

Magn. Reson. Discuss., referee comment RC1
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Comment on mr-2022-13

Anonymous Referee #1

Referee comment on "Mechanical ordering of pigment crystallites in oil binder: can electron paramagnetic resonance reveal the gesture of an artist?" by Elise Garel et al., Magn. Reson. Discuss., <https://doi.org/10.5194/mr-2022-13-RC1>, 2022

This paper determines the orientational distribution of paramagnetic pigment crystallites on painted surfaces using EPR spectroscopy. The premise is that EPR could possibly reveal the application technique of the pigments. The authors did not find a strong effect for the pigment studied, since this particular pigment has crystallites with platelet morphology, which defeat the proposed method.

The work is of interest, although not of particularly high impact. It fits within the scope of Magn. Reson. Presentation quality is good, and referencing is decent. Data quality is good. The conclusions are partially supported by the presented data (see comments below). Publication in its current stage would be premature since the work has deficiencies in a few places, as listed below in no particular order.

1.

The discussion mentions that the crystallites are platelets. Authors should provide experimental evidence that the crystallites in their samples preparations are indeed platelets. There is a reference for this (Bloise, 2016), but the preparation procedure in that cited paper appears somewhat different.

2.

It is stated that the g-parallel axis is along the crystal c axis and that the c axis is normal to the platelet plane. Evidence for this should be presented, or cited, since it is essential for the interpretation of the data.

3.

In the discussion, it is hypothesized that the orientational distribution is affected by gravity and depends on whether the sample plane is horizontal or vertical during film drying. Only the horizontal case is shown experimentally. Why not the vertical? This would

support the discussion that suggests that the platelets would then orient differently. Without experimental data on vertically dried samples, the discussion about the role of gravity is pure speculation and not useful.

4.

How are the 25x2-3 mm sample strips rotated around the axis perpendicular to the sample plane? This cannot simply be achieved by putting the sample strip into an EPR tube and rotating the EPR tube around its axis which is along the lab Y0 axis (Fig.3) in a standard EPR spectrometer. The experimental setup should be described in more detail.

5.

Were all samples dried with the application plane horizontal? This should be clarified in the Experimental section.

6.

To fully describe the experimental setup, it is not sufficient to specify just the rotation axis relative to the sample (e.g, Z and Y in Fig.6), but rather (i) the orientation of the sample in the spectrometer (lab frame), and (ii) the rotation axis in the lab frame. Only then is the description complete.

7.

In general, it is more correct to refer to "random orientation distribution" as "uniform orientational distribution" or "isotropic orientational distribution". In analogy, a "non-random distribution" is better referred to as "non-uniform". This applies to several places in the manuscript.

8.

The reduction from the triple sum in Eq.(5) to the single sum in Eq.(6) should be shown mathematically, to improve clarity and rigor. In my understanding, one angle can be dropped because of the observed rotational symmetry of the EPR spectrum when the sample rotated around the Z axis. But what is the reason the second angle is dropped? The axial symmetry of the EPR spectrum?

9.

Eq.(3) is only approximately correct, since the transition probability depends on the g-factor along the microwave B1 field - for this, all three Euler angles are in principle needed. See e.g. the textbook by J.R.Pilbrow. The approximation inherent in Eq.(3) should be explicitly stated.

10.

Spectra simulations for the case in Fig.6(a) are missing from the SI.

11.

What is the reason the spectra in Fig.6a are more noisy than all the other experimental spectra presented in the paper?

12.

The lines in Fig.5(b) and Fig.10 are misleading, as they suggest non-zero contributions for odd l . I suggest to remove these lines and present the data in these figures as is done in Fig.8.

13.

In Figs. 8 and 10, the red dashed line should be removed. It suggests a continuous function, whereas the x axis is discrete. In this context, the tick marks in Fig.10 every 0.4 on the x axis make no sense.

14.

The left-hand side of Eq.(S3) is missing the $\omega(\Omega')$ factor.

15.

What happened to the first integral in (S3)? Shouldn't there be an additional 2π factor for this integral appearing in (S5)?

16.

Figure S1 should include the simulation for all spectra in Fig. 4, not only a subset. Same applies to Figs. S2-S4.

17.

It should be stated somewhere that the odd-integer components of the orientational distribution give an EPR spectrum that appears isotropic. Therefore, as far as I understand it, odd l cannot be distinguished from $l=0$.

18.

- Line 113: matrice -> matrix
- The surname of the last author in the Hentschel reference is Spiess, not Speiss.
- The first line in SI section 2 should refer to Eq. S6, not Eq. S7.
- Eq.(S2) should say p_l and not $p_{\{l00\}}$, to be consistent with other equations.
- After Eq.(S2), it should say "determines an orientation Ω' " (prime is missing)