Resonant spin tunnel effect in mixtures of molecular magnets and superconductors

Author: Alberto José Saavedra García
Facultat de Física, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain.

Advisor: Antoni García Santiago
Departament de Física de la Matèria Condensada, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain

Abstract: The objective of this work is to study the effect of superconductors on the magnetization transition at zero field of a molecular magnet. The motivation was a strong belief that, given an adequate amount of superconductor surrounding the magnet, a much abrupter transition will happen, thus leading ultimately to many possible technological applications such as a strongly coherent THz emitter. A comparison among samples of different proportion has been made by data analysis, giving us an insight into the appropriate proportion. Additionally, while doing the analysis, some abnormalities have been found, discussed and left as future work.

I. INTRODUCTION

Since the report of resonant quantum spin tunneling for Mn_{12}-acetate was done in 1996 [1], molecular magnets have been studied for both further understanding of nature - as it is in fact an observable macroscopic quantum effect - and its possible technological applications, such as the possibility of building a THz emitter.

Molecular magnets can be magnetized and show slow relaxation once the magnetic field is switched off, even if there is a single one without external interaction with any others, and a hysteresis cycle can be tracked. This can happen due to resonant quantum spin tunneling. However, when molecular magnets are heated above their blocking temperature, they recover superparamagnetic behaviour [2].

Resonant quantum spin tunneling is known to happen mainly on molecular magnets. It is based on a quantum superposition of states, which only happens when a transverse field of some type appears. Looking for a magnetic Hamiltonian, we can see that the one for Mn_{12}-acetate is of the style

$$\mathcal{H}_0 = -DS_z^2 - CS_z^4 - g\mu_B H_z S_z \qquad (1)$$

which does not present any transverse term, but it is supposed to have a negligible one [3], sufficient for allowing this superposition of states. From here we also see that D-strain effects and similar ones are null at zero field, thus we are doing this work at zero field, as we are just left with one effect trying to demagnetize the magnet: dipolar interaction. Due to the property of symmetric energies for positive-negative spin states, at zero anisotropy field we see a superposition of states in every positive-negative value of m_s, i.e. $\Psi = \frac{1}{\sqrt{2}}|m_s\rangle \pm \frac{1}{\sqrt{2}}|-m_s\rangle$. The true magic comes when we see every state is equispaced in terms of energy, so when we apply a concrete anisotropy field, i.e. a resonant field, and break the symmetry, we can then find a new complete superposition of states, this time giving us something like $\Psi = \frac{1}{\sqrt{2}}(|m_s\rangle \pm |-m_s+2\rangle)$ or $\Psi = \frac{1}{\sqrt{2}}(|m_s-2\rangle \pm |-m_s\rangle)$, depending on the orientation of the field. Thus, supposing we are in the first case for a $S = 10$ molecular magnet, we would end up with the lower energy superposition at $\frac{1}{\sqrt{2}}(|10\rangle \pm |-8\rangle)$, but we have lower energies for $|-9\rangle$ and $|-10\rangle$ levels, to which $|-8\rangle$ states will travel. So we can imagine it as a whole transition from $|10\rangle$ to $|-10\rangle$, which is the process that leads the molecular magnet into gaining magnetization and forming a staircase in its hysteresis cycle (once for every resonant field).

One of the most known molecular magnets is the Mn_{12}-acetate, a $S = 10$ molecule that has been already mentioned, which is the material used for this study. Previous work was made with the Mn_{12}-ac described as in Lis [4], which results in a tetragonal crystalline structure and showed magnetization transitions with width in the order of the kOe. More recent work was made with the additional treatment described in JACS [5], resulting in ribbons with a triclinical crystalline structure and showing a transition width of ~ 100 Oe, with a blocking temperature of ~ 3 K.

On the other hand, physicists have known of the existence of superconductors for over a century, special materials that do not let magnetic field in their insides [6]. So, looking for sharper transitions in molecular magnets, the idea of surrounding the material with superconductor came, in order to diminish dipolar interaction, and the results did not deceive, showing a width as small as ~ 20 Oe for the Mn_{12}-ac ribbons surrounded by granular $YBa_2Cu_3O_7$ in a 1:1 mass proportion [7]. To follow up this line this work came up, with the aim of analysing a whole set of experimental data focused on the determination of the best proportion, at different temperatures, of Mn_{12}-ac and $YBa_2Cu_3O_7$.

