for raising this point, which allows us to clarify and expand the discussion on the relaxation modeling. In a second campaign (performed after around two months) we had indeed performed measurements at other B field values around 0.93 T, using Mn12-tBu crystals from the same production batch. Unfortunately, even though a similar reduction in τ_R due to ionizing radiation was observed, the absolute τ_R values were different. We attribute this phenomenon to possible chemical deterioration of the Mn12-tBu crystals over time or to possible differences in crystal alignment wrt the B field during the mounting in the two campaigns. It is however interesting to stress here that, when data taken in the two separate campaigns are rescaled each other by a scale factor which is obtained at a specific B field (0.91 T and 0.93 T for NMR and SQUID, respectively) so to get the same τ_R value, all the results follow an overall consistent trend.*
To clarify this point, we have now added Supplementary Figure 3 and 4 and Supplementary Table 1 and 2, also showing SQUID and NMR data from the second campaign. We also added Supplementary Figure 6, where it is shown that the SQUID points from the second campaign, once rescaled, are still reasonably fit by the model tuned with the first campaign data. It should be noticed that a global B-independent rescaling factor could a priori not be adequate to account for the possible effects originating the differences in τ_R observed in the two campaigns. The main text has been accordingly updated adding the following paragraphs, at line 189:

Data from a second campaign of measurements performed after about two months on crystals from the same batch as those used to acquire data reported in Fig. 3 are shown in Supplementary Fig. 3 and 4 and Supplementary Table 1 and 2. It can be noticed that a similar reduction in τ_R due to ionizing radiation is still clearly present. However, due to effects that we attribute to possible chemical deterioration of the $Mn_{12}{}^{t}BuAc$ crystals over time or to possible differences in crystal alignment wrt the *B* field during the mounting in the two campaigns, different τ_R values are obtained for both the non-emitting and emitting configurations at a given reference *B* field. Moreover, when data taken in the two separate campaigns are rescaled to each other by a scale factor which is obtained at a specific field (0.91 T and 0.93 T for NMR and SQUID, respectively) so to get the same τ_R value, all the results follow an overall consistent trend.

And at line 340:

It is worth noting that the presented model has been tuned only on the SQUID measurements acquired at $B = 0.84$ T and 0.93 T. Anyway, when considering data from the second measurement campaign, once properly rescaled (as previously reported in Experimental results), the τ_R values are still reasonably fit by the model tuned with the first campaign data (see Supplementary Fig. 6). This observation is a further verification of the confidence in the model. About the observed discrepancies, it should be noticed that a global *B*-independent rescaling factor could *a priori* not be adequate to account for the possible effects originating the differences in τ_R observed in the two campaigns.

2. One of the most significant findings in the article is the substantial decrease in relaxation time compared to the average amount of energy being delivered by the radiation. Providing the answers to a few follow-up questions would help clarify how significant this is.

2a. If the change in τ_R were caused entirely by a bulk temperature increase, what would that temperature increase be, and in terms of average energy how much radiation would be required to cause it?

A. *We thank the reviewer for giving us the opportunity to clarify this point. In a simplified "single" component implementation of the theoretical model, a global thermal increase of the order of 0.05 K allows to simulate reasonably well the measured recovery curves for the irradiated crystal, as well as the τ_R extracted from the corresponding fits.*
According to the quantitative considerations reported at lines 424-427, a T increase of around 10^{-4} K over a typical measurement period of 4 hours is expected in the non-realistic experimental hypothesis that the cryostat is not refrigerating the crystal. In conclusion, approximately a 500 times higher dose (corresponding to about 4.7 x 10^{-8} J of energy deposition) wrt the expected one would be required to account for the observed effect.
To sum up this discussion and to improve the clarity of the text, we decided to move lines 421 - 427 after line 345 and also to add the following sentence:

This is confirmed by the fact that in a simplified "single" component implementation of the theoretical model, a global thermal increase of the order of 0.05 K is needed to simulate reasonably well the measured recovery curves for the irradiated crystal, as well as the τ_R extracted from the corresponding fits.

