

## Point-by-point reply to referee # 2 for the manuscript:

*Mechanical ordering of pigment crystallites in oil binder: Can EPR reveal the gesture of an artist?*, by E. Garel, L. Binet, and D. Gourier.

We sincerely thank the reviewer for his detailed and critical reading of the manuscript, and in particular for raising two important points.

**Main comment:** *The work is performed accurately, and the results are, as whole, sound. The subject is of interest for Magn. Reason. Discussion, and is a nice tutorial on the effect of preferential orientation on EPR spectra. However I have a major point to raise as to the general applicability of the method. Indeed, while authors performed their measurements on samples prepared on purpose, the application of the proposed method on real samples would require detachment of part of the painting to study. Does not this risk to be seen as a destructive method? A comment on this should be added in the Introduction.*

**Response:** This is indeed an important issue, and we thank the reviewer for this comment. With traditional EPR, which uses a closed resonant cavity containing a small diameter tube, only small fragments of fresco could be analysed. However this is a situation that often occurs in archaeology when analysing ancient sites, where fragments of frescoes have spontaneously become detached. In some cases, and only with permission, it is possible to take small samples from a fresco. The ideal situation, towards which we should move, is the possibility to study an entire fresco *in situ* and non-invasively. In the project that finances this work, it is planned to build a portable EPR spectrometer, working at 5 GHz, based on planar resonators of the "microstrip" type. In this case, planar (or nearly planar) objects, which is the case of frescoes, can be analysed by moving the spectrometer over the surface of the object. This equipment is currently under construction (<https://anr.fr/Project-ANR-17-CE29-0002> ).

A paragraph clarifying this point has been added (in red) at the end of section 6 (lines 294-304).

**Comment #1:** *Sample preparation: How were powders ground? Does the grinding procedure affect the spectra? Can authors provide an estimate of the size and anisotropy of the microcrystals they used (e.g. by the analysis of PXRD spectra)? I can imagine that the aspect ratio of the microcrystals can be modified by grinding, and this should result in different probability density as a function of the angle. This may have major consequences for the proposed method, and has to be considered.*

**Response:** We did not observe any effect of grinding on the EPR spectra, at least in the series of experiments we performed. For example, the spectra obtained in Binet et al. 2021, carried out on raw synthetic powders, and those obtained in this work, where the powders are ground to be dispersed in a binder, are identical. The grain sizes are widely dispersed and range mainly from 1 to 20 micrometers. These sizes are too large to produce Scherrer broadening of diffraction peaks in PXRD, which would not be the case if the sizes were of the order of a few hundred nanometres or less.

**Comment #2:** *Linewidth: can authors think of extracting some further information from the empirical dependence of the linewidth they extracted from the analysis of their spectra? Or, seen from a different point of view: is there a reason for the chosen functional dependence of the linewidth?*

**Response:** The lineshape is determined by weak antiferromagnetic interactions between neighbouring  $\text{Cu}^{2+}$  ions, which average out the hyperfine interaction with  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  nuclei (Binet et al. 2021). Due to the two-dimensional character of the cuprorivaite structure, the antiferromagnetic interaction is itself anisotropic, respecting the tetragonal symmetry of the copper sites. This is responsible for the angular variation of the line width. This anisotropy is, however, quite small (1.47 mT and 1.20 mT for the parallel and perpendicular linewidths, respectively), and therefore does not provide any new information on  $\text{Cu}^{2+}$  ions and their mutual interactions. For this reason we have chosen an empirical expression for the angular variation of the line width.

**Comment #3:** *It looks like the simulation of the spectra is much better when the orientational distribution is more isotropic: indeed, the simulated spectra for the sample magnetically oriented in fluid oil are much less convincing than the remaining ones. Authors should provide a rationale for this.*

**Response:**

A potential and straightforward explanation would be the truncation of the expansion Eq. 6 of  $\mathcal{P}(\Omega)$  for numerical implementation at too a small order. The calculated spectra shown in Fig. S1 were obtained with a truncation at  $l=16$ . We checked that adding more terms in Eq. 6, up to  $l=24$ , did not improve the simulation at all, so that this explanation must be ruled out. Unfortunately, we could not figure out any explanation why the simulations in the case of the magnetically oriented sample do not match as much the experimental spectra as in the other cases.

**Comment #4:** *The description of the different frames is somehow unclear: they state “the sample frame (X, Y,Z) with X, Y and Z axes having a defined position with respect to the sample.” If I got it correctly from Figure 3, they mean that the sample frame (X,Y,Z) define the orientation of the sample with respect to the laboratory reference frame. This has to be clarified.*

**Response:**

We agree that the connection between the different frames can be confusing at some points. Indeed, the rotation axis in the laboratory frame was the  $Y_0$  axis. For rotations about the sample Y-axis (magnetic field moving from the sample Z-axis to the sample X-axis), the sample Y-axis was set parallel to the laboratory  $Y_0$  axis. This was the case of spectra or data in Figs. 4, 6b, 9 and 10. For rotations of about the sample Z-axis (Fig 6a), the latter was set parallel the laboratory  $Y_0$  axis. These settings are now specified (in red) in the captions of the corresponding figures.

**Comment #5:** *Did authors try to use larger magnetic field to orient the fluid dispersion? It appears to me that 20 mT is quite a low field, and higher fields should result in even more pronounced preferential orientation.*

**Response:** Of course we used stronger magnetic fields (at least ten times stronger) for the field orientation, but the orientation distributions were the same. What would have been interesting is to obtain orientation effects under very weak magnetic fields (Earth field). But we have not observed anything for fields of less than about 10 mT.

**Comment #6:** *The sentence “It must also be mentioned that during the film deposition and drying, the Z-axis is along the vertical direction so that the gravitational force is perpendicular to the sample*

*plane” is a bit misleading: it is not a matter of the orientation of the Z axis (which is a choice of the authors), but rather of the fact that the gravitational force is perpendicular to the sample plane.*

**Response:**

The reviewer is right. It is actually a matter of gravity being perpendicular to the sample plane during drying. The misleading phrase “the Z-axis is along the vertical direction” was removed.

**Comment #7:** *Authors state that, in case of a vertical substrate, “gravity should tend to orient the plates perpendicular to the substrate”: it is however hard to see how this could happen, given the platelet form of the pigment. I can imagine an accumulation of the pigment on the low end of the substrate, but I cannot see why they should pile differently. A more detailed explanation of the reason for the expected effect should be given.*

**Response:** We fully agree with this remark. This discussion about the effect of vertical position of the substrate is speculative and difficult to test experimentally, because in our experiments the oil containing the pigment is a viscous liquid, so the paint layer will flow along the surface if the support is placed vertically. We have therefore removed this discussion on the verticality of the substrate in Section 6. This discussion is now replaced by a sentence (lines 285-288, in red).