II. EXPERIMENTAL WORK

In order to obtain the hysteresis cycle for the different proportions and temperatures, different proportion samples were done following the JACS method [5], i.e.: 1) Prepare amorphous Mn_{12}-ac spheres in acetonitrile fol-

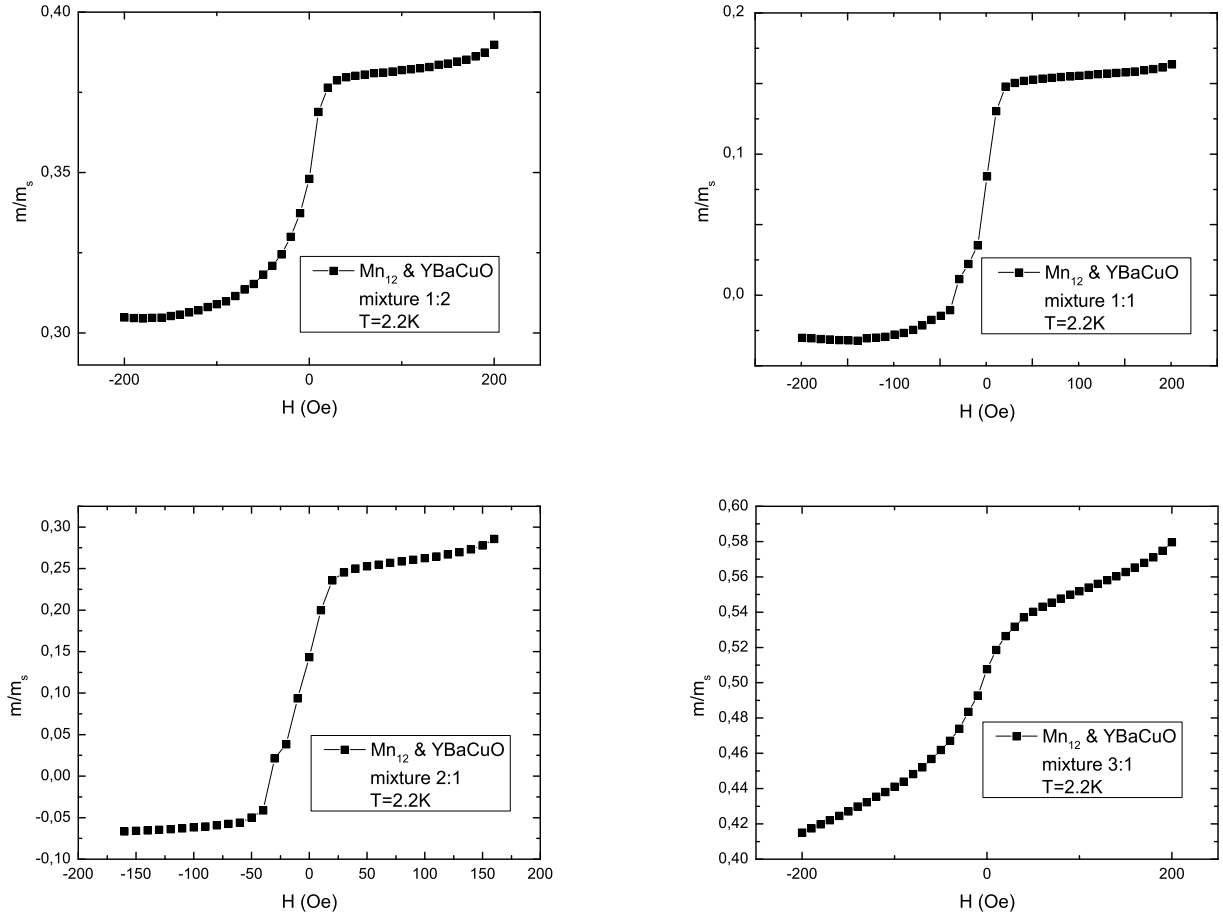

FIG. 1: Comparison among hysteresis cycles for different mixture samples at $T = 2.2$ K around $H = 0$.

lowing Lis [4], 2) add the solution into a toluene solution, 3) collect the brown precipitate using a filtrating paper. Then we do the same process adding YBaCuO on the toluene and we mix the result of the two processes as explained in [7]. Once the samples were available, magnetic measurements were made with a SQUID magnetometer, with fields as high as 5 T and temperatures as low as 1.8 K.