2b. How small is the level of detected radiation? The authors talk briefly about possible applications in sensing for fundamental physics research, how does the level of detected radiation compare to what might be necessary for such experiments? How does it compare to the sensitivity of the Mn12ac experiments from Refs. 32 and 33?

A.: *This is essentially the same point raised by Reviewer 1 in point 1, which clearly required some clarification. As for the motivation of this study, we note that it is of course very preliminary, the main aim being focused on characterizing SMMs as particle detectors. It is then too early to compare our results with what might be necessary for fundamental physics experiments.*

For the sensitivity issue, we repeat here the same point reported above in the answer to Reviewer 1.
A quantitative estimate of sensitivity is not so straightforward. Indeed, from one hand we have a continuous emitting source, on the other (beside shielding for α particles) we do not have the technical possibility (given the lack of space within our apparatuses) to reduce the rate of γ incidence, to which the energy release in the crystals is mainly related. In short, with our current setup we can only give an estimate based on the evaluation of the minimum exposition time required to detect some effect. This yields an estimate of the upper limit for the minimum detectable energy, based on the observation that the recovery of the magnetization is systematically faster under irradiation in the very first part of data acquisition (lines 225-229): during the transient time of around 180 s required to get a stable B field at the required working value, the irradiated sample systematically recovers a higher fraction of the saturation magnetization with respect to the non-irradiated one. In short, the first measurement point for the irradiated sample always shows a sensible higher magnetization value (see Fig. 3 and Supplementary Fig. 1) than for the non-irradiated one. This makes us confident that we are at least sensitive to the total amount of energy released in the time (ca. 180 s) that the SQUID magnetometer needs to change field from B $\sim$ 0 T to a stable B field at the required value. Since it is not possible to have a shorter transient time with our setup, the estimate of the sensitivity we obtain should be considered as an upper limit. Furthermore, considering that the effect is seen also when shielding for α particles, the related energy release must be mainly attributed (as confirmed by the simulation) to γ irradiation. When considering the average dose rate estimate on the crystal, we get an upper limit estimate for the sensitivity of about 6.8 MeV.

The detailed evaluation of the average dose rate estimate is now discussed in additional sentences added at line 415:

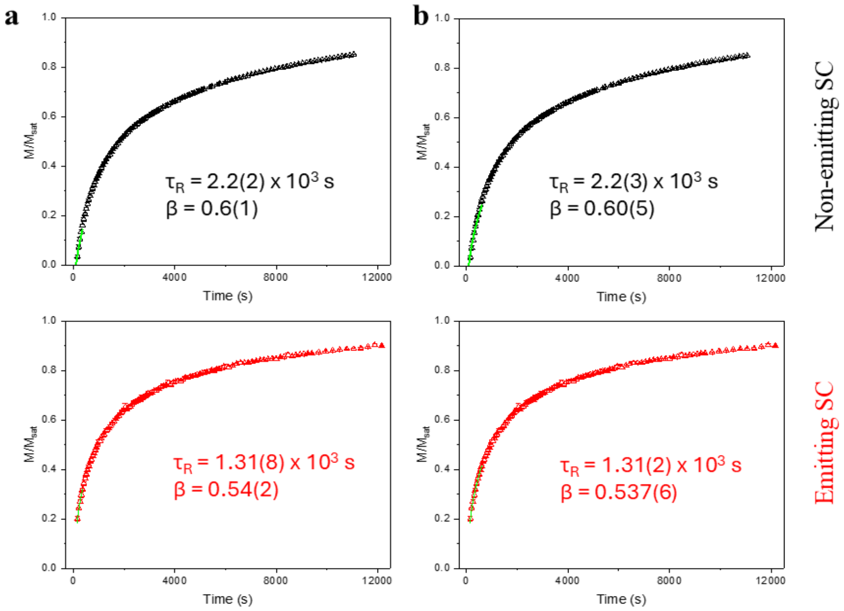
From this spectrum, a correction factor of about 1.3 has been derived for the γ surface flux, to account for the fraction of low energy photons ($E_\gamma < 59$ keV) not detected in the experimental characterization of the source. As a result, we finally estimated a dose rate on a single crystal of about $3 \cdot 10^{-8}$ Gy/min and $3.6 \cdot 10^{-7}$ Gy/min due to α and γ particles, respectively.