The protocol to follow once we have our 5 mg samples and the SQUID magnetometer is: 1) Cool the sample, 2) apply a field, such as 5 T, high enough to saturate the Mn_{12}-ac, 3) apply an intermediate field and then go to a 200 Oe field, 4) apply every time a field 10 Oe lower than the previous and measure until -200 Oe is reached.

III. RESULTS AND DISCUSSION

The analyzed data are basically the collected data, with unstable temperature cycles discarded. As we want to emphasize the zero field transition, we just straitened to its surroundings. Mixtures above 1:2 were discarded as their behaviour was practically the one of a super-

	Mixtures Mn_{12}:YBaCuO			
Temperature (K)	1:2	1:1	2:1	3:1
1.8	-	-	68.0	58.0
2.0	-	29.3	51.0	63.0
2.2	30.8	27.5	45.1	58.7
2.4	36.8	25.5	32.5	56.0
2.6	38.3	29.0	41.9	24.8*
2.8	29.5	23.6	-	-
3.0	26.0	22.3	-	-

TABLE I: Raw FWHM (expressed in Oe) for different mixtures at different temperatures, i.e. not considering any other information. Boxes filled with - correspond to the impossibility of getting any relevant data, either because the original data were not good or there was no relevant peak to analyse. The approximate uncertainty in the values is ~ 0.2 Oe. *:Value obtained not at half maximum but quite above, given the lack of information below that.

conductor, and analogously for mixtures above 3:1 being just a molecular magnet. A qualitative comparison can be made both between different mixtures at the same temperature or between different temperatures for the same mixture, the former being done as an example in FIG. 1 at 2.2 K. Although we can get a first glimpse of what is happening, this is not as easy when we compare samples at higher temperatures or for a comparison at different temperatures for each sample, so a derivative treatment has been done, analysing Full Width at Half Maximum (FWHM) of the derivative around zero field to determine how abrupt the transition is.

By doing this, we are not only being able to quantify the abruptness of the transition, but we also see some more qualitative information that we should take into account. By doing it roughly, we get values such as those summarized in TABLE I.

We can see there is a kind of pattern, as FWHM diminishes when we approach the highest temperatures, that does not work once we have too much Mn_{12}-ac. This seems reasonable given the fact that we are approaching the blocking temperature of the molecule, so that blocking should be enhanced when the mixture is highly magnetic if compared to the blocking when it is highly superconductive. Nevertheless, temperature does not seem to contribute in such a way as the composition of the mixture, which seems to be the main variable.

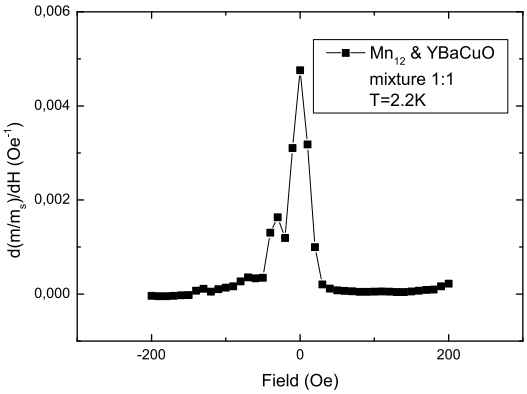

FIG. 2: Example of derivative curve. It belongs to sample 1:1 at 2.2 K, the top-right graph in FIG 1.

Now we shall pay special attention to some of those numbers, as they seem not to fit within their corresponding sample, but this is why we shall get back again to the qualitative stuff. If we take a look at FIG. 2 we can see there are two peaks, that we can relate to the protuberance in its counterpart in FIG. 1, which can lead to think that the transition is in reality a combination of a main transition with a secondary transition, but this will be left as a subject for further study. It may seem as irrelevant, but those appear for every mixture - except for 1:2 - at different heights and widths, although they tend to be at the -30 Oe field, and can be as huge as seen in FIG. 3.