The upper limit estimate is now given in line 230:

Again, this difference was systematically found in all SQUID measurements (see Supplementary Fig. 1), also when shielding for α particles. From these observations, when considering the estimated dose rate on the crystals (see Materials and methods below), we can get an upper limit estimate for the sensitivity (minimum detectable energy release) of the crystals of about 6.8 MeV with our approach. This is close to the upper limit in sensitivity of 5.486 MeV reported in ref. 32-33, obtained with the magnetic avalanches approach for α particles absorption.

A mention to our upper limit estimate has also been added to the conclusions.

As a further check, not reported in the updated manuscript, we tried to perform the evaluation of τ_R by limiting the fit to the first 5 or 10 points, corresponding to about 200 or 400 s (see Fig. below): again, a sensible lower value for τ_R is observed for the irradiated crystal. This confirms that an effect can be seen (at least in the first part of the recovery curves) on a time span of order of few minutes or lower.



Magnetization dynamics at *B* = 0.93 T with and without irradiation. SQUID recovery curves acquired with *B* = 0.93 T at *T* = 2.2 K with the $Mn_{12}{}^tBuAc$ crystal facing the non-emitting (black points) and emitting SC (red points). Green lines are fits according to Eq. (3B) considering: (**a**) the first five points of the measurement (approximately the first 200 s of each recovery curve) and (**b**) the first ten points (about 400 s).

In ref. 32 and 33 it is reported the observation of "magnetic avalanches" in Mn12-ac triggered by the absorption of a single α particle from an ^{241}Am source. Given the related α emission is characterized by an energy of 5.486 MeV, they claim an energy threshold of their setup/approach characterized by this upper limit.

2c. Are the authors able to speculate about what level of radiation would be required to trigger an avalanche in this system, and connect that to possible applications?

A.: *This is an interesting point, but it is impossible to provide a consistent answer using the current phenomenological model, given that the avalanche mechanism is not explicitly implemented. A more detailed model is currently under study, based on a "reaction-diffusion" theory for the simulation of thermal transport processes triggered by the energy deposition due to the interaction of ionizing particles with Mn12-tBu. This will be the subject of a separate publication.*

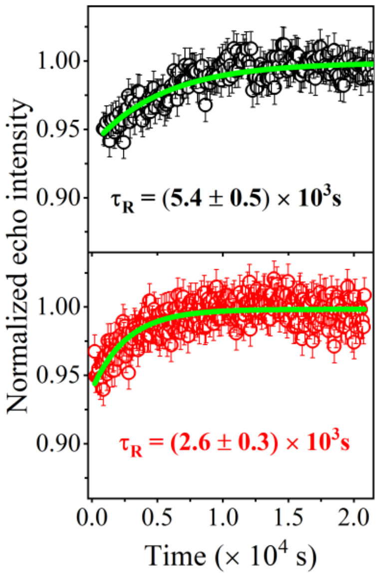
I also have a number of more minor concerns that I list separately below.

Line 88: The relaxation time up to this line has been referred to as τ, but starting on this line it is called τ_R, with no explanation of the difference. Later on multiple different relaxation times are discussed, with τ_R being the main one under study, but no such distinction has yet been made. Some more clarity in the notation would be appreciated.