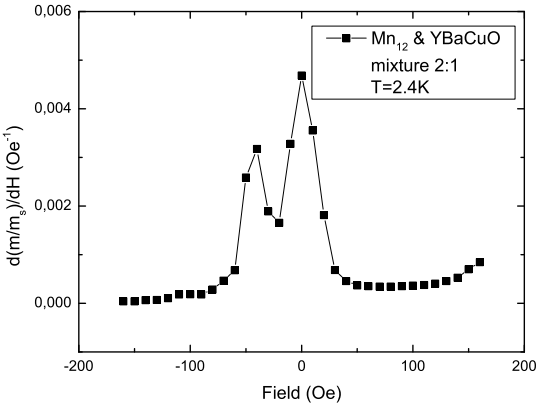

FIG. 3: Example of derivative curve. It belongs to sample 2:1 at 2.4 K.

Now the reader is obviously aware of this problem, we may recall that TABLE I was made just looking at the main peak, so it is way out of tune. Taking these peaks into account, we can do a second table with new FWHM values obtained for relevant secondary peaks (notice that this includes graphs with a clear main peak as well as those without a well defined peak, whose secondary peaks are completely irrelevant) as we can see in TABLE II.

Whereas before it seemed that sample 1:1 was the best with regard to the width of the transition, we now see that sample 1:2 has a narrower FWHM, so we could think that this is a better one from the same point of view. A possible debate could be made here, as if we look just at data like in FIG. 1 we cannot see for real if one transition is wider than the other. We may then calculate the amount of magnetization that transited, i.e. how much it decreased along the transition. We can see how while m/m_s decreases $\sim 8\%$ for sample 1:1, it decreases $\sim 18\%$ for sample 1:2. If we look into the derivative, we find the

	Mixtures Mn_{12}:YBaCuO			
Temperature (K)	1:2	1:1	2:1	3:1
1.8	-	-	68.0	58.0
2.0	-	**36.0**	51.0	63.0
2.2	30.8	**36.1**	**61.6**	58.7
2.4	36.8	**35.2**	**67.7**	56.0
2.6	38.3	**44.3**	41.9	**57***
2.8	29.5	**32.4**	-	-
3.0	26.0	**34.7**	-	-

TABLE II: More realistic version of TABLE I, with changes in bold taking into account secondary peaks. The approximate uncertainty in the values is ~ 0.2 Oe. *: Fixed by hand by extending the lines until the half maximum.

height of the main peak is $\sim 10^{-3}$ Oe^{-1} for sample 1:2 and $\sim 5 \cdot 10^{-3}$ Oe^{-1} for sample 1:1.

As another observation, we also see that 1:2 and 3:1 mixtures come from a relatively high magnetization and finish the transition at a still quite large positive value, whereas 1:1 and 1:2 mixtures start the transition at a lesser relative magnetization and always end on a very small and negative one. The ones that do not cross to negative values are easy explained, as both Mn_{12}-ac and YBaCuO have positive values during the process when being alone. This can possibly mean that it is one part strongly dominating over the other, 1:2 being dominated by YBaCuO while we need a 3:1 for a Mn_{12}-ac dominance.

Further information that should be mentioned includes the fact that the magnetization curve approaching zero field is much more abrupt than while going on to negative fields is also present in samples made solely of Mn_{12}-ac ribbons, as seen on FIG. 4.