A.: *We thank the reviewer for noting this point, which needed clarification. We have now fixed it throughout the manuscript; with the updates/corrections it should be now clear when we are referring to the intrinsic relaxation time (τ) or to the average relaxation time (τ_R parameter). We also added in the text, were needed, an "average" so to have a clearer distinction between τ and τ_R.*

Fig. 3: The fits to the NMR data both with and without radiation are not great, and the authors do comment on the error size. However, the data with radiation almost appears to have an oscillatory component to it. Is this just a coincidence from the scatter in the data?

A.: *We thank the reviewer for this comment. In NMR measurements we sometimes observe these kinds of oscillations, independently from the presence or not of irradiation: the origin of this behaviour is not clear. A more regular trend is indeed observed in other NMR data under irradiation. This is now clarified by the newly added Supplementary Fig. 2 showing the NMR echo intensity vs time, acquired with B = 0.91 T for the crystals facing the non-emitting and emitting SC.*



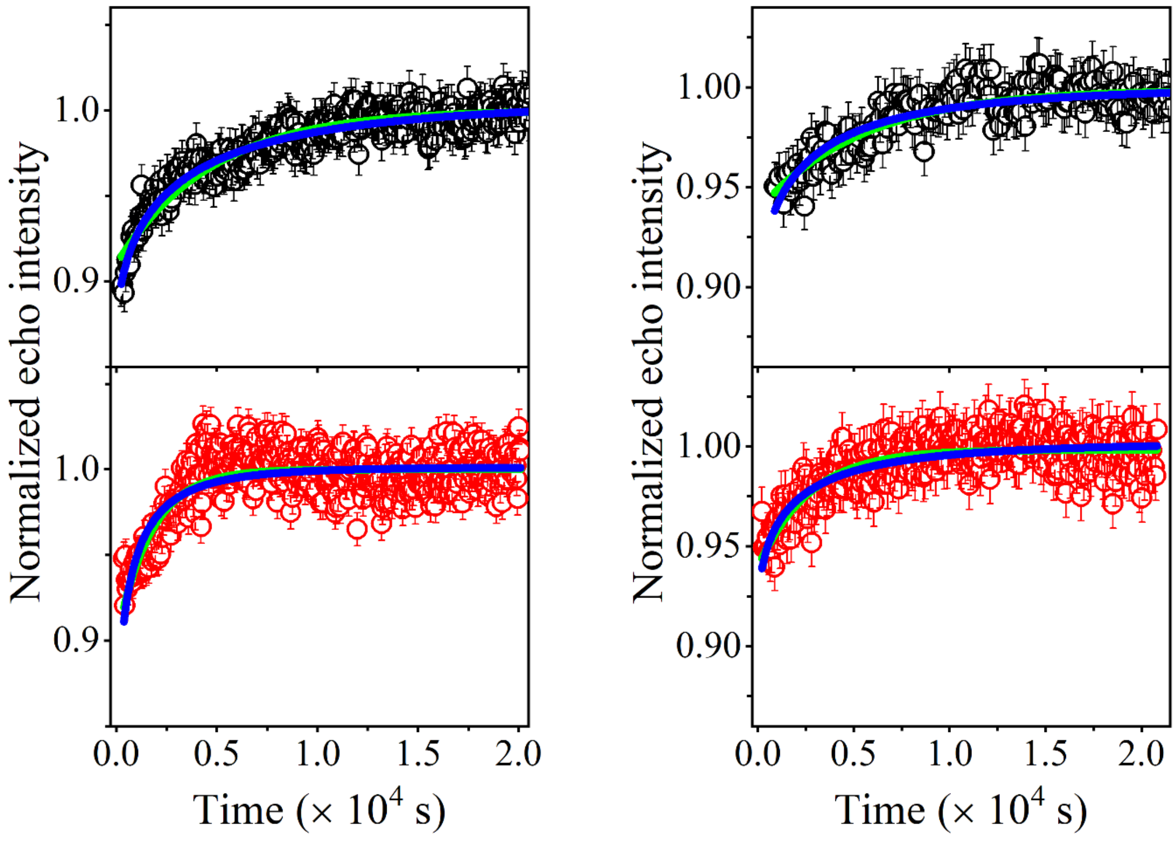
Supplementary Figure 2. Magnetization dynamics at 0.91 T with and without irradiation. NMR echo intensity *vs* time, acquired with B = 0.91 T at T = 2.2 K for the crystals facing the non-emitting (top) and emitting (bottom) SC; green lines are fit with Eq. (3A). All curves are normalized to the equilibrium values obtained by the fit procedures.

Line 170: If the main thing preventing the extraction of β from the NMR fits is the size of the noise, have the authors tried setting β from a similar SQUID run and fitting the NMR data with that value, to see whether the data is at least consistent with the SQUID β?

A.: *Yes, we did. As a first exercise, we refitted the NMR data at 0.91 T and 0.94 T with Eq. (3A) with a β starting value around 0.55, i.e., the average value obtained by the fits of the SQUID data at similar B values. Despite this, the fit procedure converges to β ~ 1, as already reported in the manuscript. By fixing the β value to 0.55, the data are still very well fitted by the new function (see Figure below), giving a different output for the τ_R parameter. We therefore decided to keep β as a free fitting parameter, avoiding assuming a value taken from fits of data obtained with another technique.*

We added in line 174:

As further check, we refitted the NMR data at 0.91 T and 0.94 T with Eq. (3A) with a β starting value around 0.55, *i.e.*, the average value obtained by the fits of the SQUID data at similar B values. Despite this, the fit procedure converges to β ~ 1. By fixing the β value to 0.55, the data are still very well fitted by the new function, giving a different output for the τ_R parameter. We therefore decided to keep β as a free fitting parameter, avoiding assuming a value taken from fits of data obtained with another technique.



Magnetization dynamics at 0.94 T (left) and 0.91 T (right) with and without irradiation. NMR echo intensity *vs* time at $T = 2.2$ K for the crystals facing the non-emitting (top) and emitting (bottom) SC. Green lines are fit with Eq. (3A) and β ~ 1, while blue lines are fit with Eq. (3A) and β = 0.55, fixed to the average value found from the fits of the SQUID data at similar *B* values. All curves are normalized to the equilibrium values obtained by the fit procedures.

Fig. 4: The lines that are guides to the eye seem somewhat misleading, as they suggest a direct comparison between NMR and SQUID values of τ_R, and the authors previously state that no such direct comparison should be made. As the more impactful comparison is the change in τ_R with and without radiation within a single experiment type, the figure might be improved by highlighting those changes, perhaps as shaded bands.

A.: *We thank the reviewer for noting this issue. We have now updated Figure 4 by drawing shaded bands as suggested by the reviewer, and we think that this improved its clarity. However, we still stress that they represent only guides for the eyes. For SQUID and NMR a minimum is expected around the anticrossing B value. While a direct comparison of the shape and of the exact minimum location between the two techniques is difficult, a clear trend around a minimum is expected for both methods, which is evidenced by the shaded bands. Moreover, the trends are even better evidenced by the shaded bands in Supplementary Figure 4, where data from the first and the second campaign are combined after proper rescaling.*

Line 283: Is "the main of its field dependence" a typo? I think there might be a word missing.
***A.**: We thank the reviewer for spotting this. The word "features" was indeed missing. We have now rephrased this sentence to account for another remark of Referee 1, as follows:*

This well-established behaviour, and the way τ depends on the B field, are independent of the fine details of the spin-Hamiltonian (Eq. (4)) and the spin-phonon coupling (Eqs. (5) and (6)).

We again thank both Reviewers for their insightful feedback and believe that the revisions have significantly improved the quality of the manuscript.

Thank you very much for your consideration.

On behalf of all co-authors

Sincerely yours,