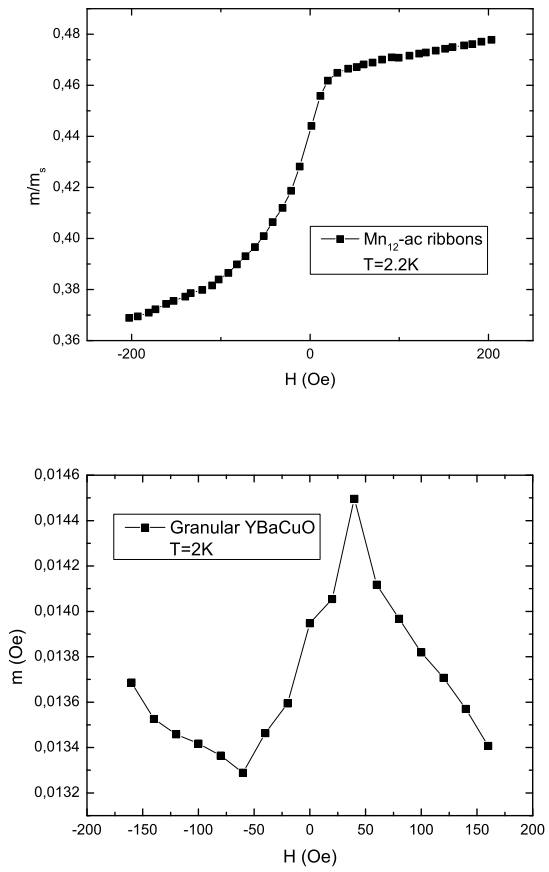

FIG. 4: Hysteresis cycle graphs of Mn_{12}-ac ribbons at 2.2 K (up) and granular YBaCuO at 2 K (down). For YBaCuO we are using just m instead of m/m_s because m_s is negative, and this could lead to doubt.

To end up, although we can see that the effect cannot be a sum of magnetizations - as both are positive and the result lead to negative -, we speculated about the secondary peak being caused by the superconductor, so we tried to simulate a hysteresis cycle of Mn_{12}-ac ribbons using data from mixtures and granular YBaCuO. While the results did not show a secondary peak, FWHM seemed too large. However, we finally obtained experimental data for Mn_{12}-ac ribbons and even though we could not say that they presented peaks as in the mixtures, their hysteresis cycles were not perfect at all. They can be interpreted as presenting small peaks around zero field, which disappear in the mixtures. We could also see that the FWHM is slightly smaller than the simulated.

IV. CONCLUSIONS

As we have done through all this work, we will let many open questions and even more further work, but this is science after all.

First of all, due to problems with the SQUID magnetometer, it was not possible to obtain more data, so the first thing to do should be a full hysteresis cycle for every sample at every temperature. This would be interesting, as in the graphs shown in FIG. 1 the cue on the range of ~ 200 Oe is almost not seen, but this could be associated with the scale of the representation, so by doing the full cycle we could really see what is happening.

Not only that, but every measurement should be done at least Oe by Oe, instead of being done in jumps of 10 Oe. This one explains itself, the more precision the better, and with that we could see what is happening in reality within those peaks and it could help to corroborate if there is really something we can call second transition or we are just trying to see more where there is nothing. This precision would also help to determine whether there is a correlation with temperature or not.

Apart from experimental details, there are some theoretical aspects that are worth bearing in mind. First of all, it may seem relevant to investigate the nature of the second peak. It could be just a tail left by the main peak, or maybe a second transition happening at $H \sim -30$ Oe. Given the latter case, a possible explanation could be some remanence trapped because of the superconductor, that would be on the ~ 30 Oe range, giving a total $H = 0$ thus leading to a second resonant spin tunneling, implying that second transition. The paper of a full hysteresis cycle also plays a role here, as we could see if those peaks do happen in the same way when coming from negative to positive, thus giving us a possible hint when trying to theorise the effect.

Secondly, we have seen how the effect of YBaCuO is not just a sum of magnetizations, as we do reach a negative one for some mixtures. We can explain this change to negative by explaining how YBaCuO is screening the Mn_{12}-ac. The screening would happen as explained in Ref. [8], by building junctions between the grains and excluding some of the volume of the Mn_{12}-ac molecules from external flux. For this reason I believe that the ra-

tios on the mixtures should have been made volume-wise rather than mass-wise, as this may be used as a starting point for other magnets and superconductors with densities that may differ from those corresponding to the components used in the current work.

In any case, we do not have only to explain why the magnetization goes to negative values for negative fields, but also why the relative magnetization decreases that much for the positive ones, because according to the screening explanation this should not be happening at all. It will require future work to find an answer and we will leave the question open.

The only solid conclusion we can reach is that the optimal mixture is somewhere between the 1:2 and 1:1 in mass, although it should be closer to 1:1. The thing is that the density for Mn_{12}-ac ribbons and for granular YBaCuO is practically the same, which happens to be a happy coincidence, and which gives us the opportunity to give the same volume-wise result. It seems pretty obvious when looked in terms of the volume that a proportion $1{:}x$ $(1 < x < 2)$ would give the sample enough superconductor to screen the magnet at its best, while still not oversaturating it, which would lead to a superconductor with impurities.

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To finish, and getting out of the research department, I would like to greatly thank my parents and my sister, who did not even know what the topic was about, but still were wishing me all the best.

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